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THE IDEAL BOSE–EINSTEIN GAS, REVISITED

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Contents:

0. Introduction 171
- 0.1. Historical remarks 171
- 0.2. Further developments 173
- 0.3. Motivation and summary of this article 174

1. Preliminaries 176
- 1.1. Introduction; basic assumptions 176
- 1.2. Quantum mechanical ensembles and density matrices 177
- 1.3. The connection with thermodynamics 179
- 1.4. The bulk limit and surface corrections 181
- 1.5. The reduced density matrices, the hierarchy and the general conservation laws 185
- 1.6. Specialization to the ideal Bose gas 191

2. Bulk properties of the ideal Bose gas 194
- 2.1. Introduction 194
- 2.2. The bulk properties 195
- 2.3. Proof of the results of section 2.2 201
- 2.4. The significance of the grand canonical ensemble 210
- 2.5. The bulk properties of an IBG in *d*-dimensions 214

Appendix 2.A. The Bose functions 216

3. The thermodynamical properties of an ideal Bose gas in a finite volume 218
- 3.1. Introduction 218
- 3.2. The grand partition function Z^{gr} 219
- 3.3. The canonical partition function 226
- 3.4. Discussion 229

Appendix 3.A. Justification of (3.14) 233

Appendix 3.B. Proof of (3.23) 234

4. The fluctuation problem for the finite ideal Bose gas 235
- 4.1. Introduction 235
- 4.2. Proof of (4.1–2) 235
- 4.3. Further comments 237

5. Local properties of an ideal Bose gas near a wall 238
- 5.1. Introduction 238
- 5.2. The density matrices of the half-infinite system 238
- 5.3. The local density and the pressure-stress tensor 241
- 5.4. The two-particle distribution function 244

Concluding remarks 245

References 246

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THE IDEAL BOSE-EINSTEIN GAS, REVISITED

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Abstract:

Some questions concerning the ideal Bose–Einstein gas are reviewed and examined further. The bulk behavior including the condensation phenomenon is characterized by the thermodynamical properties, occupations of the states and their fluctuations, and the properties of the density matrices, including the diagonal and off-diagonal long range orders. Particular attention is focused on the difference between the canonical and grand canonical ensembles and a case is made that the latter does not represent any physical system in the condensed region. The properties in a *finite* region are also examined to study the approach to the bulk limit and secondly to derive the surface properties such as the surface tension (due to the boundary). This is mainly done for the special case of a rectangular parallelopiped (box) for various boundary conditions. The question of the asymptotic behavior of the fluctuations in the occupation of the ground state in the condensed region in the canonical ensemble is examined for these systems. Finally, the local properties near the wall of a half infinite system are calculated and discussed. The surface properties also follow this way and agree with the strictly thermodynamic result. Although it is not intended to be a complete review, it is largely self-contained, with the first section containing the basic formulas and a discussion of some general concepts which will be needed. Especially discussed in detail are the extra considerations that are needed in thermodynamics and statistical mechanics to include the surface properties, and the quantum hierarchy of the density matrices and local conservation laws. In the concluding remarks several problems are mentioned which need further analysis and clarification.

0. Introduction

0.1. Historical remarks

We begin with a brief sketch of the history of the ideal Bose–Einstein gas, in which we explain what it is and why it has been (and still is) of interest.

The origins of the ideal Bose gas go back to 1924, when it was shown by Bose [1] that the Planck blackbody radiation law can be derived from the statistical mechanics of light quanta (photons), if the number of states in an energy interval are counted in a way that acknowledges the identity of the particles differently from the prescription of Boltzmann. Einstein [2–4] saw that this was "based upon the hypothesis of a far-reaching formal analogy between [light] radiation and [particulate] gas" * and believed that analogy to be "a complete one", so that the counting method of Bose should apply to a system of non-interacting particles as well as to photons. The method of counting has since been known as the Bose–Einstein (BE) statistics and the system of non-interacting particles obeying them is known as the ideal Bose–Einstein gas, or ideal Bose gas, which we abbreviate IBG.

Einstein calculated the thermodynamic properties of the IBG, and found that they approach those of the classical ideal gas in the high temperature, low density limit. He also found that the specific heat tends to zero in the low temperature limit, satisfying the principle of Nernst (unlike the classical ideal gas). Most remarkably, he found that the equations do not allow for densities greater than a critical (number) density

$$\rho_c = \zeta(\tfrac{3}{2}) \left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2} , \tag{0.1}$$

which depends only upon the temperature, T, and the mass of a single particle, besides the constants of Planck, $\hbar$, and Boltzmann, k. He asserted that when the density is made greater than ρ_c,

---

* This quotation is from the second paper of Einstein [3], which has been discussed (and partly translated into English) by Klein [5]. Many aspects of the history of the IBG, especially as related to the contributions of Paul Ehrenfest, are given in another article of Klein's [10].

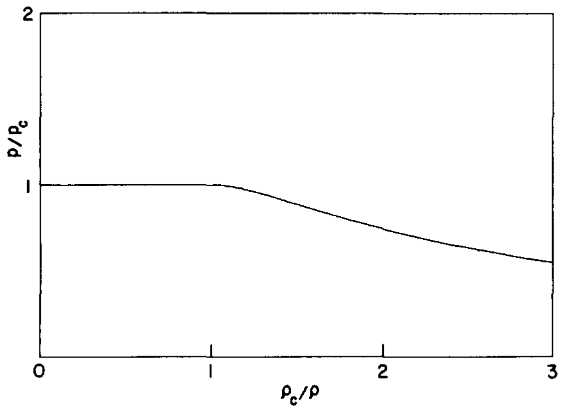

Fig. 0.1. The pressure plotted as a function of the volume per particle scaled by $p_c(T)$ (to be defined in section 2) and $\rho_c(T)$.

all additional particles (per unit volume) go into the ground state where they do not contribute to the thermodynamical properties of the system – the so-called Bose condensation. Thus the isotherm of the equation of state (the pressure, p, versus the reciprocal of the density, $1/\rho$, at constant T) is flat for $\rho > \rho_c$, as the plot in fig. 0.1 shows. In this region the system acts just like a saturated gas and condensed phase in equilibrium, where that condensed phase has no volume. Einstein believed that these effects might be important at very low temperatures for those substances that remain gaseous – most notably helium.

It should be added that in 1926 Fermi [6,7] suggested that the quantum mechanical theory of an ideal gas could be derived using a different method of counting – later known as the Fermi–Dirac (FD) statistics – by generalizing the exclusion principle that Pauli devised for the states of atomic electrons to a system of particles. The so-called ideal Fermi gas that results also behaves like the classical gas in the high temperature, low density limit, and also satisfies Nernst's principle, as does the IBG, but has no phase transition.

With the introduction of wave mechanics, it was shown in 1926 by Heisenberg [8] and Dirac [9] that the two kinds of statistics correspond to the completely symmetric (for BE) and completely anti-symmetric (for FD) wavefunctions, and in fact no other symmetry (with respect to the interchange of the particles) is possible for identical particles because of the probabilistic interpretation of the wavefunctions.

The wavefunctions for the ideal gases show quite clearly that there are spatial correlations in the system. Indeed, the BE statistics themselves imply that the particles are not statistically independent, as was recognized by Ehrenfest and Einstein [10]. Thus the gases contain a detailed structure, due to the statistics only, which is totally absent in the classical ideal gas.

Of course it was found that there are particles representing each of the two statistics, and that the appropriate choice is determined by the particle's spin. Particles with half integral spin, such as electrons, are fermions (which obey FD statistics), while particles with integral spin, such as photons and most atoms and molecules, are bosons (BE statistics). We shall restrict ourselves to the BE gas, and not pursue the FD line of development further.

Einstein's argument for the condensation of the IBG was criticised by Uhlenbeck [11] on the ground that the exact equations, before any continuum approximation is made, allow for all possible densities, and furthermore imply that there can be no singularity in the equation of state.

This was not cleared up until ten years later (see Kahn and Uhlenbeck [12]) when it was realized that the discussion of the condensation requires that the bulk limit be taken in which the number and volume are made infinite, with the density N/V fixed. (We shall explain this further in section 2. This is usually called the thermodynamic limit, but as we shall explain that name is misleading.)

The relationship of the Bose–Einstein condensation to the general problem of condensation was a new source of interest in the IBG. During the 1930's the classical and quantum statistical mechanical theories of interacting gases were developed, in a parallel form, by Mayer [13], Kahn and Uhlenbeck [12], and others *, in terms of the so-called cluster expansions of the various thermodynamic functions. However, for any non-trivial potential only the first few coefficients can be calculated, so in practice the formulas only represent the corrections to the ideal gas law for a dilute gas, and cannot be used to explain the condensation phenomenon. There is however a formal similarity between the fugacity expansions of the IBG and the cluster expansions, and since the IBG is a system in which the condensation can more or less be understood, the Bose condensation was used as a model for the discussion of a general phase transition by the above-mentioned authors.

Interest in the IBG was greatly stimulated when London [14–17] used it as a model to explain the superfluid transition in liquid helium (Isotope 4 – thus bosons). After helium was liquefied in 1908 by Kamerlingh Onnes (at 4.2°K), it slowly became clear that at about 2.17°K ($\equiv T_\lambda$) another phase transition occurs – between two liquids. First, singularities in the thermodynamic properties were noticed by Onnes, Keesom and others in the years 1911–1932, and then in 1936–1938 the extraordinary dynamical properties were discovered by Keesom, Kapitza, Allen and their co-workers **. London believed that this was *essentially* a manifestation of the Bose–Einstein condensation, even though for a liquid such as helium the intermolecular forces are quite strong and in no sense can it be considered to be an ideal gas. First of all, he noted that the predicted transition temperature T_c for an ideal gas of the same density and molecular weight as helium (given by eq. (0.1)) was 3.1°K – of the same order at T_λ. Also, the specific heats of the two systems were somewhat similar. But mainly, he suggested that the concept of condensation into a single particle state could explain the apparently dissipationless flow of liquid helium which occurs under certain circumstances. Tisza [20, 21] followed this hypothesis to propose the "two-fluid" phenomenological theory of superfluid helium, later made more complete by Landau. In this model, the superfluid carries no entropy, just like the condensate of the IBG, and in fact it has been found that the functional dependence of the superfluid fraction in helium upon T/T_λ is very close to that of the condensate fraction of the IBG upon T/T_c.

0.2. Further developments

We have seen that the motivations for the early work on the IBG were, first, to furnish a quantum mechanical theory of an ideal gas and to study its consequences; second, to study the Bose condensation as a model for a general phase transition; and third, to understand the superfluidity in liquid helium. Recent work has focused on the understanding of the theory of quantum statistical mechanics, in which the IBG plays a fundamental role, but most of the interest has stemmed from the London hypothesis about the relation with helium. The desire has been to understand both the thermodynamic and dynamical properties, and it has been hoped that the IBG serves as a sort of paradigm for the interacting boson gas.

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* For a more complete list of references, see the review article of de Boer [18].

** For a much more detailed description of liquid helium, with a history of the experimental discoveries, see London [17], also Putterman [19].

The relation of the Bose condensation to a general phase transition has not been pursued, since it is now believed that the mechanism of these two transitions is different, at least in terms of the analytic properties of the fugacity expansions at the point of condensation *.

To prove the relationship of Bose condensation to the superfluidity of helium, the meaning of Bose condensation for an interacting system must first be clarified. This was done by Penrose and Onsager [23, 24], who showed that in a general system the phenomenon of Bose condensation is evidenced by the occurrance of off diagonal long range order (ODLRO) in the first density matrix, $\rho_1(\boldsymbol{r}'\boldsymbol{r}'')$, by which it is meant that $\rho_1(\boldsymbol{r}'\boldsymbol{r}'')$ does not vanish when $\boldsymbol{r}'$ is infinitely far from $\boldsymbol{r}''$, but goes to a constant value which is called the ODLRO. Then Yang [25] developed the idea further to include the ODLRO of all of the reduced density matrices. He proposed that the superfluid density is equal to the sth root of the value of the ODLRO of the s-reduced density matrix $\rho_s(r'^s, r''^s)$, in the limit $s \to \infty$. The truth of this conjecture has not yet been determined.

We shall not attempt to give a thorough review of the more recent literature, but shall mention a few papers with some brief remarks in the text when relevant.

0.3. Motivation and summary of this article

The goal of this study is to give a survey of the properties of the IBG. We shall not make any comparisons with the properties of helium, which are known to be quite different. We do believe, however, that the mechanism of the Bose condensation is the root of the superfluidity in liquid helium, but that the resolution of this question requires more complete solution of the interacting gas than has been done so far. The complete study of the IBG represents a first step in that direction.

We will be especially interested in the thermodynamical properties, the density matrices and distribution (correlation) functions, the average occupations of the single particle states and the fluctuations about those averages. We will also discuss the surface properties and the local hydrodynamical properties.

Many of the properties have also been derived by other authors. The desire here is to give a systematic self-contained derivation, based on a single formalism, that ties the known results (and many methods) together, and fills in some gaps. In the course of this discourse, some basic questions come up, such as the question of the significance of different ensembles, which we also discuss.

In section 2 we consider the properties of the gas in the infinite volume limit, namely the bulk properties. We present a systematic derivation of all of the properties within the canonical ensemble. Although it may be redundant to go through all of the steps for both the density matrices and the thermodynamical properties (since the thermodynamical properties are well known and furthermore can be derived from the density matrices), we calculate all of the properties in a parallel manner to make the procedure more lucid.

Our emphasis in the second section is on the density matrices, which represent the complete description of the system. To make the calculation in the canonical ensemble we follow a procedure given previously by one of us (M.K.) which has not been published until now *. Consequently all of the details of this method are presented here. We discuss the resulting density matrices and distribution functions, especially with regard to their behavior in the condensed region and the insights they give into the nature of the Bose condensation. We also verify that some general relations are satisfied, such as the general fluctuation-compressibility formula.

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* See Uhlenbeck and Ford [22] p. 58.

In the course of the calculation some generating functions are introduced which are essentially equivalent to the grand canonical quantities. An examination of these quantities shows that some of them (notably the fluctuations in the ground state) differ in the canonical and grand canonical ensembles, and this leads us to question the validity and significance of the grand canonical ensemble.

In the third section we concentrate on the thermodynamical properties of an IBG in a *finite* system. The motivation is to include the asymptotic corrections to prove first of all the condensation in a "royal" way in which the leading correction terms are given. This exhibits therefore the *approach* to the bulk limit. A second reason is to study the leading correction terms themselves, which are the surface properties of the system (such as the surface density and the surface tension). For these purposes we first give a complete analysis of the grand partition function of the IBG for a gas confined in a rectangular parallelopiped box. This was partly inspired by the work of Greenspoon and Pathria [29–31] and is related to some other analyses, as will be noted in the text. The derivation given here includes all numbers of dimensions and the three boundary conditions, Dirichlet ($\Psi \to 0$), Neumann ($\partial\Psi/\partial n \to 0$), and periodic ($\Psi(r_i = 0) = \Psi(r_i = L_i)$ and $(\partial\Psi/\partial r_i)_{r_i=0} = (\partial\Psi/\partial r_i)_{r_i=L_i}$ for each fundamental direction i), and we believe is straightforward and free of arbitrary assumptions. Then we show how these results can be used to discuss the *canonical* partition function (of the finite system) as well, both in the condensed and non-condensed regions.

In the fourth section we study in detail for the finite system the fluctuation of the occupation of the ground state, mainly for the purpose of seeing whether and how the different behavior of the canonical and grand canonical ensemble already shows up for the finite system. Our results for the fluctuations in the canonical ensemble are in agreement with Hauge [32].

In the fifth section we return to the density matrices, but now to discuss their properties near a surface. To do this we calculate them for a half infinite system near the boundary. This allows the discussion of the local density and pressure variations near a wall, the relation to the pressure tensor and the hydrostatic equilibrium. We verify the so-called Bakker formula relating the surface tension with the variation of the parallel and normal pressure, and we also verify the thermodynamic relation between the surface tensions and the surface density. Most of the results in this section we believe are new.

In the concluding remarks several problems will be mentioned which need further analysis and clarification.

We begin in the first section with a review of the mathematical and physical formalism that is followed. We develop the formal relation of the thermodynamical ensembles and the density matrices, and exhibit the simplifications when the expressions are specialized to the IBG. Certain topics that are not well known are described in more detail, such as the extra considerations that must be made in thermodynamics and statistical mechanics when the surface properties are included, and the quantum hierarchy of the density matrices and the conservation laws. The hierarchy is presented because it is of general interest to clarify certain points, although only the expression for the pressure tensor, which is derived from it, is actually needed for this work.

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* This work has been presented in public lectures and discussed in the literature by Cannon [26], Lewis and Pulé [27], and Putterman [19].

The authors are grateful to Prof. E.G.D. Cohen for many helpful discussions and criticisms during the course of this work. One of us (R.Z.) would especially like to thank him for his encouragement and unfailing support.

1. Preliminaries

1.1. Introduction; basic assumptions

As mentioned in the general introduction, our main concern is the discussion of the equilibrium properties of an ideal Bose gas of N non-interacting spinless particles in a vessel of volume V and of a given shape. In this section we collect and partially derive the necessary formulae from quantum statistical mechanics and thermodynamics which are required in the discussions of the following sections.

For a general non-ideal Bose gas the state of the system is described in the Schrödinger picture and in configuration space by the wavefunction $\Psi(r^N, t)$ which satisfies the Schrödinger equation:

$$\hbar \mathrm{i} \frac{\partial \Psi(r^N, t)}{\partial t} = \hat{H}(p^N, r^N)\, \Psi(r^N, t)\,, \tag{1.1}$$

where $r^N \equiv \boldsymbol{r}_1, \boldsymbol{r}_2, \dots \boldsymbol{r}_N$, $\partial/\partial r^N \equiv \partial/\partial \boldsymbol{r}_1, \dots \partial/\partial \boldsymbol{r}_N$, the Hamiltonian operator is given by:

$$\hat{H}(p^N, r^N) = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m} + \Phi^{\mathrm{int}}(r^N) + \sum_{i=1}^{N} \phi^{\mathrm{ext}}(\boldsymbol{r}_i)\,, \tag{1.2}$$

with $\hat{p}_i = (\hbar/\mathrm{i})\partial/\partial \boldsymbol{r}_i$,* and where the assumption of Bose–Einstein statistics requires that the wavefunction Ψ must be a symmetric function of $\boldsymbol{r}_1, \boldsymbol{r}_2, \dots \boldsymbol{r}_N$. Because H is a symmetric operator in p_i and r_i it follows that if Ψ is symmetric at $t = 0$, it will remain symmetric for $t > 0$. An ideal Bose gas is defined by the assumption $\Phi^{\mathrm{int}} \equiv 0$. We consider that ϕ^{ext} includes only the potential of the wall of a vessel, and that that wall is described by an infinite potential jump (a "hard wall"), so that ϕ^{ext} can be replaced by the requirement that $\Psi \to 0$ at the wall (Dirichlet boundary condition). We shall also sometimes consider the Neumann ($\partial\Psi/\partial n \to 0$) and periodic boundary conditions which are of computational and mathematical interest, but are of less physical significance.

To describe the thermodynamical and other equilibrium properties of a Bose gas, we assume that they follow from the usual rules of quantum statistical mechanics, which we describe in the following sections. Especially we *postulate* that the proper description of the gas in contact with a very large heat reservoir of temperature T follows from the so-called canonical ensemble, in which each energy state $\Psi_E(r^N)$ of the gas occurs with the probability $\mathrm{e}^{-\beta E}/Z$, where $\beta \equiv 1/kT$ and

$$Z = \Sigma_E\, \mathrm{e}^{-\beta E}\,, \tag{1.3}$$

---

* By $\partial/\partial \boldsymbol{r}_i$ we mean the gradient with respect to $\boldsymbol{r}_i$.

is the so-called partition function. Note that for an *ideal* Bose gas there is no mechanism which could insure the approach to the canonical equilibrium state; this becomes therefore a real postulate due to the fact that the ideal gas must always be considered as a limiting case.

1.2. Quantum mechanical ensembles and density matrices [‡]

The time evolution of $\Psi(r^N, t)$ is given by the Schrödinger equation (1.1). To each observable property of the system corresponds a Hermitian operator $O(p^N, r^N, t)$ and the average value of many measurements of that property (or the expectation value in the state Ψ) is given by:

$$\langle O\rangle = \int \mathrm{d}r^N\, \Psi^*(r^N, t)\, \hat{O}\, \Psi(r^N, t)\,, \tag{1.4}$$

in which $\Psi(r^N, t)$ is assumed to be normalized to unity. In analogy with classical statistical mechanics we define a statistical *ensemble* as a collection of identical systems (described by the same Hamiltonian operator H) which are in different states $\Psi_\alpha(r^N, t)$ occurring with a given probability P_α. The ensemble average of the expectation values is given by:

$$\langle\langle O\rangle\rangle = \sum_\alpha P_\alpha \langle O\rangle_\alpha = \sum_\alpha P_\alpha \int \mathrm{d}r^N\, \Psi_\alpha^*(r^N, t)\, \hat{O}\, \Psi_\alpha(r^N, t)\,. \tag{1.5}$$

It combines the quantum mechanical and the statistical average and is therefore denoted by two brackets. We associate with $\langle\langle O\rangle\rangle$ the *macroscopic* measurement of the property O in the given ensemble and at a given time. Note that we have denoted for simplicity the different members of the ensemble by a discrete index α. This is of course not necessary and also continuous distributions of states may be considered.

Another way of writing (1.5) is obtained by introducing the so-called *density matrix*. Suppose one develops $\Psi_\alpha(r^N, t)$ in a complete orthogonal set of functions $u_j(r^N)$ according to:

$$\Psi_\alpha(r^N, t) = \sum_j a_{\alpha j}(t)\, u_j(r^N)\,. \tag{1.6}$$

Of course:

$$a_{\alpha j}(t) = \int \mathrm{d}r^N\, u_j^*(r^N)\, \Psi_\alpha(r^N, t)\,, \tag{1.7}$$

and because of the normalization of Ψ_i one has:

$$\sum_j |a_{\alpha j}(t)|^2 = 1\,, \tag{1.8}$$

$|a_{\alpha j}(t)|^2$ is the probability that in the state Ψ_α, the observable described by the functions $u_j(r^N)$ is in the state j. Introducing the density matrix:

$$\rho_{ij}(t) = \sum_\alpha P_\alpha\, a_{\alpha j}^*(t)\, a_{\alpha i}(t)\,, \tag{1.9}$$

then clearly the diagonal element $\rho_{jj}(t)$ is the probability that for the *ensemble* the observable defined by the functions u_j is in the state j. Using the expansion (1.6), one can then write the ensemble average $\langle\langle O \rangle\rangle$ as given by (1.5) in the form:

[‡] For more details see Tolman [33]; compare also de Boer [18].

$$\langle\langle O \rangle\rangle = \sum_{jk} O_{jk}\, \rho_{kj}(t) \equiv \mathrm{Tr}\, O\rho \,, \tag{1.10}$$

where

$$O_{jk} \equiv \int \mathrm{d}r^N u_j^*(r^N)\, \hat{O}\, u_k(r^N) \,, \tag{1.11}$$

is the matrix element of the observable O in the "representation" as defined by the set of functions $u_j(r^N)$. One easily verifies the following simple properties of the density matrix $\rho_{ij}(t)$:

a) $\rho_{ij}(t)$ is Hermitian: $\rho_{ij}^*(t) = \rho_{ji}(t)$. (1.12)

b) $\sum_j \rho_{jj}(t) \equiv \mathrm{Tr}\, \rho = \sum_\alpha P_\alpha = 1$. (1.13)

c) The ensemble average $\langle\langle O \rangle\rangle$ (1.10) is independent of the representation (≡ the set u_j). The change of representation will change ρ to:

$$\rho' = S^{-1} \rho S \,, \tag{1.14}$$

where S is a unitary matrix, and since also $O' = S^{-1} O S$ it follows that:

$$\mathrm{Tr}\, O'\rho' = \mathrm{Tr}\, O\rho \,. \tag{1.15}$$

d) Especially the expression (1.5) for $\langle\langle O \rangle\rangle$ can be looked upon as $\mathrm{Tr}\, O\rho$ in coordinate representation with:

$$\rho(r'^N, r''^N, t) = \sum_\alpha P_\alpha \Psi_\alpha^*(r''^N, t)\, \Psi_\alpha(r'^N, t) \,, \tag{1.16}$$

and

$$O(r'^N, r''^N) = \hat{O}\left(\frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial r'^N}, r'^N\right) \delta(r'^N - r''^N) \,, \tag{1.17}$$

so that:

$$\begin{aligned} \langle\langle O \rangle\rangle = \mathrm{Tr}\, O\rho &= \int \mathrm{d}r'^N\, \mathrm{d}r''^N\, O(r'^N, r''^N)\, \rho(r''^N, r'^N; t) \\ &= \int \mathrm{d}r'^N \left[O\left(\frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial r'^N}, r'^N\right) \rho(r'^N, r''^N; t)\right]_{r'^N = r''^N} . \end{aligned} \tag{1.18}$$

We will use this last form most of the time. Note that it also follows directly from (1.5).

The time development of the density matrix is governed by the quantum mechanical Liouville equation, which in the coordinate representation has the form:

$$\left(\hbar \mathrm{i} \frac{\partial}{\partial t} + \mathcal{L}_N\right) \rho(r'^N, r''^N; t) = 0 \,, \tag{1.19}$$

with

$$\mathcal{L}_N \equiv H\left(\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial r''^N}, r''^N\right) - H\left(\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial r'^N}, r'^N\right) . \tag{1.20}$$

It is a direct consequence of the Schrödinger equation (1.1). In general matrix form this can be written as:

$$\hbar\mathrm{i}\,\frac{\partial\rho}{\partial t} = \rho H - H\rho = [\rho, H] , \tag{1.21}$$

which is clearly analogous to the classical Liouville equation:

$$\partial\rho_{\mathrm{cl}}/\partial t = -\{\rho_{\mathrm{cl}}, H_{\mathrm{cl}}\} , \tag{1.22}$$

where the curly brackets denote the Poisson brackets.

In general the density matrix (just as ρ_{cl} in the classical theory) will depend on time. Again, just as in the classical theory, the ρ will be stationary in time if ρ depends only on constants of the motion. Especially if ρ is a function of the Hamilton operator H then the density matrix will not depend on time and can be written in the form:

$$\rho(r'^N r''^N) = \sum_E P_E \Psi_E^*(r''^N)\,\Psi_E(r'^N) , \tag{1.23}$$

where the sum goes over all eigenvalues of H and where $\Psi_E(r^N)$ are the eigenfunctions fulfilling the time independent Schrödinger equations:

$$H(p^N, r^N)\,\Psi_E(r^N) = E\,\Psi_E(r^N) . \tag{1.24}$$

This density matrix represents an ensemble of states $\Psi_E(r^N)\exp(-\mathrm{i}Et/\hbar)$ with weights P_E.

The canonical density matrix, which as mentioned in the introduction we assume to describe the thermodynamical equilibrium state of the system in contact with a heat reservoir, is a special case of (1.23) for which $P_E = \mathrm{e}^{-\beta E}/Z$ with $Z = \Sigma\,\mathrm{e}^{-\beta E}$. There are of course other stationary ensembles which are used to describe other physical situations, like the so-called *grand ensemble* which will be introduced in the next subsection.

1.3. The connection with thermodynamics

The explanation of the laws of thermodynamics is quite similar in quantum statistical mechanics as in the classical theory [‡]. The internal energy U and the generalized forces X_k are associated with the quantum statistical averages of their respective operators, which in the canonical ensemble are given by

$$U(N, T, a_1, a_2, ...) = \langle\langle H\rangle\rangle = \frac{1}{Z}\sum_E E\,\mathrm{e}^{-\beta E} , \tag{1.25}$$

$$X_k(N, T, a_1, a_2, ...) = \langle\langle(-\partial H/\partial a_k)\rangle\rangle = \frac{1}{Z}\sum_E (-\partial E/\partial a_k)\,\mathrm{e}^{-\beta E} . \tag{1.26}$$

The parameters a_1, a_2... are the generalized coordinates which characterize the outside force fields.

[‡] See for example Uhlenbeck and Ford [22] Chapter I.

Since we only consider the wall potential as an outside field, the parameters a_k describe the volume and the shape of the vessel in which the gas is enclosed. In each state of the gas the force acting "in the direction a_k" on the sources of the field is $(-\partial E/\partial a_k)$ of which X_k is the canonical average. If one changes the parameters a_k the work done *on* the gas is therefore given by:

$$\delta W = -\sum_k X_k \,\delta a_k \,. \tag{1.27}$$

If one then defines the entropy S by:

$$S(N, T, a_1, a_2, ...) = -k \sum_E \frac{\mathrm{e}^{-\beta E}}{Z} \ln \frac{\mathrm{e}^{-\beta E}}{Z} \,, \tag{1.28}$$

then one proves the first and second law, namely:

$$\delta U = T\delta S + \delta W \,. \tag{1.29}$$

Of course the second law only defines S within an additive constant. The value chosen by the definition (1.28) gives the correct ideal gas limit when $T \to \infty$. Note also that from (1.28) follows:

$$S = k \ln Z + U/T \,, \tag{1.30}$$

so that the Helmholtz free energy $F = U - TS$ is given by:

$$F(N, T, a_1, a_2, ...) = -kT \ln Z(N, T, a_1, a_2, ...) \,. \tag{1.31}$$

The partition function Z has therefore the familiar thermodynamic interpretation.

Note that the entropy is the ensemble "average" of $-k \ln (\mathrm{e}^{-\beta E}/Z)$, but since this contains Z the entropy is not the quantum-statistical average of any operator and therefore is not strictly an observable of the system. Thus the entropy (and consequently all thermodynamic potentials such as F) is a property not of a single microscopic state but instead of the ensemble itself. Note also that the thermodynamic functions only depend upon the energy levels so that the quantum mechanical "probability" only enters in the specification of those levels.

Although we are postulating that the canonical ensemble should be used to find the equilibrium properties, our calculations will lead us to the so-called grand canonical ensemble, and therefore we also give its development. To emphasize that the averages in this ensemble are different functions than in the canonical ensemble, we add the superscript gr to the symbols of the properties.

The grand canonical ensemble is a stationary ensemble composed of energy eigenstates of varying numbers of particles. To make the dependence on N explicit we now write $E_N \equiv E(N, T, a_1, a_2,...)$, $Z_N \equiv Z(N, T, a_1, a_2, ...)$. In this ensemble, each energy eigenstate $\Psi_{E_N}(r^N) \exp(\mathrm{i}E_N t/\hbar)$ is represented with the probability

$$\frac{1}{Z^{\mathrm{gr}}} \exp(-\alpha N - \beta E_N) \,. \tag{1.32a}$$

Where the normalization constant

$$Z^{\mathrm{gr}}(\alpha, T, a_1, a_2, ...) = \sum_{N, E_N} \exp(-\alpha N - \beta E_N) = \sum_{N=0}^{\infty} \mathrm{e}^{-\alpha N} Z_N \,, \tag{1.32b}$$

is called the grand partition function. Again $\beta = 1/kT$, and α will be defined soon. The role of the density matrices is not quite the same in the grand canonical ensemble; there is no complete density matrix since the number of particles is not fixed. It is necessary to consider only the so-called reduced density matrices, as we shall discuss in section 1.4. First we concentrate on the thermodynamic functions, which only depend upon the energy levels.

Again, the "mechanical" properties U and X_k are the quantum statistical averages of their respective operators, which are given by

$$U^{\mathrm{gr}}(\alpha, T, a_1, a_2, \ldots) = \langle\langle H\rangle\rangle^{\mathrm{gr}} = \frac{1}{Z^{\mathrm{gr}}} \sum_{N, E_N} E_N \exp(-\alpha N - \beta E_N) \,, \tag{1.33}$$

$$X_k^{\mathrm{gr}}(\alpha, T, a_1, a_2, \ldots) = \left\langle\left\langle -\frac{\partial H}{\partial a_k}\right\rangle\right\rangle^{\mathrm{gr}} = \frac{1}{Z^{\mathrm{gr}}} \sum_{N, E_N} \left(\frac{-\partial E_N}{\partial a_k}\right) \exp(-\alpha N - \beta E_N) \,. \tag{1.34}$$

The (average) number of particles in the system is associated with the quantum-statistical average of N,

$$N^{\mathrm{gr}}(\alpha, T, a_1, a_2, \ldots) = \langle\langle N\rangle\rangle^{\mathrm{gr}} = \frac{1}{Z^{\mathrm{gr}}} \sum_{N, E_N} N \exp(-\alpha N - \beta E_N) \,. \tag{1.35}$$

Then, one proves that the first and second laws of thermodynamics for a system with a variable number of particles

$$\delta U^{\mathrm{gr}} = T \delta S^{\mathrm{gr}} + \delta W^{\mathrm{gr}} + \mu \delta N^{\mathrm{gr}} \,, \tag{1.36}$$

(where μ is the chemical potential) is satisfied if the entropy is defined as

$$\begin{aligned} S^{\mathrm{gr}}(\alpha, T, a_1, a_2, \ldots) &= -k \sum_{N, E_N} \frac{\exp(-\alpha N - \beta E_N)}{Z^{\mathrm{gr}}} \ln \frac{\exp(-\alpha N - \beta E_N)}{Z^{\mathrm{gr}}} \\ &= \frac{1}{T}\left(\frac{\alpha}{\beta} N^{\mathrm{gr}} + U^{\mathrm{gr}} + kT \ln Z^{\mathrm{gr}}\right) , \end{aligned} \tag{1.37}$$

and the association $\alpha = -\beta\mu$ is made. It follows that the thermodynamic potential $\Omega \equiv U - TS - \mu N$ is directly related to the grand partition function as follows:

$$\Omega^{\mathrm{gr}}(\alpha, T, a_1, a_2, \ldots) = -kT \ln Z^{\mathrm{gr}}(\alpha, T, a_1, a_2, \ldots) \,. \tag{1.38}$$

Usually the ensembles are considered to be practically equivalent for large systems, even though they are meant to describe different physical situations. In fact as we shall show in section 3 this can be proved in general in a one phase region. However when the system is in a two phase region, the equivalence of the two ensembles becomes problematical. We will come back to this in the next section, in which this difference is one of our main concerns.

1.4. The bulk limit and surface corrections

1.4.1. Thermodynamical considerations

For a given thermodynamic system, there are a set of generalized coordinates a_i and forces X_i such that the work is given by (1.27). Usually these coordinates characterize the boundary of the region, especially the volume. In fact, almost always the volume is the only coordinate that enters in the work, so that

$$\delta W = -p \delta V \,. \tag{1.39}$$

This is actually valid in two different situations. On one hand, it is rigorously true for any finite system in which work is only done through changing the volume (compression), and in which there is only one way to change that volume, say by moving a piston in a cylinder, or by expanding the boundaries of the system in all directions while keeping the shape the same. Then the function $p(V, T)$ is peculiar to that specific system. But on the other hand, if one assumes that the system is spatially homogeneous, and that there are no effects from the surface, then the only (compression) work can come from changing the volume, and here too the work would be given by (1.39). Now the function p can depend only on T and the density $\rho = N/V$, and must be the same function for systems of all shapes and sizes. In fact this is usually assumed, although not always explicitly stated. This homogeneity property holds empirically for many large systems and simplifies their thermodynamic description. It is an assumption and does not *follow* from thermodynamics.

With the single work term (1.39) the laws of thermodynamics (allowing for a variation in N)

$$dU = T\,dS - p\,dV + \mu\,dN\,, \tag{1.40}$$

which implies that U is a function of S, V and N, and likewise T, p and μ are functions of S, V and N since $T = (\partial U/\partial S)_{V,N}$ etc. The assumption of the existence of the bulk limit implies that U is a homogeneous function of the first order in S, V and N so that for any positive number λ,

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)\,. \tag{1.41}$$

This implies in turn that T, p and μ are homogeneous functions of the zeroth order in S, V and N; they do not change if one increases the size of the system by λ, and are therefore called *intensive* variables in contrast to the *extensive* variables U, S, V and N. Differentiating (1.41) with respect to λ and setting $\lambda = 1$, this implies

$$U(S, V, N) = S\left(\frac{\partial U}{\partial S}\right)_{V,N} + V\left(\frac{\partial U}{\partial V}\right)_{S,N} + N\left(\frac{\partial U}{\partial N}\right)_{S,V} = TS - pV + \mu N\,. \tag{1.42}$$

Then also

$$F \equiv U - TS = -pV + \mu N\,, \tag{1.43}$$

$$\Omega \equiv F - \mu N = -pV\,. \tag{1.44}$$

Thus, for a homogeneous system, μ is the Gibbs free energy per particle $(U - TS + pV)/N$. An independent variable can be eliminated in (1.41) by setting λ equal to $1/S$, $1/V$, or $1/N$. The most common choice is the latter, but it will be convenient for the discussion of the surface tension to choose $\lambda = 1/V$. Then,

$$U = V\,U(S/V, 1, N/V) \equiv V u(s, \rho)\,, \tag{1.45}$$

where $s \equiv S/V$ and $\rho \equiv N/V$. With these definitions, (1.40) and (1.42) become respectively

$$du = T\,ds + \mu\,d\rho\,, \tag{1.46}$$

and

$$\rho\mu = u - Ts + p\,. \tag{1.47}$$

These imply the Gibbs–Duhem relation:

$$\mathrm{d}p = \rho\,\mathrm{d}\mu + s\,\mathrm{d}T\,. \tag{1.48}$$

Then (1.46) can be viewed as the basic "law" between the variables u, T, s, μ, and ρ, with p defined by (1.47), or equivalently (1.48) can be viewed as the basic law between p, ρ, μ, s, and T, with (1.47) serving as the definition of u.

If the functional relationship between u, s, and ρ is known (such as $u(s, \rho)$) then from (1.46) and (1.47) the other thermodynamic variables μ, T, and p follow. Similarly, if the relation between μ, p, and T is known (such as $p(\mu, T)$) then from (1.47) and (1.48) the variables ρ, s, and u follow. However, neither the functions $u(s, \rho)$ nor $p(\mu, T)$ are usually measured directly. Instead, one measures the equation of state $p(\rho, T)$. Using the Maxwell relation

$$\left(\frac{\partial(s/\rho)}{\partial(1/\rho)}\right)_T = \left(\frac{\partial p}{\partial T}\right)_\rho\,, \tag{1.49}$$

which follows from (1.48), $s(\rho, T)$ can be deduced from $p(\rho, T)$ except for a function of the temperature, which can be determined by a specific heat measurement. Then all of the thermodynamic functions follow.

This is the usual theory of bulk thermodynamics. Yet the property of homogeneity can never be exactly true, as there must always be local variations near the surface at least. If these variations are restricted to within a finite distance from the wall that is small compared with the size of the system and the local radius of curvature, then one would expect that the nature of the surface variations is the same all around and that they contribute a correction to the extensive thermodynamic properties of the system that is proportional to the surface area A. We now derive the various relations between these bulk and surface properties that follow from the laws of thermodynamics. These considerations are similar to Gibbs' theory of surface tension ‡, which deals especially with the free surface between two separated fluid phases. The surface corrections that we are considering correspond to the surface tension between a fluid and a solid wall, which is a less familiar form of surface tension.

Thus we assume firstly that both the volume V and the area A play a role in the thermodynamics, so that the work term is $\delta W = -p\delta V + \gamma\delta A$, and γ is the force associated with changing the area without changing the volume – the so-called surface tension. The basic law replacing (1.40) is

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \gamma\,\mathrm{d}A + \mu\,\mathrm{d}N\,. \tag{1.50}$$

It is convenient to introduce the potential $\Omega \equiv U - TS - \mu N$, so that

$$\mathrm{d}\Omega = -S\,\mathrm{d}T - p\,\mathrm{d}V + \gamma\,\mathrm{d}A - N\,\mathrm{d}\mu\,, \tag{1.51}$$

and $\Omega = \Omega(T, V, A, \mu)$. Besides V and A, Ω depends only upon the intensive quantities T and μ. Our second assumption is that Ω is a sum of functions proportional to the volume and the area:

$$\Omega(T, V, A, \mu) = V\omega(T, \mu) + A\omega'(T, \mu)\,. \tag{1.52}$$

This is an extension of the bulk homogeneity assumption (1.45), which in terms of the potential Ω is just the first term above. Of course this is meant to hold only in the asymptotic sense when both V and A are very large. Now it follows from (1.51) and (1.52) that

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‡ Gibbs [34]. A concise treatment has been given by Ono and Kondo [35].

$$p = -(\partial\Omega/\partial V)_{T,A,\mu} = -\omega\,, \tag{1.53}$$

$$\gamma = (\partial\Omega/\partial A)_{T,V,\mu} = \omega'\,, \tag{1.54}$$

$$S = -(\partial\Omega/\partial T)_{V,A,\mu} = V(\partial p/\partial T)_\mu + A(-\partial\gamma/\partial T)_\mu \equiv Vs + As'\,, \tag{1.55}$$

$$N = -(\partial\Omega/\partial\mu)_{T,V,A} = V(\partial p/\partial\mu)_T + A(\partial\gamma/\partial\mu)_T \equiv V\rho + A\rho'\,, \tag{1.56}$$

and

$$\mathrm{d}p = \rho\,\mathrm{d}\mu + s\,\mathrm{d}T\,, \tag{1.57}$$

$$-\mathrm{d}\gamma = \rho'\,\mathrm{d}\mu + s'\,\mathrm{d}T\,. \tag{1.58}$$

Likewise, all potentials have a volume part and a surface part. For example, the internal energy which is related to Ω by $U = \Omega + TS + \mu N$ is given by $Vu + Au'$, where u and u' are

$$u = -p + Ts + \rho\mu\,, \tag{1.59}$$

$$u' = \gamma + Ts' + \rho'\mu\,. \tag{1.60}$$

These follow directly from (1.53)–(1.56). As one would expect, the volume parts are identical to the bulk properties, as (1.57) is identical to (1.48). The area parts act like another phase (although two-dimensional) with the equation of state (1.58), and linked to the bulk phase by the common T and μ.

As we have shown, measuring $\rho(p, T)$ and c_V determines all of the bulk properties, such as $\mu(\rho, T)$. Therefore, if one also measures $\gamma(\rho, T)$ (say), then $\gamma(\mu, T)$ follows, and then using (1.58) all of the surface properties can be found.

The function p can be shown to be the pressure far from the surface. One way to see this is to consider a bounded system that is enlarged in such a way that the shape remains the same, so that both the volume and the surface area of the system change. Say δV and δA are the changes of the volume and area associated with a small element of the surface. Then the normal pressure on the surface is given by

$$p_n = -\delta W/\delta V = p - \gamma\,\delta A/\delta V\,, \tag{1.61}$$

where we have used that $\delta W = -p\delta V + \gamma\delta A$. A simple geometrical argument shows that the ratio of the change of the area to the change of the volume of a small element of the surface with the shape invariant is given by [‡]

$$\delta A/\delta V = 1/R_1 + 1/R_2\,, \tag{1.62}$$

where R_1 and R_2 are the principle radii of curvature at that point of the surface. Combining (1.61) and (1.62) gives the Laplace formula for the surface tension – if p is the pressure far from the surface.

1.4.2. Statistical interpretation

As we have shown in section 1.3, the partition functions are directly related to the thermodynamical properties. In the canonical ensemble,

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[‡] See for example Landau and Lifshitz [36] p. 230.

$$F = -kT \ln Z\,, \tag{1.63}$$

and in the grand canonical ensemble,

$$\Omega^{\mathrm{gr}} = -kT \ln Z^{\mathrm{gr}}\,. \tag{1.64}$$

These associations are strictly true for a finite system, for which there are always surface effects due to the discrete (particulate) nature of matter. To calculate the bulk thermodynamic properties, for which there are no contributions from the surface and for which the condensation is marked by a singularity in the equation of state, it is necessary to make the volume of the system infinite with the density $N/V = \rho$ fixed. *In this limit* the bulk properties can be calculated from the partition functions:

$$\lim_{V\to\infty} -\frac{kT}{V} \ln Z = f = -p + \rho\mu\,, \tag{1.65}$$

$$\lim_{V\to\infty} -\frac{kT}{V} \ln Z^{\mathrm{gr}} = \omega^{\mathrm{gr}} = -p^{\mathrm{gr}}\,, \tag{1.66}$$

where $-p + \rho\mu$ and $-p^{\mathrm{gr}}$ depend only upon ρ and T. Note that in the grand canonical ensemble, the N above refers to the average value N^{gr} defined in (1.35).

We call the limit $V \to \infty$ with $N/V = \rho$ the "bulk limit" because it enables the bulk properties to be calculated from the partition functions. We use this name rather than the more familiar "thermodynamic limit" because the latter gives the misleading impression that thermodynamics is only related to statistical mechanics in that limit, which is not true. In the case of thermodynamics, the bulk limit is simply *assumed* (namely the assumption of homogeneity) while in statistical mechanics it must be *proven*. That proof must be carried out for a particular system and is not simple to do.

We expect that the next leading term in the asymptotic expansion is proportional to the surface area, and that the thermodynamic theory of the surface corrections that we have presented should apply. Namely,

$$-kT \ln Z \sim (-p + \rho\mu)V + (\gamma + \rho'\mu)A\,, \tag{1.69}$$

$$-kT \ln Z^{\mathrm{gr}} \sim -p^{\mathrm{gr}} V + \gamma^{\mathrm{gr}} A\,. \tag{1.70}$$

This again requires proof for every system under consideration, in which case the surface tension can be calculated directly from the partition functions as shown above. Using (1.50) one can also write the surface tension as follows:

$$\gamma = (\partial F/\partial A)_{T,V,N} = (\partial/\partial A)_{T,V,N}(-kT \ln Z)\,, \tag{1.71}$$

$$\gamma^{\mathrm{gr}} = (\partial \Omega^{\mathrm{gr}}/\partial A)_{\mu,V,T} = (\partial/\partial A)_{\mu,V,T}(-kT \ln Z^{\mathrm{gr}})\,. \tag{1.72}$$

Again the problem arises whether the two ensembles give identical results for the surface tension and the other surface properties.

1.5. The reduced density matrices, the hierarchy, and the general conservation laws

In this subsection we go back to the temporal development of the general density matrix of a non-ideal gas (not necessarily in equilibrium) as described by the quantum Liouville equation (1.19). Our main purpose is to develop the quantum mechanical analogue of the so-called B-B-G-K-Y hierarchy of equations in classical statistical mechanics, and to develop the corresponding conservation laws.

Consider a system of N particles in a region Λ of volume V, whose density matrix is $\rho(\boldsymbol{r}'_1, \ldots \boldsymbol{r}'_N, \boldsymbol{r}''_1, \ldots \boldsymbol{r}''_N; N, \Lambda, t)$ as given by (1.16). The so-called s-particle reduced density matrices are defined by ‡:

$$\rho_s(\boldsymbol{r}'_1, \ldots \boldsymbol{r}'_s, \boldsymbol{r}''_1, \ldots \boldsymbol{r}''_s; N, \Lambda, t) \equiv \frac{N!}{(N-s)!} \int_\Lambda \mathrm{d}\boldsymbol{r}^{s+1} \ldots \int_\Lambda \mathrm{d}\boldsymbol{r}^N$$

$$\times\ \rho(\boldsymbol{r}'_1, \ldots \boldsymbol{r}'_s, \boldsymbol{r}_{s+1}, \ldots \boldsymbol{r}_N, \boldsymbol{r}''_1, \ldots \boldsymbol{r}''_s, \boldsymbol{r}_{s+1}, \ldots \boldsymbol{r}_N; N, \Lambda, t)\,. \tag{1.73}$$

For simplicity we will supress the dependence on N, Λ, and t, and use as before the abbreviated notation $r'^s \equiv \boldsymbol{r}'_1, \ldots \boldsymbol{r}'_s$ etc. Note that $\rho_N(r'^N, r''^N) = N!\rho(r'^N, r''^N)$. From the normalization

$$\int_\Lambda \mathrm{d}r^N\, \rho(r^N, r^N) = 1\,, \tag{1.74}$$

which is equivalent to (1.13) it follows that

$$\int_\Lambda \mathrm{d}r^s\, \rho_s(r^s, r^s) = \frac{N!}{(N-s)!}\,, \tag{1.75}$$

and that the successive matrices are interrelated by

$$(N-s)\,\rho_s(r'^s, r''^s) = \int_\Lambda \rho_{s+1}(r'^s, \boldsymbol{r}_{s+1}, r''^s, \boldsymbol{r}_{s+1})\, \mathrm{d}\boldsymbol{r}_{s+1}\,. \tag{1.76}$$

The equations of motion for ρ_s follow from the quantum Liouville equation (1.19). In the coordinate representation and for a general Hamiltonian

$$H(p^N, r^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \Phi(r^N)\,, \tag{1.77}$$

(where now Φ contains both interaction and external potentials) one obtains by directly integrating (1.19–20):

$$\left[\hbar \mathrm{i}\,\frac{\partial}{\partial t} + \sum_{i=1}^{s} \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial \boldsymbol{r}'^2_i} - \frac{\partial^2}{\partial \boldsymbol{r}''^2_i}\right)\right]\rho_s(r'^s, r''^s)$$

$$= \frac{N!}{(N-s)!} \int_\Lambda \mathrm{d}r^{N-s}\, \{\Phi(r'^s, r^{N-s}) - \Phi(r''^s, r^{N-s})\}\; \rho(r'^s, r^{N-s}, r''^s, r^{N-s})\,. \tag{1.78}$$

We have used the abbreviations $r^{N-s} \equiv \boldsymbol{r}_{s+1}, \ldots \boldsymbol{r}_N$ and $\mathrm{d}r^{N-s} \equiv \mathrm{d}\boldsymbol{r}_{s+1} \ldots \mathrm{d}\boldsymbol{r}_N$.

The diagonal element of the s-particle density matrix defines the so-called s-particle (reduced) distribution functions. We shall write

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‡ These were first discussed in detail by Husimi [37] and de Boer [18].

$$n_s(r^s) \equiv \rho_s(r^s, r^s)\,. \tag{1.79}$$

Especially $n_1(r)$ is the density of particles and $\int n_1(r)\,\mathrm{d}r = N$ as follows from (1.75). By putting $r'^s = r''^s$ in (1.78) one obtains the equations of motion for the distribution functions. For $s = 1$ for example one gets:

$$\frac{\partial n_1(r)}{\partial t} + \frac{\hbar}{2m\mathrm{i}}\left[\left(\frac{\partial^2}{\partial r'^2} - \frac{\partial^2}{\partial r''^2}\right)\rho_1(r', r'')\right]_{r'=r''=r} = 0\,. \tag{1.80}$$

This can be cast in the form of a continuity equation:

$$\frac{\partial}{\partial t}(mn_1(r)) + \frac{\partial}{\partial r_\alpha}(mn_1(r)\,v_\alpha(r)) = 0\,, \tag{1.81}$$

where $mn_1(r)$ is the mass density (often called $\rho(r)$) and

$$mn_1(r)\,v_\alpha(r) \equiv \frac{\hbar}{\mathrm{i}}\left[\frac{\partial}{\partial \xi_\alpha}\tilde{\rho}_1(r, \xi)\right]_{\xi=0}\,, \tag{1.82}$$

is the α-component of the momentum current. In (1.81) the sum over α is implied according to the usual convention with repeated indices. We have introduced $\tilde{\rho}_1$ according to

$$\tilde{\rho}_1(r, \xi) \equiv \rho_1(r + \tfrac{1}{2}\xi, r - \tfrac{1}{2}\xi) = \rho_1(r', r'')\,. \tag{1.83}$$

That is, $\tilde{\rho}_1$ is just ρ_1 with the change of variables

$$r = \tfrac{1}{2}(r' + r'')\,, \qquad \xi = r' - r''\,. \tag{1.84}$$

Note that for a single particle system in a pure state* ψ, $\rho_1(r', r'') = \psi^*(r'')\,\psi(r')$ and (1.82) becomes the familiar expression for the probability current density:

$$\psi^*(r)\,\psi(r)\,v_\alpha(r) = \frac{\hbar}{2m\mathrm{i}}\left\{\psi^*(r)\frac{\partial}{\partial r_\alpha}\psi(r) - \psi(r)\frac{\partial}{\partial r_\alpha}\psi^*(r)\right\}. \tag{1.85}$$

For a non-ideal gas in which the interaction between the particles is due to a pair potential $\phi(r_{ij})$ (where $r_{ij} \equiv |r_i - r_j|$) so that the total potential is of the form

$$\Phi(r^N) = \sum_{i<j=1}^{N}\phi(r_{ij}) + \sum_{i=1}^{N}\Phi^{\mathrm{ext}}(r_i)\,, \tag{1.86}$$

the equations (1.78) can be further simplified. One obtains:

$$\left(\hbar\mathrm{i}\frac{\partial}{\partial t} + \mathcal{L}_s\right)\rho_s(r'^s, r''^s) = \sum_{i=1}^{s}\int\{\phi(|r_i' - r_{s+1}|) - \phi(|r_i'' - r_{s+1}|)\}\,\rho_{s+1}(r'^s, r_{s+1}, r''^s, r_{s+1})\,\mathrm{d}r_{s+1}\,, \tag{1.87}$$

$$\mathcal{L}_s \equiv \sum_{i=1}^{s}\left[\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r_i'^2} - \frac{\partial^2}{\partial r_i''^2}\right) - \Phi^{\mathrm{ext}}(r_i') + \Phi^{\mathrm{ext}}(r_i'') - \sum_{j>i}[\phi(r_{ij}') - \phi(r_{ij}'')]\right]. \tag{1.88}$$

This is the hierarchy of coupled equations for the density matrices, which is the analogue of the B-B-G-K-Y hierarchy for the reduced phase space distributions in classical statistical mechanics. It has also recently been given by Putterman [19], and had been partially derived by Penrose [23] and Frohlich [38] among others [‡]. The first equation is:

$$\hbar \mathrm{i} \frac{\partial \rho_1(\boldsymbol{r}_1' \boldsymbol{r}_1'')}{\partial t} + \left\{ \frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial \boldsymbol{r}_1'^2} - \frac{\partial^2}{\partial \boldsymbol{r}_1''^2} \right) - \Phi^{\mathrm{ext}}(\boldsymbol{r}_1') + \Phi^{\mathrm{ext}}(\boldsymbol{r}_1'') \right\} \rho_1(\boldsymbol{r}_1' \boldsymbol{r}_1'')$$

$$= \int [\phi(|\boldsymbol{r}_1' - \boldsymbol{r}_2|) - \phi(|\boldsymbol{r}_1'' - \boldsymbol{r}_2|)]\, \rho_2(\boldsymbol{r}_1', \boldsymbol{r}_2, \boldsymbol{r}_1'', \boldsymbol{r}_2)\, \mathrm{d}\boldsymbol{r}_2 \,. \tag{1.89}$$

Just as in the classical theory [‡‡], basic consequences of the hierarchy (1.87–1.88) are the general conservation laws of mass, momentum and energy with the corresponding expressions for the fluxes. The local conservation laws are:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial r_\alpha} (\rho v_\alpha) = 0 \,, \tag{1.90}$$

$$\frac{\partial}{\partial t} (\rho v_\alpha) + \frac{\partial}{\partial r_\beta} (\rho v_\alpha v_\beta + P_{\alpha\beta}) = -\rho \frac{\partial}{\partial r_\alpha} \frac{\Phi^{\mathrm{ext}}}{m} \,, \tag{1.91}$$

$$\frac{\partial}{\partial t} (\rho \epsilon) + \frac{\partial}{\partial r_\alpha} (\rho \epsilon v_\alpha + J_\alpha) = -\tfrac{1}{2} \left\{ \frac{\partial v_\alpha}{\partial r_\beta} + \frac{\partial v_\beta}{\partial r_\alpha} \right\} P_{\alpha\beta} \,, \tag{1.92}$$

where $\rho = \rho(\boldsymbol{r})$ is the mass density, $P_{\alpha\beta} = P_{\alpha\beta}(\boldsymbol{r})$ is the local stress tensor, $\epsilon = \epsilon(\boldsymbol{r})$ is the local specific energy (energy per unit mass), and $J_\alpha = J_\alpha(\boldsymbol{r})$ is the local current density. Following the usual convention in hydrodynamics, we use *in this section only* for the mass density $mn_1(\boldsymbol{r})$ the symbol $\rho(\boldsymbol{r})$ and for the specific energy the symbol ϵ, whereas in the rest of this thesis ρ will be used for the *average number density* N/V, and ϵ will be used for the single particle energy levels.

The derivation of the conservation laws from the hierarchy is similar to the classical theory, except that there is an ambiguity in the expressions for the local quantities which is due to the non-commutability of the operators which enter in their definitions. This requires an additional rule, the so-called Weyl correspondence of the classical operators as we shall explain later.

The mass conservation law (1.90) follows from the first hierarchy equation (1.89) as before with the mass current density given by (1.82). Note that here there is already an ambiguity in the definition of $\rho \boldsymbol{v}$ since one could add any vector whose divergence is zero.

Next, the equation of motion for $\boldsymbol{v}$ (that is, the momentum conservation law) (1.91) can be derived by taking $(\hbar/\mathrm{i})(\partial/\partial \xi_\alpha)$ of (1.89) after making the change of variables (1.84) and again letting $\boldsymbol{\xi} \to 0$. The result can be cast in the form of (1.91), giving for the stress tensor $P_{\alpha\beta} = P^{\mathrm{k}}_{\alpha\beta} + P^{\phi}_{\alpha\beta}$, where

$$P^{\mathrm{k}}_{\alpha\beta}(\boldsymbol{r}) = \frac{1}{m} \left[\left(\frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \xi_\alpha} - m v_\alpha(\boldsymbol{r}) \right) \left(\frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \xi_\beta} - m v_\beta(\boldsymbol{r}) \right) \tilde{\rho}_1(\boldsymbol{r}, \boldsymbol{\xi}) \right]_{\boldsymbol{\xi}=0} \,, \tag{1.93}$$

$$P^{\phi}_{\alpha\beta}(\boldsymbol{r}) = \tfrac{1}{2} \int \frac{R_\alpha R_\beta}{R^2} \phi'(R)\, \mathrm{d}\boldsymbol{R} \int_0^R \mathrm{d}\lambda\, n_2\!\left(\boldsymbol{r} + (\lambda - R) \frac{\boldsymbol{R}}{R} \,, \boldsymbol{r} + \lambda \frac{\boldsymbol{R}}{R} \right). \tag{1.94}$$

The steps that give $P^{\mathrm{k}}_{\alpha\beta}$ are straightforward, and those that lead to $P^{\phi}_{\alpha\beta}$ are identical to the classical derivation, to which the reader is referred [‡‡] (in fact (1.94) is formally identical to the classical expression). Note that $n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the two particle distribution function defined by (1.79).

[‡] Also, the hierarchy of equations of the so-called Wigner distribution functions, which are a kind of Fourier transform of the density matrices, have been given by Irving and Zwanzig [39].

[‡‡] See Uhlenbeck and Ford [22] Chapter 7.

Finally, defining the local internal energy density $\rho\epsilon = \rho(\epsilon^{\mathrm{k}} + \epsilon^{\phi} + \Phi^{\mathrm{ext}}/m)$ with:

$$\rho\,\epsilon^{\mathrm{k}}(\boldsymbol{r}) = \frac{1}{2m}\left[\left(\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \xi_\beta} - m v_\beta(\boldsymbol{r})\right)^2 \tilde{\rho}_1(\boldsymbol{r}, \boldsymbol{\xi})\right]_{\boldsymbol{\xi}=0} \tag{1.95}$$

$$\rho\,\epsilon^{\phi}(\boldsymbol{r}) = \tfrac{1}{2}\int \phi(r_{12})\, n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)\,\mathrm{d}\boldsymbol{r}_2\,, \tag{1.96}$$

the conservation of energy (1.91) can be derived. Note that in ϵ^{k} the transport kinetic energy $\frac{1}{2}\rho v^2$ has been subtracted off, and only the *internal* energy density enters in (1.95).

To derive the conservation law (1.91) one must find the rate of change of both ϵ^{k} and ϵ^{ϕ}. The equation for ϵ^{k} follows from (1.89) in a way similar to the derivation of the momentum equation. To find the equation for ϵ^{ϕ} the second hierarchy equation (eq. (1.87–88) for $s = 2$) is needed. The derivation is completely analogous to the classical case, with the result that the energy flux is a sum of the following three terms:

$$J^{\mathrm{k}}_\alpha(\boldsymbol{r}) = \left[\frac{1}{m}\left\{\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \xi_\alpha} - m v_\alpha(\boldsymbol{r})\right\}\frac{1}{2m}\left|\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \xi_\beta} - m v_\beta(\boldsymbol{r})\right|^2 \tilde{\rho}_1(\boldsymbol{r}, \boldsymbol{\xi})\right]_{\boldsymbol{\xi}=0}, \tag{1.97}$$

$$J^{\phi 1}_\alpha(\boldsymbol{r}) = \int \frac{\phi(|\boldsymbol{r}-\boldsymbol{r}_2|)}{2}\,\frac{1}{m}\left[\left\{\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \xi_{1\alpha}} - m v_\alpha(\boldsymbol{r})\right\}\tilde{\rho}_2(\boldsymbol{r}, \boldsymbol{r}_2; \boldsymbol{\xi}_1, \boldsymbol{\xi}_2)\right]_{\boldsymbol{\xi}_1,\boldsymbol{\xi}_2=0} \mathrm{d}\boldsymbol{r}_2\,, \tag{1.98}$$

$$\begin{aligned} J^{\phi 2}_\alpha(\boldsymbol{r}) = \int \frac{R_\alpha R_\beta}{2R^2}\,\phi'(R)\,\mathrm{d}\boldsymbol{R}\int_0^R \mathrm{d}\lambda\,\Bigg[\frac{1}{m}\left\{\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \xi_{1\beta}} - m v_\beta(\boldsymbol{r}) + \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \xi_{2\beta}} - m v_\beta(\boldsymbol{r})\right\} \\ \times\, \tilde{\rho}_2\!\left(\boldsymbol{r} + (\lambda - R)\frac{\boldsymbol{R}}{R}, \boldsymbol{r} + \lambda\frac{\boldsymbol{R}}{R}; \boldsymbol{\xi}_1, \boldsymbol{\xi}_2\right)\Bigg]_{\boldsymbol{\xi}_1,\boldsymbol{\xi}_2=0}, \end{aligned} \tag{1.99}$$

where $\tilde{\rho}_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{\xi}_1, \boldsymbol{\xi}_2) \equiv \rho_2(\boldsymbol{r}_1 + \frac{1}{2}\boldsymbol{\xi}_1, \boldsymbol{r}_2 + \frac{1}{2}\boldsymbol{\xi}_2; \boldsymbol{r}_1 - \frac{1}{2}\boldsymbol{\xi}_1, \boldsymbol{r}_2 - \frac{1}{2}\boldsymbol{\xi}_2)$, similar to the definition of $\tilde{\rho}_1$ given by (1.83). In general we can write these as:

$$\tilde{\rho}_s(r^s, \xi^s) = \rho_s(r^s + \tfrac{1}{2}\xi^s, r^s - \tfrac{1}{2}\xi^s)\,. \tag{1.100}$$

We now return to the ambiguity mentioned earlier. To illustrate the problem let us consider only the three local quantities $\rho(\boldsymbol{r})$, $\rho(\boldsymbol{r})\,\boldsymbol{v}(\boldsymbol{r})$, and $\rho(\boldsymbol{r})\,\epsilon^{\mathrm{k}}_{\mathrm{tot}}(\boldsymbol{r}) \equiv \rho(\boldsymbol{r})\,[\epsilon^{\mathrm{k}}(\boldsymbol{r}) + \frac{1}{2}v(\boldsymbol{r})^2]$, which are respectively the mass density, momentum density, and total kinetic energy density. One would like them to be quantum mechanical averages of operators of the form $\mathcal{O}(p^N, r^N)$ similar to the functions $\mathcal{O}_{\mathrm{cl}}(p^N, r^N)$ which lead to the local classical quantities. For the mass density $\rho(\boldsymbol{r})$ there is no difficulty; the corresponding operator is clearly

$$\mathcal{O}^{(1)} = m\sum_{i=1}^{N}\delta(\boldsymbol{r} - \boldsymbol{r}_i) = \mathcal{O}^{(1)}_{\mathrm{cl}}\,, \tag{1.101}$$

where the coordinate $\boldsymbol{r}$ is a parameter in the operator. However, for the momentum density, the classical function is

$$\mathcal{O}^{(2)}_{\mathrm{cl},\alpha} = \sum_{i=1}^{N} p_{i\alpha}\,\delta(\boldsymbol{r} - \boldsymbol{r}_i)\,, \tag{1.102}$$

which would not itself be an Hermitian quantum mechanical operator, if p_i and r_i were taken to be operators. The same is true for the kinetic energy density, for which the classical function is

$$\mathcal{O}_{\mathrm{cl}}^{(3)} = \sum_{i=1}^{N} \frac{p_i^2}{2m}\,\delta(\boldsymbol{r}-\boldsymbol{r}_i)\,. \tag{1.103}$$

The operators $\mathcal{O}^{(2)}$ and $\mathcal{O}^{(3)}$ must be Hermitian so that $\rho\, v_\alpha$ and $\rho\,\epsilon_{\mathrm{tot}}^{\mathrm{k}}$ are real. Also one must require that

$$\int_\Lambda \rho\, v_\alpha\, \mathrm{d}\boldsymbol{r} = \int_\Lambda \langle \mathcal{O}_\alpha^{(2)} \rangle\, \mathrm{d}\boldsymbol{r} = \sum_{i=1}^{N} \hat{p}_{i\alpha}\,, \tag{1.104}$$

and

$$\int_\Lambda \rho\, \epsilon_{\mathrm{tot}}^{\mathrm{k}}\, \mathrm{d}r = \int_\Lambda \langle \mathcal{O}^{(3)} \rangle\, \mathrm{d}\boldsymbol{r} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m}\,. \tag{1.105}$$

One might hope that by properly symmetrizing the classical functions one could guess the operators $\mathcal{O}^{(2)}$ and $\mathcal{O}^{(3)}$. For example one might replace $p_{i\alpha}\delta(\boldsymbol{r}-\boldsymbol{r}_i)$ in (1.102) by

$$\tfrac{1}{2}\,[\hat{p}_{i\alpha}\delta(\boldsymbol{r}-\boldsymbol{r}_i) + \delta(\boldsymbol{r}-\boldsymbol{r}_i)\,\hat{p}_{i\alpha}]\,, \tag{1.106}$$

which in fact leads to the local momentum density (1.82). But already for the local energy density the summand in (1.103) can be symmetrized in different ways, such as

$$\frac{1}{2}\,\frac{1}{2m}\,[\hat{p}_i^2\delta(\boldsymbol{r}-\boldsymbol{r}_i) + \delta(\boldsymbol{r}-\boldsymbol{r}_i)\hat{p}_i^2]\,, \tag{1.107}$$

$$\frac{1}{2m}\,[\hat{p}_{i\alpha}\delta(\boldsymbol{r}-\boldsymbol{r}_i)\,\hat{p}_{i\alpha}]\,, \tag{1.108}$$

$$\frac{1}{4}\,\frac{1}{2m}\,[\hat{p}_i^2\delta(\boldsymbol{r}-\boldsymbol{r}_i) + 2\hat{p}_{i\alpha}\delta(\boldsymbol{r}-\boldsymbol{r}_i)\hat{p}_{i\alpha} + \delta(\boldsymbol{r}-\boldsymbol{r}_i)\hat{p}_i^2]\,. \tag{1.109}$$

It can be verified that each of these is Hermitian and also satisfies (1.105), yet they give different expressions for the local kinetic energy. Using (1.18) one finds respectively:

$$\rho\epsilon_{\mathrm{tot}}^{\mathrm{k}_1} = -\frac{\hbar^2}{4m}\left[\left\{\frac{\partial^2}{\partial \boldsymbol{r}'^2} + \frac{\partial^2}{\partial \boldsymbol{r}''^2}\right\}\rho_1(\boldsymbol{r}',\boldsymbol{r}'')\right]_{\boldsymbol{r}'=\boldsymbol{r}''=\boldsymbol{r}} = -\frac{\hbar^2}{2m}\left[\left\{\frac{\partial^2}{\partial \boldsymbol{\xi}^2} + \frac{1}{4}\frac{\partial^2}{\partial \boldsymbol{r}^2}\right\}\tilde{\rho}_1(\boldsymbol{r},\boldsymbol{\xi})\right]_{\boldsymbol{\xi}=0}, \tag{1.110}$$

$$\rho\epsilon_{\mathrm{tot}}^{\mathrm{k}_2} = -\frac{\hbar^2}{2m}\left[\frac{\partial}{\partial r'_\alpha}\,\frac{\partial}{\partial r''_\alpha}\,\rho_1(\boldsymbol{r}',\boldsymbol{r}'')\right]_{\boldsymbol{r}'=\boldsymbol{r}''=\boldsymbol{r}} = -\frac{\hbar^2}{2m}\left[\left\{\frac{\partial^2}{\partial \boldsymbol{\xi}^2} - \frac{1}{4}\frac{\partial^2}{\partial \boldsymbol{r}^2}\right\}\tilde{\rho}_1(\boldsymbol{r},\boldsymbol{\xi})\right]_{\boldsymbol{\xi}=0}, \tag{1.111}$$

$$\rho\epsilon_{\mathrm{tot}}^{\mathrm{k}_3} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial \boldsymbol{\xi}^2}\,\tilde{\rho}_1(\boldsymbol{r},\boldsymbol{\xi})\right]_{\boldsymbol{\xi}=0}. \tag{1.112}$$

A solution to the problem is given by the Weyl correspondence rule (see [40]) which defines a unique Hermitian quantum mechanical operator $\mathcal{O}(p^N, r^N)$ for each classical function $\mathcal{O}_{\mathrm{cl}}(p^N, r^N)$. It can be stated directly in terms of the quantum mechanical average itself as follows (Irving and Zwanzig [39]): For a given classical function $\mathcal{O}_{\mathrm{cl}}(r^N, p^N)$ the corresponding quantum statistical average is given by

$$\langle \mathcal{O} \rangle = \int \mathrm{d}r^N \left[\mathcal{O}_{\mathrm{cl}}\left(\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \xi^N}\,, r^N\right)\,\tilde{\rho}(r^N, \xi^N)\right]_{\xi^N=0}. \tag{1.113}$$

It should be stressed however that this correspondence is *ad hoc*. For the momentum density this gives our expression (1.82) and implies in turn that the operator is symmetrized according to (1.106). For the kinetic energy density $O_{\mathrm{cl}}^{(3)}$ it gives the expression (1.112) above, which implies that the operator is symmetrized according to (1.109), and implies that the local kinetic energy density is given by the expression (1.95) that we have used ‡.

In the following we are only concerned with the equilibrium properties, in which case the density matrices $\rho_s(r'^s, r''^s; N, \Lambda, t)$ are replaced by the corresponding canonical equilibrium density matrices $\rho_s(r'^s, r''^s; N, \Lambda, T)$ which are time independent. The conservation laws simplify because the properties are time independent and also because $v = 0$. The equation of motion (1.91) becomes simply the statement of hydrostatic equilibrium:

$$\frac{\partial}{\partial r_\beta} P_{\alpha\beta}(\boldsymbol{r}) = -\rho(\boldsymbol{r}) \frac{\partial}{\partial r_\alpha} \frac{\Phi^{\mathrm{ext}}(\boldsymbol{r})}{m} . \tag{1.114}$$

Furthermore (1.92) implies that J_α must everywhere be zero.

In the grand canonical ensemble the density matrices are defined as averages of the canonical reduced density matrices as follows:

$$\rho_s^{\mathrm{gr}}(r'^s, r''^s; \alpha, \Lambda, T) \equiv \sum_{N=s}^{\infty} \frac{\mathrm{e}^{-\alpha N} Z(N, \Lambda, T)}{Z^{\mathrm{gr}}(\alpha, \Lambda, T)} \rho_s(r'^s, r''^s; N, \Lambda, T) . \tag{1.115}$$

The role of these density matrices are similar to those of the canonical ensemble. Making use of the fact that the canonical density matrices satisfy the equilibrium hierarchy, it can be verified that the grand canonical ones also satisfy it and lead therefore to the same conservation laws. Note however that there is no "complete" density matrix in the grand canonical ensemble. Note also that ρ_s^{gr} are normalized by

$$\int_\Lambda \mathrm{d}r^s\, \rho_s^{\mathrm{gr}}(r'^s, r''^s; \alpha, \Lambda, T) = \left\langle \frac{N!}{(N-s)!} \right\rangle^{\mathrm{gr}} , \tag{1.116}$$

and inter-related by

$$\left(-\frac{\partial}{\partial\alpha} + N^{\mathrm{gr}} - s\right) \rho_s^{\mathrm{gr}}(r'^s, r''^s; \alpha, \Lambda, T) = \int_\Lambda \rho_{s+1}^{\mathrm{gr}}(r'^s, \boldsymbol{r}, r''^s, \boldsymbol{r}; \alpha, \Lambda, T)\, \mathrm{d}\boldsymbol{r} . \tag{1.117}$$

In (1.116) and in the following we use one bracket instead of two for simplicity to denote the quantum statistical averages.

1.6. Specialization to the ideal Bose gas

Since the Hamiltonian of the ideal gas is a sum of single particle Hamiltonians

$$\hat{H}(p^N, r^N) = \sum_{i=1}^{N} \hat{H}_0(\boldsymbol{p}_i, \boldsymbol{r}_i) , \tag{1.118}$$

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‡ Putterman [19] has also derived the conservation laws with the corresponding expressions for the fluxes, based upon using (1.110) for the definition of the local energy density.

with

$$\hat{H}_0(\boldsymbol{p}_i, \boldsymbol{r}_i) \equiv \frac{\hat{p}_i^2}{2m} + \phi^{\text{ext}}(\boldsymbol{r}_i) \,, \tag{1.119}$$

the energy eigenvalues E and eigenfunctions $\Psi_E(r^N)$ can all be expressed in the single particle energy states ϵ_k and eigenfunctions $\psi_k(\boldsymbol{r})$ defined by:

$$\hat{H}_0(\boldsymbol{p}, \boldsymbol{r})\, \psi_k(\boldsymbol{r}) = \epsilon_k\, \psi_k(\boldsymbol{r}) \,. \tag{1.120}$$

(This ϵ_k should not be confused with the specific energy of the previous subsection.) One gets

$$E = E_{n_0 n_1 \ldots} = \sum_{k=0}^{\infty} n_k \epsilon_k \,, \tag{1.121}$$

where the occupation numbers $n_0, n_1, n_2, \ldots$ of the states ϵ_k satisfy

$$\sum_{k=0}^{\infty} n_k = N \,. \tag{1.122}$$

To satisfy the requirement of Bose statistics the $\Psi_E(r^N)$ must be the symmetrized sum of the products of the corresponding single particle functions $\psi_k(\boldsymbol{r})$, so that

$$\Psi_E(r^N) = \Psi_{n_0 n_1 n_2 \ldots}(r^N) = \frac{1}{\sqrt{N!\, n_0!\, n_1! \ldots}} \sum_{\mathrm{P}\{r^N\}} \underbrace{\underbrace{\psi_0(\boldsymbol{r}_1) \ldots \psi_0(\boldsymbol{r}_{n_0})}_{n_0} \; \underbrace{\psi_1(\boldsymbol{r}_{n_0+1}) \ldots}_{n_1} \qquad \ldots}_{} \,, \tag{1.123}$$

where the sum is over all permutations of the coordinates $r^N \equiv \boldsymbol{r}_1 \ldots \boldsymbol{r}_N$. These $\Psi(r^N)$ are normalized to unity in the $\psi_k(\boldsymbol{r})$.

With the energy levels all of the thermodynamic functions follow. The canonical partition function (1.3) for the IBG is

$$Z(N, \Lambda, T) = \sum_{\{n_k\}}^{N} \exp(-\beta \textstyle\sum_k n_k \epsilon_k) \,, \tag{1.124}$$

where the summation is over all occupation sets $\{n_k\}$ satisfying (1.122) and Λ symbolizes as before the boundary of the region and the outside fields described by the parameters $a_1, a_2, \ldots$. Likewise, the internal energy (1.25) and the generalized external forces X_k (1.26) become

$$U(N, \Lambda, T) = \frac{1}{Z} \sum_{\{n_k\}}^{N} (\textstyle\sum_l n_l \epsilon_l) \exp(-\beta \textstyle\sum_k n_k \epsilon_k) \,, \tag{1.125}$$

$$X_i(N, \Lambda, T) = \frac{1}{Z} \sum_{\{n_k\}}^{N} \textstyle\sum_l n_l(-\partial \epsilon_l / \partial a_i) \exp(-\beta \textstyle\sum_k n_k \epsilon_k) \,. \tag{1.126}$$

The entropy follows from $\ln Z$ and U according to (1.30).

These expressions imply evidently that the probability for the occupation set $\{n_0 n_1 \ldots\}$ is

$$\frac{1}{Z} \exp(-\beta \textstyle\sum_k n_k \epsilon_k) \,, \tag{1.127}$$

so that the average occupation number of the state ϵ_i must be given by

$$\langle n_i \rangle = \frac{1}{Z} \sum_{\{n_k\}}^{N} n_i \exp(-\beta \textstyle\sum_k n_k \epsilon_k) \,, \tag{1.128}$$

and the corresponding mean square occupation by

$$\langle n_i^2 \rangle = \frac{1}{Z} \sum_{\{n_k\}}^{N} n_i^2 \exp(-\beta \textstyle\sum_k n_k \epsilon_k) \,. \tag{1.129}$$

The equilibrium density matrix (1.23) for the IBG is

$$\rho(r'^N, r''^N; N, \Lambda, T) = \frac{1}{Z} \sum_{\{n_k\}}^{N} \Psi^*_{n_0 n_1 \ldots}(r''^N)\, \Psi_{n_0 n_1 \ldots}(r'^N) \exp(-\beta \textstyle\sum_k n_k \epsilon_k) \,. \tag{1.130}$$

In terms of the single particle states this can be written

$$\rho(r'^N, r''^N; N, \Lambda, T) = \frac{1}{N! Z} \sum_{\mathrm{P}\{r'^N\}} \sum_{i=1}^{N} \prod_{k=0}^{\infty} \exp(-\beta \epsilon_k)\, \psi^*_k(r''_i)\, \psi_k(r'_i) \,, \tag{1.131}$$

using (1.123) for Ψ and elementary combinatorial identities. The reduced density matrices then follow by direct integration, according to (1.73), and the following expression results:

$$\rho_s(r'^s, r''^s; N, \Lambda, T) = \sum_{\{n_j\}}^{s} \Psi^*_{n_0 n_1 \ldots}(r''^s)\, \Psi_{n_0 n_1 \ldots}(r'^s) \frac{s!}{Z} \sum_{\{n'_k\}}^{N} \prod_{i=1}^{\infty} \frac{(n'_i)!}{n_i!\,(n'_i - n_i)!} \exp(-\beta \textstyle\sum_k n'_k \epsilon_k) \,, \tag{1.132}$$

where the set $\{n_j\}$ satisfies the restriction $\sum n_j = s$, and the set $\{n'_k\}$ satisfies $\sum n'_k = N$. The Ψ's are the s-particle wavefunctions given by (1.123) with N replaced by s. For example, when $s = 1$, the only possible occupation sets $\{n_j\}$ are $n_k = 1$, $n_l = 0$ $(l \neq k)$ for $k = 0, 1, 2, \ldots$, and (1.132) becomes

$$\rho_1(r'_1, r''_1; N, \Lambda, T) = \sum_{k=0}^{\infty} \psi^*_k(r''_1)\, \psi_k(r'_1) \frac{1}{Z} \sum_{\{n_l\}}^{N} n_k \exp(-\beta \textstyle\sum_l n_l \epsilon_l) = \displaystyle\sum_{k=0}^{\infty} \langle n_k \rangle\, \psi^*_k(r'_1)\, \psi_k(r'_1) \,. \tag{1.133}$$

The grand partition function defined in (1.32) becomes for the IBG:

$$Z^{\mathrm{gr}}(\alpha, \Lambda, T) = \sum_{N=0}^{\infty} \mathrm{e}^{-\alpha N} \sum_{\{n_k\}}^{N} \exp(-\beta \textstyle\sum_k n_k \epsilon_k) = \displaystyle\prod_{k=0}^{\infty} \sum_{n_k=0}^{\infty} (\exp(-\alpha - \beta \epsilon_k))^{n_k}$$

$$= \prod_{k=0}^{\infty} (1 - \exp(-\alpha - \beta \epsilon_k))^{-1} \,. \tag{1.134}$$

Likewise, one easily verifies that the thermodynamical functions (1.33)–(1.35) for the IBG are given by the following well known expressions:

$$N^{\mathrm{gr}}(\alpha, \Lambda, T) = \sum_{k=0}^{\infty} \langle n_k \rangle^{\mathrm{gr}} , \tag{1.135}$$

$$U^{\mathrm{gr}}(\alpha, \Lambda, T) = \sum_{k=0}^{\infty} \epsilon_k \langle n_k \rangle^{\mathrm{gr}} , \tag{1.136}$$

$$X_j^{\mathrm{gr}}(\alpha, \Lambda, T) = \sum_{k=0}^{\infty} (-\partial \epsilon_k / \partial a_j) \langle n_k \rangle^{\mathrm{gr}} , \tag{1.137}$$

and the entropy is given in terms of N^{gr}, U^{gr}, and Z^{gr} according to (1.37), and where

$$\langle n_k \rangle^{\mathrm{gr}} = (\exp(\alpha + \beta\epsilon_k) - 1)^{-1} , \tag{1.138}$$

is the grand canonical occupation of the state k. The mean square occupation is

$$\langle n_k^2 \rangle^{\mathrm{gr}} = \langle n_k \rangle^{\mathrm{gr}} + 2(\langle n_k \rangle^{\mathrm{gr}})^2 . \tag{1.139}$$

For the grand canonical density matrices of the IBG one finds

$$\rho_s^{\mathrm{gr}}(r'^s, r''^s; \alpha, \Lambda, T) = \sum_{\mathrm{P}\{r'^s\}} \prod_{i=1}^{s} \rho_1^{\mathrm{gr}}(\boldsymbol{r}_i', \boldsymbol{r}_i''; \alpha, \Lambda, T) , \tag{1.140}$$

where the first density matrix is given by the simple expression

$$\rho_1^{\mathrm{gr}}(\boldsymbol{r}', \boldsymbol{r}''; \alpha, \Lambda, T) = \sum_{k=0}^{\infty} \langle n_k \rangle^{\mathrm{gr}} \psi_k^*(\boldsymbol{r}'') \, \psi_k(\boldsymbol{r}') . \tag{1.141}$$

Evidently the s-particle grand canonical density matrix is just a symmetrized sum of products of the single particle density matrix[‡].

2. Bulk properties of the ideal Bose gas

2.1. Introduction

In this section the bulk properties of the ideal Bose gas are discussed and then derived. Following our remarks in section 1.4.2, these are found by means of the bulk limit, in which a sequence of similar systems of increasing N and V is considered with $N/V = \rho$ fixed, and the bulk properties are found in the limit $V \to \infty$. In this limit, the Bose condensation will be evident. As a product of the calculation, also the grand canonical properties are derived, and it turns out that some of them *differ* from the corresponding canonical properties – even in the bulk limit! The origin and

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[‡] Note that these results can also be found directly by using the construction operator definition of the reduced density matrices. Namely, in terms of the creation and annihilation operators $\hat{\psi}(\boldsymbol{r})$ and $\hat{\psi}^\dagger(\boldsymbol{r})$ which obey the Bose commutation rule, and in which the coordinate $\boldsymbol{r}$ is a parameter, the first two reduced density matrices are:

$$\rho_1(\boldsymbol{r}_1', \boldsymbol{r}_1'') = \mathrm{Tr}\, \hat{\rho}\, \hat{\psi}^\dagger(\boldsymbol{r}_1'')\, \psi(\boldsymbol{r}_1') , \qquad \rho_2(\boldsymbol{r}_1', \boldsymbol{r}_2'; \boldsymbol{r}_1'', \boldsymbol{r}_2'') = \mathrm{Tr}\, \hat{\rho}\, \hat{\psi}^\dagger(\boldsymbol{r}_1'')\, \hat{\psi}^\dagger(\boldsymbol{r}_2'')\, \hat{\psi}(\boldsymbol{r}_2')\, \hat{\psi}(\boldsymbol{r}_1') .$$

This holds in both the grand canonical and canonical ensembles, with the appropriate definition of the density operator $\hat{\rho}$ and the trace (Tr). From this point of view the density matrices themselves can be thought of as quantum statistical averages of these construction operators. One can show that the above definition is identical to (1.73) and (1.115). For more details see for example de Boer [41].

meaning of the unexpected difference, which has also been noted by some other authors, will be discussed in section 2.4. Finally, in section 2.5, the bulk canonical properties of a system whose number of dimensions is other than three are briefly considered.

2.2. The bulk properties

Here we simply list and discuss the bulk properties of a three dimensional ideal Bose gas. As one would expect for a bulk system, there are only two independent thermodynamic variables, which we choose to be ρ and T.[‡]

The pressure and energy density are given by

$$p(\rho, T) = \tfrac{2}{3}u(\rho, T) = \begin{cases} \dfrac{kT}{\lambda^3} g_{5/2}(\alpha)\,, & \rho < \rho_c\,, \\[2ex] \dfrac{kT}{\lambda^3} \zeta(\tfrac{5}{2})\,, & \rho > \rho_c\,, \end{cases} \tag{2.1}$$

where $\lambda^2 \equiv 2\pi\hbar^2/mkT$,

$$\rho_c = \rho_c(T) \equiv \zeta(\tfrac{3}{2})/\lambda^3\,, \tag{2.2}$$

and for $\rho < \rho_c$, $\alpha = \alpha(\rho, T)$ is the unique root of

$$\rho = \frac{1}{\lambda^3} g_{3/2}(\alpha)\,. \tag{2.3}$$

We have introduced the Bose functions

$$g_n(\alpha) \equiv \sum_{j=1}^{\infty} j^{-n}\, e^{-\alpha j}\,, \tag{2.4}$$

whose properties are discussed in Appendix 2.A.

The equation of state (2.1) is divided into two analytic segments by the density ρ_c. For $\rho > \rho_c$, the pressure is independent of the density and equal to $p_c = p_c(T) \equiv kT\,\zeta(\tfrac{5}{2})/\lambda^3$, while for $\rho < \rho_c$ it is found by eliminating α between (2.1) and (2.3). The isotherm of p versus ρ, scaled by p_c and ρ_c, is given in fig. 0.1. With this scaling the isotherms for all temperatures fall on this one curve. Note that there is no critical point beyond which the condensation ceases to occur, and that the subscript c refers here to the point of condensation. One can also define the temperature T_c at which the condensation occurs for a given ρ, determined by

$$\rho\lambda_c^3 = \zeta(\tfrac{3}{2})\,, \qquad \lambda_c^2 = 2\pi\hbar^2/mkT_c\,, \tag{2.5}$$

which also defines the thermal length at condensation λ_c. The two phase region $\rho > \rho_c$ corresponds to $T < T_c$ and $\lambda > \lambda_c$.

For low densities $\rho \ll \rho_c$, the pressure is given by

$$p = \rho kT\Big(1 - \frac{\zeta(\tfrac{3}{2})}{4\sqrt{2}}\,\frac{\rho}{\rho_c} \ldots\Big)\,, \tag{2.6}$$

[‡] The following *thermodynamical* properties are of course well known. Compare for example Einstein [2–4], Kahn [42], London [17] and Huang [43–44].

and clearly approaches the classical ideal gas behavior as $\rho/\rho_c \to 0$. As ρ approaches ρ_c the pressure reaches p_c with zero slope, and when $\rho > \rho_c$ the isotherm is flat. At ρ_c there is a discontinuity in the second derivative.

In analogy to a regular (first order) phase transition, where there is also a horizontal piece in the isotherm, a state for $\rho > \rho_c$ can be interpreted as a two phase system, with ρ_c non-condensed particles of specific volume $1/\rho_c$ and $\rho - \rho_c$ condensed particles of specific volume zero, in each unit volume. The fraction of condensed particles is therefore

$$1 - \rho_c/\rho = 1 - (T/T_c)^{3/2} . \tag{2.7}$$

That the condensed particles have no volume follows from the fact that they do not contribute to the pressure. This of course is where this transition differs most from the usual ones.

The entropy density (that is, entropy per unit volume) s, Helmholtz free energy density f, and chemical potential μ ($\equiv$ Gibbs free energy per *particle*) are given by

$$s(\rho, T) = \begin{cases} \dfrac{5}{2}\dfrac{k}{\lambda^3} g_{5/2}(\alpha) + k\rho\alpha , & \rho < \rho_c , \\ \dfrac{5}{2}\dfrac{k}{\lambda^3} \zeta(\tfrac{5}{2}) , & \rho > \rho_c , \end{cases} \tag{2.8}$$

$$f(\rho, T) = u - Ts = \begin{cases} -\dfrac{kT}{\lambda^3} g_{5/2}(\alpha) - kT\rho\alpha , & \rho < \rho_c , \\ -\dfrac{kT}{\lambda^3} \zeta(\tfrac{5}{2}) , & \rho > \rho_c , \end{cases} \tag{2.9}$$

$$\mu(\rho, T) = (f + p)/\rho = \begin{cases} -kT\alpha , & \rho < \rho_c , \\ 0 , & \rho > \rho_c , \end{cases} \tag{2.10}$$

where for each of these, α is determined by (2.3) when $\rho < \rho_c$. One can verify that these satisfy the thermodynamical relations (1.46–47).

Note that for a given fixed temperature, when the density is increased beyond ρ_c the entropy density and also the density of non-condensed particles ($= \rho_c$) are fixed, while the density of condensed particles ($= \rho - \rho_c$) varies. Therefore one can say that the condensed particles carry no entropy, and the difference in the specific entropy and specific volume of the two phases satisfy the Clapeyron equation, as in a first order transition:

$$\frac{\mathrm{d}p_c(T)}{\mathrm{d}T} = \frac{\Delta(s/\rho)}{\Delta(1/\rho)} = \frac{5}{2}\,\frac{k\zeta(\frac{5}{2})}{\lambda^3} . \tag{2.11}$$

Similarly, u, f, and $\rho\mu$ depend only upon T when $\rho > \rho_c$, and therefore the condensed particles do not contribute at all to the thermodynamical properties.

These functions can also be written in terms of T and T_c. For example, for the internal energy per particle we have

$$u/\rho = \begin{cases} \frac{3}{2}kT\,\dfrac{g_{5/2}(\alpha)}{g_{3/2}(\alpha)}, & T > T_c\,, \\[2ex] \frac{3}{2}kT\left(\dfrac{T}{T_c}\right)^{3/2}\dfrac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}, & T < T_c\,. \end{cases} \tag{2.12}$$

As $T \to \infty$, u/ρ approaches the classical value $\frac{3}{2}kT$. At T_c there is a discontinuity in the second derivative. The derivative of u/ρ with respect to T is the specific heat per particle at constant volume (density), which in terms of T and T_c is given by

$$c_v/k = \begin{cases} \dfrac{15}{4}\dfrac{g_{5/2}(\alpha)}{g_{3/2}(\alpha)} - \dfrac{9}{4}\dfrac{g_{3/2}(\alpha)}{g_{1/2}(\alpha)}, & T > T_c\,, \\[2ex] \dfrac{15}{4}\left(\dfrac{T}{T_c}\right)^{3/2}\dfrac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}, & T < T_c\,. \end{cases} \tag{2.13}$$

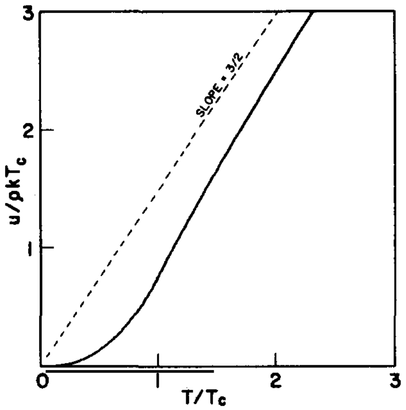

Fig. 2.1. The energy per particle u/ρ divided by kT_c plotted as a function of the temperature T divided by T_c, at constant density ρ.

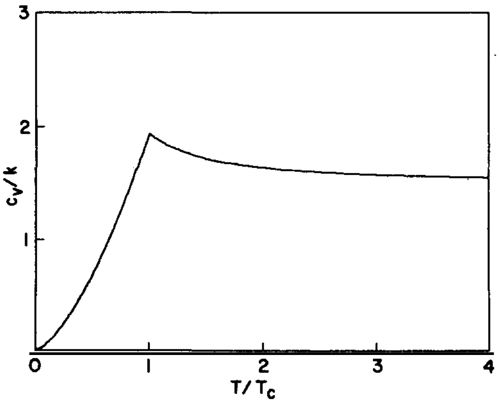

Fig. 2.2. The specific heat at constant density c_v/k as a function of T/T_c.

We have plotted the energy and specific heat per particle as functions of the temperature in figs. 2.1 and 2.2 respectively. At $T = T_c$, c_v/k reaches a maximum value of $15\zeta(\frac{5}{2})/4\zeta(\frac{3}{2}) \simeq 1.926$, with a discontinuity in the first derivative given by:

$$\left[\frac{\partial(c_v/k)}{\partial(T/T_c)}\right]^{-} - \left[\frac{\partial(c_v/k)}{\partial(T/T_c)}\right]^{+} = \frac{27}{16\pi}(\zeta(\tfrac{3}{2}))^2 \simeq 3.66 \,, \tag{2.14}$$

and as $T \to \infty$, it reaches the classical value $\frac{3}{2}$.

In the bulk limit, the average occupation of the lowest single particle state, divided by the volume, is given by:

$$\lim_{V\to\infty} \frac{\langle n_0\rangle}{V} = \begin{cases} 0\,, & \rho < \rho_c\,, \\ \rho - \rho_c\,, & \rho > \rho_c\,. \end{cases} \tag{2.15}$$

It is non-zero only for $\rho > \rho_c$. On the other hand, the density of particles in the other states always goes to zero. They are represented by a continuum in the energy distribution. Thus we see that the condensation found from the thermodynamical properties is comprised of particles occupying the ground state.

The fluctuations around the average values, divided by V^2, goes to zero for all states including the ground state and for all densities:

$$\lim_{V\to\infty} \frac{\langle n_k^2\rangle - \langle n_k\rangle^2}{V^2} = \lim_{V\to\infty} \frac{\langle(\Delta n_k)^2\rangle}{V^2} = 0\,. \tag{2.16}$$

In particular, there are no "macroscopic fluctuations" in the occupation of the ground state, in the two phase region. We will discuss this further in the section 2.4.

The properties that we have discussed so far are well known. Now we turn to the density matrices, which have not previously been discussed completely. For all s, they can be written

$$\rho_s(r'^s, r''^s; \alpha, T) = \begin{cases} \displaystyle\sum_{\mathrm{P}\{r'^s\}} \prod_{i=1}^{s} F(|\boldsymbol{r}_i' - \boldsymbol{r}_i''|, \alpha, T)\,, & \rho < \rho_c\,, \\ \displaystyle\frac{1}{2\pi \mathrm{i}} \oint \frac{\mathrm{d}t}{t} \exp\{t(\rho-\rho_c)\} \sum_{\mathrm{P}\{r'^s\}} \prod_{i=1}^{s} \left(F(|\boldsymbol{r}_i' - \boldsymbol{r}_i''|, 0, T) + \frac{1}{t}\right), & \rho > \rho_c\,, \end{cases} \tag{2.17}$$

where

$$F(r, \alpha, T) = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} j^{-3/2} \exp\{-\alpha j - \pi r^2/j\lambda^2\}\,, \tag{2.18}$$

and again $\alpha = \alpha(\rho, T)$ as determined by (2.3). Note that

$$\frac{1}{2\pi \mathrm{i}} \oint \frac{\mathrm{d}t}{t} \exp\{t(\rho - \rho_c)\} t^{-k} = \frac{(\rho - \rho_c)^k}{k!}\,, \tag{2.19}$$

where the contour goes around the origin in the positive sense. To find an explicit expression for the density matrix when $\rho > \rho_c$, the products of the expression

$$\sum_{\mathrm{P}\{r'^s\}} \prod_{i=1}^{s} \left(F(|\boldsymbol{r}_i' - \boldsymbol{r}_i''|, 0, T) + \frac{1}{t}\right)\,, \tag{2.20}$$

must be multiplied out, and the contour integral carried out. According the (2.19), that means simply replacing the factor $(1/t)^k$ in each term by $(\rho - \rho_c)^k/k!$. This gives an alternative expression for ρ_s in the two phase region $\rho > \rho_c$:

$$\rho_s(r'^s, r''^s; \rho, T) = \sum_{k=1}^{s} \frac{(\rho - \rho_c)^{s-k}}{k!} \prod_{i=1}^{k} \sum_{l_i,} \sum_{l_i'=1}^{s} F(|\boldsymbol{r}_{l_i} - \boldsymbol{r}'_{l_i'}|, 0, T) , \tag{2.21}$$

with the restriction on the multiple sums that $l_i \neq l_j$ $(i \neq j)$ and $l_i' \neq l_j'$ $(i \neq j)$.

The one particle density matrix is given by

$$\rho_1(\boldsymbol{r}_1', \boldsymbol{r}_1''; \rho, T) = \begin{cases} F(|\boldsymbol{r}_1' - \boldsymbol{r}_1''|, \alpha, T) , & \rho < \rho_c , \\ F(|\boldsymbol{r}_1' - \boldsymbol{r}_1''|, 0, T) + \rho - \rho_c , & \rho > \rho_c . \end{cases} \tag{2.22}$$

The diagonal element (which according to (1.79) is the local density) is independent of position as it should be. When $|\boldsymbol{r}_1' - \boldsymbol{r}_1''| \to \infty$, $F \to 0$, and

$$\rho_1(\boldsymbol{r}_1', \boldsymbol{r}_1''; \rho, T) \to \begin{cases} 0 , & \rho < \rho_c , \\ \rho - \rho_c , & \rho > \rho_c . \end{cases} \tag{2.23}$$

The non-zero value for $\rho > \rho_c$ is described as off diagonal long range order (ODLRO).

Note that $F(r, \alpha, T)$ can also be written as

$$\begin{aligned} \lambda^3 F(r, \alpha, T) &= \frac{\lambda}{r} \exp(-2\sqrt{\pi\alpha}\, r/\lambda) + \sum_{s=1}^{\infty} \frac{\lambda}{r} \exp(-A^+ r/\lambda)\, 2\cos(A^- r/\lambda) , \\ A^{\pm} &\equiv \sqrt{2\pi}\,(\alpha^2 + 4\pi^2 s^2)^{1/4} \left[1 \pm \frac{\alpha}{(\alpha^2 + 4\pi^2 s^2)^{1/2}}\right]^{1/2} . \end{aligned} \tag{2.24}$$

The proof will be given in Appendix 3.A. When $r/\lambda \gg 1$ the first term dominates, from which it can be seen that the limiting behavior for $r \to \infty$ is an exponential decay, except when $\alpha = 0$, when F goes to zero as $1/\lambda^2 r$. Actually, for small but positive α there is a regime in which $F \sim 1/\lambda^2 r$, namely for $r \ll \lambda/\sqrt{\alpha}$. When $\alpha \to 0$ this bound goes to infinity, which explains how the transition from exponential to reciprocal behavior takes place.

The "curvature" of ρ_1 about $|r_1' - r_1''| = 0$ is related to the local energy density, according to (1.95). One can verify that this gives a value for the energy that is identical to (2.1).

For the two particle density matrix $\rho_2(r_1' r_2', r_1'' r_2''; \rho, T)$, we have from (2.17) for $\rho < \rho_c$:

$$\rho_2 = F(|\boldsymbol{r}_1' - \boldsymbol{r}_1''|, \alpha, T)\, F(|\boldsymbol{r}_2' - \boldsymbol{r}_2''|, \alpha, T) + F(|\boldsymbol{r}_1' - \boldsymbol{r}_2''|, \alpha, T)\, F(|\boldsymbol{r}_2' - \boldsymbol{r}_1''|, \alpha, T) , \tag{2.25a}$$

and for $\rho > \rho_c$:

$$\begin{aligned} \rho_2 = {} & F(|\boldsymbol{r}_1' - \boldsymbol{r}_1''|, 0, T)\, F(|\boldsymbol{r}_2' - \boldsymbol{r}_2''|, 0, T) + F(|\boldsymbol{r}_1' - \boldsymbol{r}_2''|, 0, T)\, F(|\boldsymbol{r}_2' - \boldsymbol{r}_1''|, 0, T) \\ & + (\rho - \rho_c)[F(|\boldsymbol{r}_1' - \boldsymbol{r}_1''|, 0, T) + F(|\boldsymbol{r}_2' - \boldsymbol{r}_2''|, 0, T) + F(|\boldsymbol{r}_1' - \boldsymbol{r}_2''|, 0, T) \\ & + F(|\boldsymbol{r}_2' - \boldsymbol{r}_1''|, 0, T)] + (\rho - \rho_c)^2 . \end{aligned} \tag{2.25b}$$

When both primed coordinates are far from both double primed ones,

$$\rho_2 \to \begin{cases} 0\,, & \rho < \rho_c\,, \\ (\rho - \rho_c)^2\,, & \rho > \rho_c\,, \end{cases} \tag{2.26}$$

and ρ_2 also exhibits ODLRO when $\rho > \rho_c$. The diagonal element $\boldsymbol{r}_1' = \boldsymbol{r}_1'', \boldsymbol{r}_2' = \boldsymbol{r}_2''$ is the two particle distribution function, according to (1.79):

$$n_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \rho, T) = \begin{cases} \rho^2 + [F(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, \alpha, T)]^2\,, & \rho < \rho_c\,, \\ \rho^2 + [F(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, 0, T)]^2 + 2(\rho - \rho_c)F(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, 0, T)\,, & \rho > \rho_c\,. \end{cases} \tag{2.27}$$

When $|\boldsymbol{r}_1 - \boldsymbol{r}_2| \to \infty$, $n_2 \to \rho^2$ for all ρ, or equivalently the cluster function $\chi_2(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) - n_1(\boldsymbol{r}_1) n_1(\boldsymbol{r}_2) \to 0$. Since the distribution functions are the diagonal elements of the density matrices, we express this behaviour by saying that there is no *diagonal* long range order (DLRO). This in turn implies that there is no spatial separation of the phases [‡]. When $\rho < \rho_c$, this cluster function can be integrated over all space:

$$\int \chi_2(\boldsymbol{r}_1, \boldsymbol{r}_2)\,\mathrm{d}\boldsymbol{r}_2 = \int [F(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, \alpha, T)]^2\,\mathrm{d}\boldsymbol{r}_2 = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} j^{-3/2}(j-1)\,\mathrm{e}^{-\alpha j}$$

$$= \left(-\frac{\partial}{\partial \alpha} - 1\right) \rho(\alpha, T) = \left(kT\rho \frac{\partial}{\partial p} - 1\right) \rho(p, T)\,, \tag{2.28}$$

using the fact that $\partial p/\partial \alpha = -kT\rho$ at constant T. This result agrees with the fluctuation-compressibility formula of Ornstein and Zernike [47].

Now we extend these considerations to all ρ_s. First of all, when all $\{r'^s\}$ are far from all $\{r''^s\}$ then it is clear from (2.17) that

$$\rho_s \to \begin{cases} 0\,, & \rho < \rho_c\,, \\ (\rho - \rho_c)^s\,, & \rho > \rho_c\,. \end{cases} \tag{2.29}$$

This is namely the general ODLRO of the density matrices, as has been given by Yang [25].

To discuss the DLRO, we introduce the general cluster functions χ_s by the scheme of Ursell:

$$\begin{aligned} &n_1(\boldsymbol{r}_1) = \chi_1(\boldsymbol{r}_1)\,, \\ &n_2(\boldsymbol{r}_1\boldsymbol{r}_2) = \chi_2(\boldsymbol{r}_1\boldsymbol{r}_2) + \chi_1(\boldsymbol{r}_1)\chi_1(\boldsymbol{r}_2)\,, \\ &n_3(\boldsymbol{r}_1\boldsymbol{r}_2\boldsymbol{r}_3) = \chi_3(\boldsymbol{r}_1\boldsymbol{r}_2\boldsymbol{r}_3) + \chi_1(\boldsymbol{r}_1)\chi_2(\boldsymbol{r}_2\boldsymbol{r}_3) + \chi_1(\boldsymbol{r}_2)\chi_2(\boldsymbol{r}_3\boldsymbol{r}_1) + \chi_1(\boldsymbol{r}_3)\chi_2(\boldsymbol{r}_1\boldsymbol{r}_2) + \chi_1(\boldsymbol{r}_1)\chi_1(\boldsymbol{r}_2)\chi_1(\boldsymbol{r}_3) \\ &\cdots \end{aligned} \tag{2.30}$$

On the right hand side there are terms representing each possible partition of the set $\{r^s\}$. These equations determine the functions χ_s successively in terms of the n_s. The relations can be inverted [‡‡] to give explicit expressions for the χ_s but they will not be needed here. The importance of these χ_s is that they have the so-called cluster property if and only if the distribution functions have the co-called product property. These properties are defined as follows. If the particles $\{r^s\}$ are split into two groups $\{r^a\}$ and $\{r^b\}$ which are separated far from each other and contain a and b particles respectively, then n_s is said to obey the product property if

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[‡] See Uhlenbeck, Hemmer and Kac [45]; also Kac [46].

[‡‡] See for example Kahn and Uhlenbeck [12].

$$n_s(r^s) \to n_a(r^a)\, n_b(r^b)\,, \tag{2.31}$$

and χ_s is said to obey the cluster property if under such a separation it goes to zero. That one property implies the other follows immediately from the definition of χ_s given in (2.30).

For the IBG, the distribution functions which follow as the diagonal elements of (2.17) all satisfy the product property (2.31). This can be verified using (2.17) (or (2.21) for $\rho > \rho_c$) and the fact that $F(|\boldsymbol{r}_i - \boldsymbol{r}_j|, \alpha, T) = 0$ if $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$ belong to the two different groups. Hence it follows that the functions χ_s satisfy the cluster property, and therefore that χ_s must be composed of just those terms of n_s that vanish under every possible separation of the particles. By inspection of n_s implied by (2.17) or (2.21) one finds

$$\chi_s(r^s, \rho, T) = \begin{cases} \sum' F(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, \alpha, T)\, F(|\boldsymbol{r}_2 - \boldsymbol{r}_3|, \alpha, T) \ldots F(|\boldsymbol{r}_s - \boldsymbol{r}_1|, \alpha, T)\,, & \rho < \rho_c\,, \\ \sum' F(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, 0, T)\, F(|\boldsymbol{r}_2 - \boldsymbol{r}_3|, 0, T) \ldots F(|\boldsymbol{r}_s - \boldsymbol{r}_1|, 0, T) & \\ \quad + (\rho - \rho_c) \sum F(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, 0, T) \ldots F(|\boldsymbol{r}_{s-1} - \boldsymbol{r}_s|, 0, T)\,, & \rho > \rho_c\,, \end{cases} \tag{2.32}$$

in which $\sum'$ indicates a sum over permutations of $\{\boldsymbol{r}_2 \ldots \boldsymbol{r}_s\}$ and $\sum$ indicates summation over permutations of *all* $\{\boldsymbol{r}_1 \ldots \boldsymbol{r}_s\}$. It is interesting to note that the explicit expressions for χ_s are much simpler than the expressions for n_s, especially when $\rho > \rho_c$.

When $\rho < \rho_c$, $\chi_s(r^s)$ given above can be integrated over all space and the result satisfies the generalized fluctuation-compressibility formula

$$\int \chi_s(r^s, \rho, T)\, \mathrm{d}r^{s-1} = \left\{ \prod_{n=1}^{s-1} \left(kT\rho \frac{\partial}{\partial p} - n \right) \right\} \rho(p, T)\,, \tag{2.33}$$

as has been given by Hemmer [48] for a general system. For the case $s = 2$ this agrees with (2.28). Note that when $\rho > \rho_c$ both sides of this equation diverges.

Therefore we have characterized the structure of the Bose condensation by the presence of ODLRO in all of the density matrices, without DLRO. This is consistent with the absence of a phase separation. The long range behavior can also be shown to be consistent with the macroscopic occupation of the ground state (2.15) and their fluctuations (2.16).

2.3. Proof of the results of section 2.2

a. The notion of the generating function. For the calculation of the bulk limit of a given canonical function $f(N, \Lambda, T)$ (where Λ represents the bounded region, with volume V), it turns out to be useful to introduce the corresponding generating function $f^{\mathrm{g}}(\alpha, \Lambda, T)$ defined by

$$f^{\mathrm{g}}(\alpha, \Lambda, T) \equiv \sum_{N=0}^{\infty} \frac{\mathrm{e}^{-\alpha N} Z(N, \Lambda, T)}{Z^{\mathrm{gr}}(\alpha, \Lambda, T)}\, f(N, \Lambda, T)\,. \tag{2.34}$$

Clearly these functions are closely related to the grand canonical quantities discussed in section 1. In fact, inspection shows that the generating functions of N, U, χ_k (including p), and the reduced density matrices ρ_s are identical to their grand canonical averages. For instance, the grand canonical energy as defined by (1.33) can also be written as

$$U^{\mathrm{gr}}(\alpha, \Lambda, T) = \sum_{N=0}^{\infty} \frac{\mathrm{e}^{-\alpha N} Z(N, \Lambda, T)}{Z^{\mathrm{gr}}(\alpha, \Lambda, T)} U(N, \Lambda, T) , \tag{2.35}$$

where U is the canonical energy defined by (1.25). All of the above quantities are quantum-statistical averages of operators that depend only upon E and N, and therefore can be called "mechanical". It is clear that for all such quantities f^{g} defined above is identical to f^{gr} defined in section 1. Note however that this is not the case for the entropy, since its generating function is

$$S^{\mathrm{g}} = -k \sum_{N} \frac{\mathrm{e}^{-\alpha N} Z_N}{Z^{\mathrm{gr}}} \sum_{E_N} \frac{\exp(-\beta E_N)}{Z_N} \ln \frac{\exp(-\beta E_N)}{Z_N} , \tag{2.36}$$

(where $E_N \equiv E(N, \Lambda)$ and $Z_N \equiv Z(N, \Lambda, T)$) which differs from the grand canonical entropy S^{gr} of (1.37) by the amount

$$S^{\mathrm{gr}} - S^{\mathrm{g}} = -k \sum_{N} \frac{\mathrm{e}^{-\alpha N} Z_N}{Z^{\mathrm{gr}}} \ln \frac{\mathrm{e}^{-\alpha N} Z_N}{Z^{\mathrm{gr}}} . \tag{2.37}$$

Similarly for all the thermodynamic potentials such as F and Ω one must distinguish between the grand canonical definitions denoted by the superscript gr and the generating functions denoted by the superscript g. The origin of this difference is that the entropy and these other thermodynamic potentials describe the *ensemble* and are not strictly quantum statistical averages.

From now on we will always use the superscript gr *instead of* g *when the expressions are the same* (namely for the mechanical quantities). But for the entropy and the thermodynamic potentials the different superscripts must be watched! For an *unspecified* quantity f we must always use the superscript g to denote the generating function.

b. Outline of the method. For a given intensive canonical quantity $f(N, \Lambda, T)$ the bulk limit is defined by

$$f(\rho, T) \equiv \lim_{V\to\infty} f(N, \Lambda, T) , \tag{2.38}$$

where $\rho = N/V$. This can be accomplished for the ideal Bose gas by first introducing the generating function defined by (2.34) and calculating the limit

$$f^{\mathrm{g}}(\rho, T) \equiv \lim_{V\to\infty} f^{\mathrm{g}}(\alpha, \Lambda, T) , \tag{2.39}$$

where $\alpha = \alpha(\rho, \Lambda, T)$ is determined by:

$$\rho = \frac{N^{\mathrm{gr}}}{V} = \frac{1}{V} \sum_{N=0}^{\infty} N \frac{\mathrm{e}^{-\alpha N} Z(N, \Lambda, T)}{Z^{\mathrm{gr}}(\alpha, \Lambda, T)} . \tag{2.40}$$

Evidently $f(\rho, T)$ and $f^{\mathrm{g}}(\rho, T)$ are related by

$$f^{\mathrm{g}}(\rho, T) = \int_{0}^{\infty} \nu(x, \rho; T) f(x, T)\, \mathrm{d}x , \tag{2.41}$$

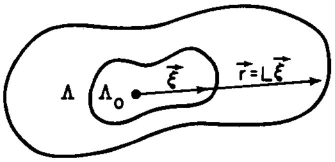
where

$$\nu(x, \rho; T) \equiv \lim_{V\to\infty} \frac{V \mathrm{e}^{-\alpha N} Z(N, \Lambda, T)}{Z^{\mathrm{gr}}(\alpha, \Lambda, T)} , \tag{2.42}$$

with $N/V = x$ and $\alpha = \alpha(\rho, \Lambda, T)$ as determined by (2.40). Therefore $f(\rho, T)$ can be found from $f^{g}(\rho, T)$ by inverting (2.41).

All of these steps can be accomplished for the IBG. First of all, the generating functions can be written in simple terms – indeed, for all of the functions that we will consider except for the entropy they are identical to the corresponding grand canonical expressions which have already been given in section 1.5. Then for all of the functions the limit (2.39–40) can be calculated. Note that $f^{g}(\rho, T)$ in (2.39) is written as a function of ρ instead of α because the limit $V \to \infty$ is taken not with α fixed but with the average density $\rho = N^{gr}/V$ fixed. The function $\nu(x, \rho; T)$ is calculated in the same way. That function can be interpreted as the distribution of overall density in the grand canonical *ensemble* when the average density is equal to ρ, in the bulk limit. In the one phase region we shall find that it is a delta function and the bulk properties in the two ensembles are therefore identical; this can be proven even for a general one phase system using the method of steepest descents, as we shall sketch in section 3. However, in the two phase region of the IBG we shall find that $\nu(x, \rho; T)$ is not a delta function and that therefore the inverse of (2.41) is not completely trivial, but still can be done. The function ν has been named the Kac density.

c. Application to the thermodynamical properties. First of all the limit $V \to \infty$ has to be defined precisely, especially with reference to the *shape* of the system. It is most reasonable to assume that as $V \to \infty$ the shape does not change and the region Λ is simply enlarged in all directions. This can be accomplished by scaling the coordinates of Λ to a "unit" cell Λ_0 of volume unity by the factor L, as shown below:



Then as L is increased, Λ expands uniformly about the origin of the coordinate system, assuming that that origin is chosen somewhere inside of Λ_0. The bulk limit is found by making N and L infinite while keeping N/L^3 fixed. One expects that the properties in that limit will not depend upon the shape of Λ_0 nor on the location of the origin within it.

The single particle wavefunctions in Λ, $\psi_k(\boldsymbol{r})$ and the energy levels ϵ_k (ordered so that $\epsilon_0 \leqq \epsilon_1 \leqq \epsilon_2 \ldots$) satisfy the Schrödinger equation (1.120), namely:

$$\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \boldsymbol{r}^2}\,\psi_k(\boldsymbol{r}) + \epsilon_k\,\psi_k(\boldsymbol{r}) = 0\ , \tag{2.43}$$

and are normalized to unity:

$$\int_{\Lambda} |\psi_k(\boldsymbol{r})|^2\,\mathrm{d}\boldsymbol{r} = 1\ . \tag{2.44}$$

We consider that ψ_k satisfy either the Neumann ($\partial\psi/\partial n \to 0$) or the Dirichlet ($\psi \to 0$) boundary conditions. When L is increased, the states scale in the following way:

$$\psi_k(\boldsymbol{r}) = \frac{1}{L^{3/2}}\,y_k(\boldsymbol{r}/L)\ , \tag{2.45}$$

$$\beta\epsilon_k = \frac{2\pi\hbar^2}{mL^2}\beta e_k = \frac{\lambda^2}{L^2} e_k \,, \tag{2.46}$$

where y_k and e_k satisfy

$$\frac{\partial^2}{\partial\xi^2} y_k(\xi) + 4\pi e_k y_k(\xi) = 0 \,, \tag{2.47}$$

and

$$\int_{\Lambda_0} |y_k(\xi)|^2 \, d\xi = 1 \,, \tag{2.48}$$

as can easily verified, letting $\xi = \boldsymbol{r}/L$. Also y_k must satisfy the same given boundary condition of the boundary of Λ_0 as does ψ_k on the boundary of Λ. Thus y_k and e_k satisfy the dimensionless Schrödinger equation (2.47) in the region Λ_0 and are independent of L. Note that e_k are defined so as to make the dependence of ϵ_k on λ as well as on L explicit.

By a theorem of H. Weyl [‡], the number of eigenstates $g(e)\,de$ between e and $e + de$ goes as

$$g(e)\, de \sim \frac{2}{\sqrt{\pi}} e^{1/2} \, de \,, \tag{2.49}$$

asymptotically as $e \to \infty$ independent of the shape of Λ_0, and for either Dirichlet or Neumann boundary conditions. This means that the limit of the ratio of the two sides of (2.49) is equal to 1 for $e \to \infty$. This result enables us to calculate the limit (2.39–40) without specifying the shape of Λ_0.

First we consider for the function $f(N, \Lambda, T)$ the pressure, whose generating function is given by (1.137). In terms of e_k this is:

$$\frac{p^{\mathrm{gr}}}{kT} = \frac{2}{3L^3} \sum_{k=0}^{\infty} \frac{\lambda^2 e_k/L^2}{\exp(\alpha + \lambda^2 e_k/L^2) - 1} \,, \tag{2.50}$$

and (2.40), which determines α, becomes

$$\rho = \frac{1}{L^3} \sum_{k=0}^{\infty} \frac{1}{\exp(\alpha + \lambda^2 e_k/L^2) - 1} \,. \tag{2.51}$$

This pressure is the average of $(-\partial\epsilon/\partial V) = (-\partial\epsilon/\partial L)/3L^2$ and therefore represents the force related to changing the volume of Λ without changing its shape.

To obtain the equation of state $p^{\mathrm{gr}}(\rho, T)$ in the bulk limit one should first eliminate α between (2.50) and (2.51) and then let $L \to \infty$. On the other hand for a fixed $\alpha > 0$, the limit $L \to \infty$ for the two functions (2.50–51) can be taken right away since the sums go over to integrals by definition. Then one gets, using (2.49):

$$\frac{p^{\mathrm{gr}}}{kT} \sim \frac{2}{3\lambda^3} \int_0^{\infty} \frac{x}{e^{\alpha+x} - 1} \frac{2}{\sqrt{\pi}} x^{1/2} \, dx = \frac{1}{\lambda^3} g_{5/2}(\alpha) \,, \tag{2.52}$$

[‡] See Kac [49]; also McKean and Singer [50].

$$\rho \sim \frac{1}{\lambda^3} \int_0^\infty \frac{1}{e^{\alpha+x}-1} \frac{2}{\sqrt{\pi}} x^{1/2}\, dx = \frac{1}{\lambda^3} g_{3/2}(\alpha) . \tag{2.53}$$

A difficulty arises (as Einstein already noted) when α approaches zero. Since $g_{3/2}(\alpha)$ is monotonically decreasing with the maximum value $g_{3/2}(0) = \zeta(\frac{3}{2})$ at $\alpha = 0$, it seems that there would be a maximum value of the density equal to $\rho_c(T) = \zeta(\frac{3}{2})/\lambda^3$. In fact, the Bose functions $g_n(\alpha)$ are analytic functions only for $\alpha > 0$ (see Appendix 2.A), and the procedure of letting $L \to \infty$ with α fixed is not valid for $\alpha = 0$. To resolve this difficulty one must allow for the possibility that $\alpha \to 0$ *as* $L \to \infty$, and clearly one must be careful with the order of the two limits. First we consider that $e_0 = 0$, which is the case for Neumann and periodic boundary conditions. Indeed, for any finite L it follows from (2.51) that ρ is infinite when $\alpha = 0$. Suppose that $\alpha \sim c/L^3$ as $L \to \infty$, where c is a constant. Then the $k = 0$ term of (2.51) is

$$\frac{1}{L^3} \frac{1}{e^\alpha - 1} \sim \frac{1}{L^3 \alpha} \sim \frac{1}{c} . \tag{2.54}$$

On the other hand, for $k > 0$, α is negligible compared to $\lambda^2 e_k/L^2$ (note that e_k is a *number*); therefore one can put $\alpha = 0$ in all these terms and for $L \to \infty$ their sum can again be replaced by an integral, giving $\zeta(\frac{3}{2})/\lambda^3 \equiv \rho_c$. If one now chooses $c = 1/(\rho - \rho_c)$ so that $\alpha \sim 1/[L^3(\rho - \rho_c)]$, then (2.51) becomes the identity $\rho = \rho_c + (\rho - \rho_c)$ when $L \to \infty$ and this must therefore be the correct asymptotic behavior of α. Then for the pressure one sees that with this α even the first term of (2.50) goes to zero for $L \to \infty$, so one concludes that (2.52) remains valid for all $\alpha \geqq 0$. Thus for $\rho > \rho_c$ the pressure stays constant and is equal to:

$$p^{gr}(\rho, T) = \frac{kT}{\lambda^3} g_{5/2}(0) = \frac{kT}{\lambda^3} \zeta(\tfrac{5}{2}) , \qquad \rho > \rho_c . \tag{2.55}$$

Clearly this argument needs more mathematical scrutiny. It has been made mathematically respectable by Lewis and Pulé [27].

For the more physical Dirichlet boundary conditions the argument must be modified slightly because then $e_0 > 0$. From (2.50) and (2.51) one sees that the smallest value of α is now negative, namely $-\lambda^2 e_0/L^2$. When $\rho > \rho_c$ one must now consider that α goes to zero as $\alpha + \lambda^2 e_0/L^2 \sim 1/[L^3(\rho - \rho_c)]$ and one obtains the same results as before.

Therefore for both the Dirichlet and Neumann boundary conditions we have

$$p^{gr}(\rho, T) = \begin{cases} \dfrac{kT}{\lambda^3} g_{5/2}(\alpha) , & \rho < \rho_c , \\[2ex] \dfrac{kT}{\lambda^3} \zeta(\tfrac{5}{2}) , & \rho > \rho_c . \end{cases} \tag{2.56}$$

The results for the generating function of the energy density $u^{gr} = U^{gr}/V$ follow immediately since $u^{gr} = \frac{3}{2} p^{gr}$ as is evident from (1.136) and (2.50). Note that we introduce the energy *density* u^{gr} so that the bulk limit exists.

For the entropy there is the difficulty that the generating function S^g as given by (2.36) cannot be calculated simply in terms of the single particle states. However, the grand canonical entropy (1.37) can be used in its place, because the difference between the two, which is given by (2.37), vanishes in the bulk limit. This can be argued simply by noting that the factor $e^{-\alpha N} Z_N / Z^{gr}$ must go as $1/V$ as $V \to \infty$ to maintain its normalization to unity, and therefore that (2.37) goes only as $\ln V$, while S^{g} and S^{gr} are proportional to V. In the bulk limit $s^{\mathrm{gr}} \equiv S^{\mathrm{gr}}/V$ can be found in a manner similar to p^{gr}, with the result that

$$s^{\mathrm{gr}}(\rho, T) = s^{\mathrm{g}}(\rho, T) = \begin{cases} \dfrac{5}{2}\dfrac{k}{\lambda^3}\, g_{5/2}(\alpha) + k\rho\alpha\,, & \rho < \rho_{\mathrm{c}}\,, \\ \dfrac{5}{2}\dfrac{k}{\lambda^3}\, \zeta(\tfrac{5}{2})\,, & \rho > \rho_{\mathrm{c}}\,. \end{cases} \tag{2.57}$$

Next we calculate the Kac density $\nu(x, \rho) = \nu(x, \rho; T)$, by means of the characteristic function of the distribution:

$$\langle \mathrm{e}^{\mathrm{i}\xi N/V} \rangle \equiv \sum_{N=0}^{\infty} \mathrm{e}^{\mathrm{i}\xi N/V}\, \frac{\mathrm{e}^{-\alpha N} Z(N, \Lambda, T)}{Z^{\mathrm{gr}}(\alpha, \Lambda, T)} = \frac{Z^{\mathrm{gr}}(\alpha - \mathrm{i}\xi/V, \Lambda, T)}{Z^{\mathrm{gr}}(\alpha, \Lambda, T)}\,. \tag{2.58}$$

Evidently this is the Fourier transform of $\nu(x, \rho)$ in the limit of $V \to \infty$, if $\alpha = \alpha(\rho, \Lambda, T)$ is determined by (2.40):

$$\lim_{V \to \infty} \langle \mathrm{e}^{\mathrm{i}\xi N/V} \rangle = \int_0^{\infty} \nu(x, \rho)\, \mathrm{e}^{\mathrm{i}\xi x}\, \mathrm{d}x\,. \tag{2.59}$$

The limit of (2.58) can be calculated in a manner similar to the generating functions such as the pressure. When $\rho < \rho_{\mathrm{c}}$, α can be fixed and determined by (2.53), and using (1.134) for Z^{gr} and (2.49) for the density of states, it follows that

$$\ln \langle \mathrm{e}^{\mathrm{i}\xi N/V} \rangle \sim \frac{L^3}{\lambda^3}\, g_{5/2}(\alpha - \mathrm{i}\xi/V) - \frac{L^3}{\lambda^3}\, g_{5/2}(\alpha) \sim \mathrm{i}\frac{\xi}{\lambda^3}\, g_{3/2}(\alpha) = \mathrm{i}\,\xi\,\rho\,, \tag{2.60}$$

as $L \to \infty$. Again when $\rho > \rho_{\mathrm{c}}$ it is necessary to take $\alpha + \lambda^2 e_0/L^2 \sim 1/[L^3(\rho - \rho_{\mathrm{c}})]$ for the $k = 0$ term of Z^{gr} (1.134), while for the rest α can be taken to be zero and the sum replaced by an integral. This gives

$$\begin{aligned} \ln \langle \mathrm{e}^{\mathrm{i}\xi N/V} \rangle &\sim \frac{L^3}{\lambda^3}\, g_{5/2}(\alpha) - \ln \left\{ \frac{1}{L^3(\rho - \rho_{\mathrm{c}})} - \frac{\mathrm{i}\xi}{V} \right\} - \frac{L^3}{\lambda^3}\, g_{5/2}(0) + \ln \frac{1}{L^3(\rho - \rho_{\mathrm{c}})} \\ &\sim \frac{\mathrm{i}\xi}{\lambda^3}\, \zeta(\tfrac{3}{2}) - \ln(1 - \mathrm{i}\xi(\rho - \rho_{\mathrm{c}}))\,, \end{aligned} \tag{2.61}$$

as $L \to \infty$, or

$$\langle \mathrm{e}^{\mathrm{i}\xi N/V} \rangle \sim \frac{\mathrm{e}^{\mathrm{i}\xi\rho_{\mathrm{c}}}}{1 - \mathrm{i}\xi(\rho - \rho_{\mathrm{c}})} = \frac{1}{\rho - \rho_{\mathrm{c}}} \int_{\rho_0}^{\infty} \mathrm{d}x\, \exp\left\{ -\frac{x - \rho_{\mathrm{c}}}{\rho - \rho_{\mathrm{c}}} - \mathrm{i}\xi x \right\}. \tag{2.62}$$

By virtue of (2.59), the results (2.60) and (2.62) imply that

$\underline{\rho < \rho_{\mathrm{c}}}$

$$\nu(x, \rho) = \delta(x - \rho)\,, \tag{2.63}$$

$\underline{\rho > \rho_c}$

$$\nu(x, \rho) = \begin{cases} 0\,, & x < \rho_c\,, \\ \dfrac{1}{\rho - \rho_c} \exp\left\{-\dfrac{x - \rho_c}{\rho - \rho_c}\right\}, & x > \rho_c\,. \end{cases} \tag{2.64}$$

For $\rho < \rho_c$, this implies by (2.41) that all $f(\rho, T)$ are identical to their corresponding $f^g(\rho, T)$. When $\rho > \rho_c$, $\nu(x, \rho)$ as a function of x is distributed over all densities greater than ρ_c. A plot of $\nu(x, \rho)$ as a function of x is given in fig. 2.3. In this case $f^g(\rho, T)$ is an integral transform of $f(\rho, T)$. The inversion is simple because all of the f^g that we have calculated depend upon ρ only in integral powers of $\rho - \rho_c$, and from (2.64) one can verify directly that

$$(\rho - \rho_c)^k = \int_0^\infty \nu(x, \rho) \frac{(x - \rho_c)^k}{k!}\, \mathrm{d}x\,. \tag{2.65}$$

Therefore the transformation from $f^g(\rho, T)$ to $f(\rho, T)$ for $\rho > \rho_c$ can be accomplished by replacing the factor $(\rho - \rho_c)^k$ in each term of the former by $(\rho - \rho_c)/k!$. This can be written formally as

$$f(\rho, T) = \frac{1}{2\pi \mathrm{i}} \oint \frac{\mathrm{d}t}{t} \exp\{(\rho - \rho_c)t\}\, f^g(\tfrac{1}{t} + \rho_c, T)\,, \tag{2.66}$$

by virtue of (2.19). In fact, the integral transformation with $\nu(x, \rho)$ of (2.64) is basically a Laplace transform, and (2.66) can be recognized as the general inversion formula.

Especially if $f^g(\rho, T)$ is independent of, or proportional to, $\rho - \rho_c$, then it is identical to $f(\rho, T)$, and *vice versa*.

Therefore p, u, and s are identical to p^{gr}, u^{gr}, and s^{gr}, since for $\rho > \rho_c$ the latter are all independent of ρ. This proves the results (2.1) and (2.8) of the previous subsection. Note that this also implies that all of the bulk thermodynamical properties are identical in the canonical and grand canonical ensembles, for all values of the density.

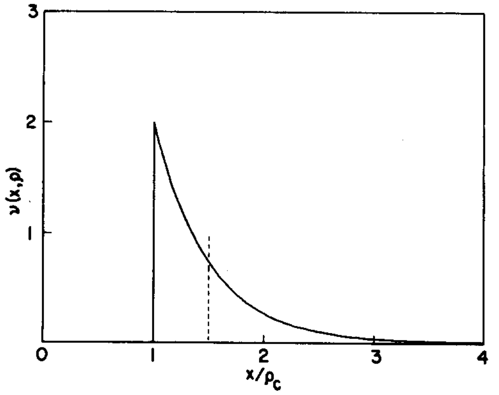


Fig. 2.3. The Kac density $\nu(x, \rho)$ plotted as a function of x for a given fixed ρ (greater than ρ_c) and at a fixed temperature. The mean at $x = \rho$ is shown by the dotted line.

d. Calculation of the occupations of the states and their fluctuations. The generating functions are given by (1.138–139), and the discussion of the limit $V \to \infty$ with ρ determined by (2.40) is similar to that of the pressure. One finds for the *excited states* $k > 0$,

$$\lim_{V\to\infty} \frac{\langle n_k \rangle^{\rm gr}}{V} = \lim_{V\to\infty} \frac{\langle n_k^2 \rangle^{\rm gr}}{V^2} = 0 \,, \tag{2.67}$$

while for the ground state,

$$\lim_{V\to\infty} \frac{\langle n_0 \rangle^{\rm gr}}{V} = \begin{cases} 0 \,, & \rho < \rho_{\rm c} \,, \\ \rho - \rho_{\rm c} \,, & \rho > \rho_{\rm c} \,, \end{cases} \tag{2.68}$$

$$\lim_{V\to\infty} \frac{\langle n_0^2 \rangle^{\rm gr}}{V^2} = \begin{cases} 0 \,, & \rho < \rho_{\rm c} \,, \\ 2(\rho - \rho_{\rm c})^2 \,, & \rho > \rho_{\rm c} \,. \end{cases} \tag{2.69}$$

Note that we must divide by V and V^2 to make the quantities intensive. Using the inversion method that has been derived, the corresponding canonical quantities can be calculated. Thus it follows that these occupations and their fluctuations are the same in the canonical ensemble, except for the mean square occupation of the ground state, which is $2(\rho - \rho_{\rm c})^2$ above but according to (2.65) or (2.66) is equal to $(\rho - \rho_{\rm c})^2$ in the canonical ensemble (when $\rho > \rho_{\rm c}$). Hence, the fluctuations are zero, as stated in (2.16).

Note that we have also found that the fluctuation of the density of particles in the ground state in the grand canonical ensemble is not zero, since according to (2.68) and (2.69),

$$\lim_{V\to\infty} \frac{\langle (\Delta n_0)^2 \rangle^{\rm gr}}{V^2} \equiv \lim_{V\to\infty} \frac{\langle n_0^2 \rangle^{\rm gr} - (\langle n_0 \rangle^{\rm gr})^2}{V^2} = (\rho - \rho_{\rm c})^2 \,. \tag{2.70}$$

These are huge fluctuations in an infinite system that occur even at $T = 0$. This is in sharp contrast to the canonical case. We will discuss this result further in section 2.4.

e. Calculation of the density matrices. In the bulk limit (2.39–40) the generating function of the s-particle reduced density matrix (1.140) clearly becomes

$$\rho_s^{\rm gr}(r'^s, r''^s; \rho, T) = \sum_{{\rm P}\{r'^s\}} \prod_{i=1}^{s} \rho_1^{\rm gr}(r_i', r_i''; \rho, T) \,, \tag{2.71}$$

for all ρ, and we need only consider $\rho_1^{\rm gr}$ (1.141). In terms of y_k and e_k it is

$$\rho_1^{\rm gr}(\boldsymbol{r}', \boldsymbol{r}''; \alpha, \Lambda, T) = \sum_{k=0}^{\infty} \frac{1}{L^3} \frac{1}{\exp(\alpha + \lambda^2 e_k/L^2) - 1} \, y_k^*(\boldsymbol{r}''/L) y_k(\boldsymbol{r}'/L) \,. \tag{2.72}$$

In the one phase region $\rho < \rho_{\rm c}$ the limit $L \to \infty$ can be taken with α fixed and determined by (2.53), with the result:

$$\rho_1^{\rm gr}(\boldsymbol{r}', \boldsymbol{r}''; \rho, T) = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} j^{-3/2} \exp\{-\alpha j - \pi |\boldsymbol{r}' - \boldsymbol{r}''|^2/j\lambda^2\} \equiv F(|\boldsymbol{r}' - \boldsymbol{r}''|, \alpha, T) \,. \tag{2.73}$$

This follows by expanding (2.72) in powers of $e^{-\alpha}$ and using a generalization of Weyl's theorem, which states that

$$\sum_{k=0}^{\infty} \exp(-te_k)\, y_k^*(\boldsymbol{r}'')\, y_k(\boldsymbol{r}') \sim t^{-3/2} \exp\{-\pi|\boldsymbol{r}' - \boldsymbol{r}''|^2/t\} \,, \tag{2.74}$$

as $t \to 0$, for all shapes of the region Λ_0 and for all boundary conditions as long as neither $\boldsymbol{r}'$ nor $\boldsymbol{r}''$ is on the boundary of the region. When $\rho > \rho_c$ one must take $\alpha \to 0$ as before, in which case the $k = 0$ term of (2.72) gives a special contribution while for all the terms $k > 0$ one can set $\alpha = 0$ and use (2.74), with the result [‡]

$$\rho_1^{\text{gr}}(\boldsymbol{r}', \boldsymbol{r}''; \rho, T) = F(|\boldsymbol{r}' - \boldsymbol{r}''|, 0, T) + (\rho - \rho_c)|y_0(0)|^2 \,. \tag{2.75}$$

This result leads to the following difficulty. With the Neumann boundary conditions, y_0 = const. = 1 and therefore the diagonal element of ρ_1^{gr} becomes $\rho_c + (\rho - \rho_c) = \rho$ as it should. However with the more physical Dirichlet boundary condition, the ground state $y_0(\xi)$ is not constant so that $y_0(0) \neq 1$ in general, and therefore the diagonal element which is the local density differs from the *average* density ρ and depends even upon the choice of the origin! The reason is that the ground state (which is macroscopically occupied) varies smoothly over the whole region Λ, and when the volume is made infinite the local density is any finite region about the origin becomes constant at a value that depends upon $y_0(0)$. Thus the bulk limit for the density does not exist in the usual way. If the average density were fixed not at ρ but at a value that makes the local density given by the diagonal element of ρ_1^{gr} equal to ρ, then clearly (2.75) would be replaced by

$$\rho_1^{\text{gr}}(\boldsymbol{r}', \boldsymbol{r}''; \rho, T) = F(|\boldsymbol{r}' - \boldsymbol{r}''|, 0, T) + (\rho - \rho_c) \,, \qquad \rho > \rho_c \,. \tag{2.76}$$

We will use this expression in all of the following. Note that it also follows from (2.75) by averaging the latter over all choices of the origin. In any case, this "renormalization" of the density does not change any of the relations between the thermodynamical properties since they are all independent of the density when $\rho < \rho_c$. Clearly the variation of the density is a pathology of the ideal gas, and one would expect that for an interacting system (say with a hard core repulsion) that this problem would be removed.

Thus, the bulk generating functions of the s-particle density matrix is given by (2.71), (2.73) and (2.76). Evidently it depends upon powers of $\rho - \rho_c$ (when $\rho > \rho_c$) from zero to s, and the general inversion (2.66) applies and leads to (2.17) for the canonical density matrices. This completes the derivation of the bulk canonical properties.

Actually, it should be pointed out that the fact that the bulk canonical properties and the bulk generating functions are related by the integral transform (2.41) does not really follow simply from (2.34), since there is the delicate question of interchanging limits. This step has been justified by Cannon [26]. Also, he was the first to derive the general expression for the density matrix (2.17) [‡‡].

Since the generating functions are all identical to the corresponding grand canonical averages (in the bulk limit), we have been led inadvertantly to the following surprising situation: The canonical and grand canonical ensembles differ in their predictions for some of the *bulk* properties of the IBG, especially $\langle(\Delta n_0)^2\rangle$ and ρ_s for $s \geqq 2$, in the condensed region, while $\langle n_0\rangle$, ρ_1, and all of the thermodynamical properties are the same. The fluctuations in the average occupation of the ground state according to (2.69) and (2.70) are quite different in the two ensembles, as we have already noted. Compare also the density matrices, which in the grand canonical ensemble are given by (2.71, 73, 76). In the off diagonal limit, in which *all* primed coordinates are far from the double-primed ones, they evidently behave as

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[‡] This expression has been derived with more mathematical detail by Lewis and Pulé [27].

[‡‡] (Unpublished notes.) Note that the two particle distribution function (2.27) was first derived by London [16] and also by Placzek [51] in the one phase region only, and is called the London–Placzek formula. Note also that in the grand canonical ensemble the density matrices have been given recently by Girard [52], and the distribution functions in the one phase region by Jaen [53].

$$\rho_s^{\text{gr}}(r'^s, r''^s; \rho, T) \to \begin{cases} 0\,, & \rho < \rho_c\,, \\ s!\,(\rho - \rho_c)^s\,, & \rho > \rho_c\,, \end{cases} \tag{2.77}$$

which differs from the canonical ODLRO $(\rho - \rho_c)^s$ as given in (2.29), when $\rho > \rho_c$. The diagonal elements of the density matrices are the grand canonical distribution functions, and one can show from (2.71) that their cluster functions defined according to (2.30) are given by

$$\chi_s^{\text{gr}}(r^s; \rho, T) = \sum_{\mathrm{p}\{r_2 \dots r_s\}} \rho_1^{\text{gr}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \rho, T)\, \rho_1^{\text{gr}}(\boldsymbol{r}_2, \boldsymbol{r}_3; \rho, T) \dots \rho_1^{\text{gr}}(\boldsymbol{r}_s, \boldsymbol{r}_1; \rho, T)\,, \tag{2.78}$$

for *all* ρ. When $\rho > \rho_c$ these differ from the canonical cluster functions (2.32) for $s \geqq 2$, and do not satisfy the cluster property, since in the limit that all coordinates $\boldsymbol{r}_1 \dots \boldsymbol{r}_s$ are separated far apart,

$$\chi_s^{\text{gr}} \to \begin{cases} 0\,, & \rho < \rho_c\,, \\ (s-1)!\,(\rho - \rho_c)^s\,, & \rho > \rho_c\,. \end{cases} \tag{2.79}$$

The grand canonical system exhibits therefore DLRO in the condensed region.

In the grand canonical ensemble, the fraction of systems containing N particles is given by $\mathrm{e}^{-\alpha N} Z(N, \Lambda, T)/Z^{\text{gr}}(\alpha, \Lambda, T)$. The mean of that distribution is $\langle N\rangle^{\text{gr}} = N^{\text{gr}}$ of (2.40), and about that mean there is a fluctuation in number. In the bulk limit this can become a fluctuation in the average density which evidently can be calculated directly from $\nu(x, \rho)$:

$$\lim_{V\to\infty} \frac{\langle(\Delta N)^2\rangle^{\text{gr}}}{V^2} = \int_0^\infty (x - \rho)^2\, \nu(x, \rho)\, \mathrm{d}x = \begin{cases} 0\,, & \rho < \rho_c\,, \\ (\rho - \rho_c)^2\,, & \rho > \rho_c\,, \end{cases} \tag{2.80}$$

using (2.65). Thus in the condensed region there are fluctuations in the density of the entire system. These cannot be directly compared to the canonical ensemble since by assumption the number of particles in that ensemble is fixed. Since (2.80) is identical to the fluctuations in the average occupation of the ground state, the latter must be due to the former. And finally the DLRO (2.79) can also be attributed to these density fluctuations, since the normalization of the grand canonical density matrices is related to the distribution of N, by (1.116).

2.4. The significance of the grand canonical ensemble

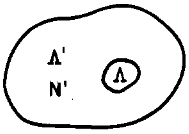
The differences that we have just found between some bulk properties in the canonical and the grand canonical ensembles are particularly striking because they represent infinite systems for which it is usually supposed that the ensembles are equivalent. Therefore one might wonder at this point which of the results are correct and why we have been preferring the canonical ensemble.

Indeed, in terms of calculational convenience the grand canonical ensemble is clearly preferred, as we have seen. In this section we investigate the grand canonical ensemble and show that it *loses its validity* for the IBG in the condensed region [‡].

This ensemble, as defined in section 1.3, is normally thought to represent an "open system" which exchanges particles with a resevoir that determines the temperature and the average density. This is based upon the simple derivation of the grand canonical distribution (1.32) as the most probable distribution when the exact number of particles and energy are not specified but only their average values. Then according to (2.80) there should be huge density fluctuations in a condensed "open" IBG.

However, the relationship between this open system and the most probable distribution (1.32) is not entirely clear. A more fundamental derivation of the ensemble for an open system is to consider the properties of a system Λ that is part of a much larger system Λ' described by the canonical ensemble (which in turn is in contact with a heat resevoir that determines the temperature). In this way the grand canonical distribution also can be derived [ǂ], but a careful examination shows that some of the steps might be suspect in a two phase region. We will return to this point later.

In this subsection we will derive the fluctuations in density in the subregion Λ of an IBG by direct calculation. That is, we consider that the system Λ (of volume V) is part of a larger system Λ' (of volume V') containing N' particles, as represented below:



The boundary between Λ and $\Lambda' - \Lambda$ is an imaginary surface separating the regions, and Λ can contain any number of particles N between zero and N'. The spatial distributions of the N' particles are described by the complete distribution function $n(r^{N'}; N', \Lambda')$ (which we shall later take to be the canonical distribution but for now can leave general), from which the probability that there are N particles in Λ follows:

$$P(N, \Lambda; N', \Lambda') = \frac{N'!}{(N'-N)!\,N!} \int_{\Lambda} \mathrm{d}r^N \int_{\Lambda'-\Lambda} \mathrm{d}r^{N'-N} n(r^{N'}, N', \Lambda) \,. \tag{2.81}$$

Letting $V' \to \infty$ with $N'/V' = \rho = \text{const.}$, this gives the probability that there are N particles in Λ when the total (infinite) system has a density ρ, namely:

$$P(N, \Lambda; \rho) = \lim_{V' \to \infty} P(N, \Lambda; \rho V', \Lambda') \,. \tag{2.82}$$

Now letting $V \to \infty$ with $N/V = x$, this gives the probability that Λ (which is now also infinite) is at density x when the larger total system is at density ρ, namely:

$$P(x, \rho) = \lim_{V \to \infty} VP(xV, \Lambda; \rho) \,. \tag{2.83}$$

If indeed Λ were described by the grand canonical ensemble, then this should be precisely the Kac distribution $\nu(x, \rho)$, according to (2.42).

[‡] This point has also been discussed by Johnston [28].

[ǂ] See for example Huang [43].

First we consider that $n(r^{N'};N',\Lambda')$ is constant, which is the case for the IBG in the classical limit ($T\to\infty$) and also when $T=0$. Then, to satisfy the normalization requirement it must be equal to $(V')^{-N'}$, and it is easy to show that

$$P(N,\Lambda;N',\Lambda')=\frac{N'!}{(N'-N)!\,N!}\left(\frac{V}{V'}\right)^{N}\left(1-\frac{V}{V'}\right)^{N'-N}, \tag{2.84}$$

$$P(N,\Lambda;\rho)=\frac{1}{N!}(\rho V)^{N}\,\mathrm{e}^{-\rho V}, \tag{2.85}$$

$$P(x,\rho)=\delta(x-\rho)\,. \tag{2.86}$$

This final result is in sharp contradiction with $\nu(x,\rho)$ (2.64) at $T=0$, where $\rho_{\mathrm{c}}=0$.

We now consider all temperatures. In general, (2.81) can be written in terms of the reduced distribution functions as follows:

$$P(N,\Lambda;N',\Lambda')=\sum_{s=N}^{N'}\frac{(-1)^{s-N}}{(s-N)!\,N!}\int\limits_{\Lambda} n_s(r^s;N',\Lambda')\,\mathrm{d}r^s, \tag{2.87}$$

where n_s are defined according to (1.73, 79), namely

$$n_s(r^s;N',\Lambda')\equiv\frac{N'!}{(N'-s)!}\int\limits_{\Lambda'} n(r^N;N',\Lambda')\,\mathrm{d}r^{N'-s}\,. \tag{2.88}$$

Note that in (2.87) the integral is over the subregion Λ while in (2.88) it is over the entire region Λ'. Eq. (2.87) can be proven by the inclusion-exclusion method, namely by writing

$$\int\limits_{\Lambda'-\Lambda}\mathrm{d}r^{N'-N}=\int\limits_{\Lambda'}\mathrm{d}r^{N'-N}\prod_{i=N'-N+1}^{N'}(1-\Theta(\boldsymbol{r}_i)), \tag{2.89}$$

where $\Theta(\boldsymbol{r})$ is unity when $r\in\Lambda$ and zero when $r\in\Lambda'-\Lambda$, and multiplying out the products of the integrand. Now, letting $V'\to\infty$ with $N'/V'=\rho$, (2.87) becomes:

$$P(N,\Lambda;\rho)=\sum_{s=N}^{\infty}\frac{(-1)^{s-N}}{(s-N)!\,N!}\int\limits_{\Lambda} n_s(r^s;\rho)\,\mathrm{d}r^s, \tag{2.90}$$

where this n_s represents the bulk limit of (2.88). To take the next limit $V\to\infty$ we must first introduce the characteristic function of the distribution (compare with (2.60–62)):

$$\begin{aligned}\langle \mathrm{e}^{\mathrm{i}\xi N/V}\rangle &\equiv \sum_{N=0}^{\infty}\mathrm{e}^{\mathrm{i}\xi N/V}P(N,\Lambda;\rho)=\sum_{s=0}^{\infty}\frac{(\mathrm{e}^{\mathrm{i}\xi/V}-1)^s}{s!}\int\limits_{\Lambda} n_s(r^s;\rho)\,\mathrm{d}r^s\\ &=\exp\left\{\sum_{s=1}^{\infty}\frac{(\mathrm{e}^{\mathrm{i}\xi/V}-1)^s}{s!}\int\limits_{\Lambda}\chi_s(r^s;\rho)\,\mathrm{d}r^s\right\}.\end{aligned} \tag{2.91}$$

The last step is a consequence of the first theorem of Mayer[‡]. Since in the limit $V\to\infty$ the charac-

[‡] See Uhlenbeck and Ford [22], [55] Ch. 2. Note that (2.90) and (2.92) have been given recently by Vezzetti [54]. Compare also Kac and Luttinger [56].

teristic function is evidently the Fourier transform of $P(x, \rho)$,

$$\lim_{V\to\infty} \langle e^{i\xi N/V} \rangle = \int_0^\infty e^{i\xi x} P(x, \rho)\, dx\ , \tag{2.92}$$

the function $P(x, \rho)$ can be found by inversion. Now, for the $s = 1$ term of (2.91):

$$(e^{i\xi/V} - 1) \int_\Lambda \chi_1(\boldsymbol{r}, \rho)\, d\boldsymbol{r} = \left(i\frac{\xi}{V} - \frac{1}{2}\frac{\xi^2}{V^2} \dots\right)\rho V \sim i\xi\rho\ , \tag{2.93}$$

as $V \to \infty$ since $\chi_1 = \rho$ always. For $s \geqq 2$ we must refer to the explicit expression for χ_s (2.32) in the *canonical ensemble*; when $\rho < \rho_c$,

$$\lim_{V\to\infty} \frac{1}{V} \int_\Lambda \chi_s(r^s; \rho, T)\, dr^s\ , \tag{2.94}$$

clearly exists in which case all terms $s \geqq 2$ in (2.91) must vanish at least as fast as $1/V$, as $V \to \infty$, and then from (2.91–93) it follows that:

$$P(x, \rho) = \delta(x - \rho)\ , \tag{2.95}$$

which agrees with $\nu(x, \rho)$ of (2.63). When $\rho \geqq \rho_c$, the $s = 2$ term of (2.91) is given by

$$\tfrac{1}{2}(e^{i\xi/V} - 1)^2 \int_\Lambda \chi_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \rho, T)\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 =$$

$$= \left(-\frac{\xi^2}{4V^2} + \dots\right) \int_\Lambda \{[F(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, 0, T)]^2 + 2(\rho - \rho_c) F(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, 0, T)\}\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2\ . \tag{2.96}$$

Since according to (2.24) $F(r, 0, T) \sim 1/r$ for large r, both terms of this integral go to zero as $V \to \infty$:

$$\frac{1}{V^2} \int_\Lambda F(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, 0, T)\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 \sim \frac{1}{V} \int_0^{V^{1/3}} \frac{4\pi r^2}{r}\, dr \sim V^{-1/3}\ , \tag{2.97a}$$

$$\frac{1}{V^2} \int_\Lambda [F(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, 0, T)]^2\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2 \sim \frac{1}{V} \int_0^{V^{1/3}} \frac{4\pi r^2}{r^2}\, dr \sim V^{-2/3}\ , \tag{2.97b}$$

although not as fast as when $\rho < \rho_c$. Further inspection shows that all terms for $s > 2$ vanish at least as fast. Again only (2.93) remains and therefore $P(x, \rho)$ is a delta function (2.95) for $\rho > \rho_c$ also, sharply contradicting the prediction of the grand canonical ensemble (2.64). In particular there are *no* fluctuations in the overall density.

Therefore, the properties of an IBG in a region Λ which is part of a larger system Λ' are always identical to those predicted by the canonical ensemble, in the double limit V, $V' \to \infty$. The grand canonical ensemble does not represent this (and probably not any) physical situation for the condensed IBG, and therefore its anomalous predictions should be ignored.

In the general derivation of the grand canonical ensemble for an open system, the basic assumption is that the properties in the two parts Λ' and $\Lambda' - \Lambda$ are independent, at least to the extent that the interaction is a surface term. This is not the case for the condensed IBG and must be due to the ODLRO.

Finally one might wonder how the grand canonical ensemble gives any property correctly of the condensed IBG, as it does for the thermodynamical properties and the first reduced density matrix. From the argument following (2.66) it follows that any canonical property $f(\rho, T)$ that is either independent of or proportional to the density ρ is also given by $f^{\mathrm{g}}(\rho, T) = f^{\mathrm{gr}}(\rho, T)$. This only makes use of the fact that the density distribution $\nu(x, \rho)$ is normalized to unity and its mean is at $x = \rho$, and these two properties are basic requirements of *any* density ensemble.

2.5. The bulk properties of an IBG in d-dimensions

The methods of section 2.3 can easily be generalized for any number of dimensions d making use of the generalization of the Weyl theorem, namely that the density of states $g(e)$ is $e^{d/2-1}/\Gamma(d/2)$. Here we just list the results and omit the proofs.

The pressure, energy density, chemical potential, and entropy density are given by

$$p(\rho, T) = \frac{2}{d}\, u(\rho, T) = \begin{cases} \dfrac{kT}{\lambda^d}\, g_{1+d/2}(\alpha)\,, & \rho < \rho_{\mathrm{c}}\,, \\[2ex] \dfrac{kT}{\lambda^d}\, \zeta(1 + d/2)\,, & \rho > \rho_{\mathrm{c}}\,, \end{cases} \tag{2.98}$$

$$\mu(\rho, T) = (u - Ts + p)/\rho = \begin{cases} kT\alpha\,, & \rho < \rho_{\mathrm{c}}\,, \\ 0\,, & \rho > \rho_{\mathrm{c}}\,, \end{cases} \tag{2.99}$$

where $\alpha = \alpha(\rho, T)$ is the unique root of

$$\rho = \frac{1}{\lambda^d}\, g_{d/2}(\alpha)\,, \tag{2.100}$$

and

$$\rho_{\mathrm{c}} = \rho_{\mathrm{c}}(T) \equiv \zeta(d/2)/\lambda^d\,, \qquad d \geqq 3\,. \tag{2.101}$$

For $d \leqq 2$ there is no condensation and ρ_{c} is infinite. The expressions for $\rho > \rho_{\mathrm{c}}$ refer only to $d \geqq 3$.

For $d \geqq 3$ there is a first order phase transition at $\rho = \rho_{\mathrm{c}}$ such that for greater densities (at constant temperature) the pressure is constant and equal to $p_{\mathrm{c}} \equiv kT\zeta(1 + d/2)/\lambda^d$. We have plotted the pressure isotherms, scaled by p_{c} and ρ_{c}, in fig. 2.4. Also included are the curves for $d = 1$ and 2 for which there is no phase transition, and for which the quantity $\rho_0 = \rho_0(T) \equiv 1/\lambda^d$ is used for scaling the density. The analytic properties of the curves can be found using the properties of the Bose functions $g_n(\alpha)$ given in Appendix 2.A. The one dimensional IBG has no phase transition; its isotherm is never flat and approaches the ordinate ($\rho = 0$) with slope

$$\left(\frac{\mathrm{d}(p/p_{\mathrm{c}})}{\mathrm{d}(\rho_0/\rho)}\right)_{\rho = \rho_0} = \frac{-2\pi}{\zeta(3/2)} \simeq -2.405\,, \tag{2.102}$$

while in two dimensions *all* derivatives are zero at $\rho = \rho_0$. In three dimensions the first derivative is zero and the second derivative is discontinuous at $\rho = \rho_{\mathrm{c}}$, as we have already noted, and in four dimensions the first derivative is continuous and zero while all higher ones are infinite, at the tran-

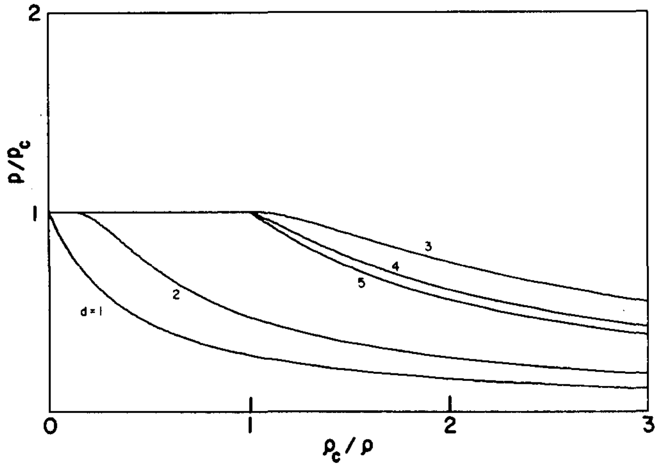


Fig. 2.4. The isotherm of the bulk pressure p (scaled by p_c) versus the specific volume $1/\rho$ (scaled by $1/\rho_c$ for $d \geqq 3$ and $1/\rho_0$ for $d \leqq 2$), for dimensionality $d = 1$ to 5.

sition point. For $d \geqq 5$ the condensation point is reached with slope

$$\left(\frac{\mathrm{d}(p/p_c)}{\mathrm{d}(\rho_c/\rho)}\right)_{\rho=\rho_c} = \frac{[\zeta(d/2)]^2}{\zeta(d/2+1)\,\zeta(d/2-1)}\,, \tag{2.103}$$

which approaches −1 as $d \to \infty$.

The condensed region $\rho > \rho_c$ can again be interpreted as consisting of two phases with the fraction of condensed particles given by $(\rho - \rho_c)/\rho = 1 - (T/T_c)^{d/2}$, where T_c is defined analogous to the case $d = 3$. Again the thermodynamical properties are independent of the density for a given temperature in the condensed region and therefore the condensed phase does not contribute to the thermodynamics. One can also verify that the Clapeyron equation is satisfied.

The specific heat per particle at constant volume (density) follows from (2.98) and is given by ‡:

$$\frac{c_v}{k} \equiv \frac{1}{k}\left(\frac{\partial}{\partial T}\right)_\rho \frac{u}{\rho} = \begin{cases} \dfrac{d}{2}\left(\dfrac{d}{2}+1\right)\dfrac{g_{1+d/2}(\alpha)}{g_{d/2}(\alpha)} - \left(\dfrac{d}{2}\right)^2 \dfrac{g_{d/2}(\alpha)}{g_{d/2-1}(\alpha)}\,, & \rho < \rho_c\,, \\ \dfrac{d}{2}\left(\dfrac{d}{2}+1\right)\left(\dfrac{T}{T_c}\right)^{d/2} \dfrac{\zeta(1+d/2)}{\zeta(d/2)}\,, & \rho > \rho_c\,. \end{cases} \tag{2.104}$$

It is plotted in fig. 2.5 as a function of the temperature, scaled by T_c for $d = 3$, 4, and 5, and T_0 for $d = 1$ and 2, where $T_0(\rho)$ is the solution of $\rho_0(T_0) = \rho$, as T_c is the solution of $\rho_c(T_c) = \rho$.

As we have noted earlier, at $T = T_c$ there is a discontinuity in the first derivative of the specific heat, for $d = 3$. When $d = 4$ the specific heat itself is continuous, but on the right hand side of the transition point $T \to T_c^+$ the second and all higher derivatives are infinite. For $d \geqq 5$ there is a discontinuity in the specific heat itself. Note that by virtue of the relation $u = (d/2)p$ (valid only for an ideal gas) there is a direct relation between the discontinuities in the specific heat and those in the equation of state.

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‡ This formula has been given by May [57].

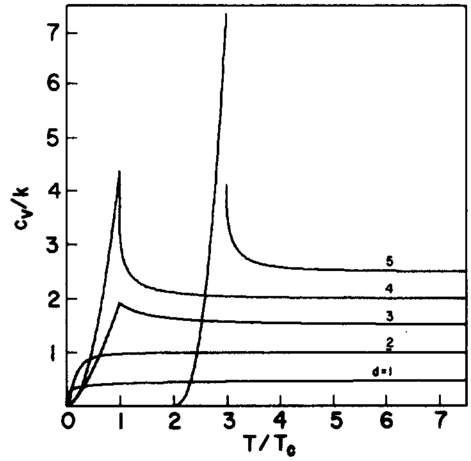

Fig. 2.5. The specific heat per particle as a function of the scaled temperature, for $d = 1$ to 5. For $d = 5$ the curve is shifted.

The average occupations of the energy levels and their fluctuations can be calculated, and the bulk behavior for all $d > 3$ is exactly like the three dimensional case. Likewise the bulk density matrices are the same except that F is now

$$F(r, \alpha, T) = \frac{1}{\lambda^d} \sum_{j=1}^{\infty} j^{-d/2} \exp(-\alpha j - \pi r^2/j\lambda^2) . \tag{2.105}$$

The discussion of the DLRO and the ODLRO in the condensed region for $d > 3$ is the same as that for $d = 3$.

Appendix 2.A: The Bose functions

These functions are defined by

$$g_n(\alpha) \equiv \frac{1}{\Gamma(n)} \int_0^{\infty} \frac{t^{n-1}\,\mathrm{d}t}{\mathrm{e}^{t+\alpha} - 1} = \sum_{j=1}^{\infty} j^{-n}\, \mathrm{e}^{-\alpha j} , \tag{2.A1}$$

for $\alpha > 0$ and all n, and also $\alpha = 0$ and $n > 1$. In the latter case,

$$g_n(0) = \sum_{j=1}^{\infty} j^{-n} = \zeta(n) , \tag{2.A2}$$

which is the zeta function of Riemann. The behavior of the Bose functions about $\alpha = 0$ is given by

$$g_n(\alpha) = \begin{cases} \Gamma(1-n)\alpha^{n-1} + \sum\limits_{k=0}^{\infty} \zeta(n-k)\dfrac{(-\alpha)^k}{k!}\,, & n \neq 1, 2, 3, \ldots \\[2ex] \dfrac{(-\alpha)^{n-1}}{(n-1)!}\left[-\ln\alpha + \sum\limits_{m=1}^{n-1}\dfrac{1}{m}\right] + \sum\limits_{\substack{k=0\\ \neq n-1}}^{\infty} \zeta(n-k)\dfrac{(-\alpha)^k}{k!}\,, & n = 1, 2, 3, \ldots\,. \end{cases} \tag{2.A3}$$

(In the second formula, for the case $n = 1$, the sum over m should be interpreted as zero.) At $\alpha = 0$, $g_n(\alpha)$ diverges for $n \leqq 1$; indeed for all n there is some kind of singularity at $\alpha = 0$, such as a branch point.

The expansions (2.A3) are in terms of $\zeta(n)$, which for $n \leqq 1$ must be found by analytically continuing (2.A2). With the asymptotic properties of the zeta function it can be shown that the k series in (2.A3) are convergent for $|\alpha| < 2\pi$. Consequently (2.A3) also represents an analytic continuation of $g_n(\alpha)$ for $\alpha < 0$. As shown by Robinson [58], these expansions can be derived most simply by means of the Mellin transformation,

$$G_n(s) = \int_0^{\infty} g_n(\alpha)\alpha^{s-1}\,\mathrm{d}\alpha = \zeta(n+s)\,\Gamma(s)\,, \tag{2.A4}$$

which can be formally inverted as follows:

$$g_n(\alpha) = \frac{1}{2\pi\mathrm{i}}\int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty} G_n(s)\,\alpha^{-s}\,\mathrm{d}s\,, \tag{2.A5}$$

where c is to the right of all the singularities of $G_n(s)$. The contour can be deformed to encircle just the singularities, and since the contribution of the semi-circles vanish, $g_n(\alpha)$ can be found by evaluating the residues, and this gives (2.A3).

When $\alpha \gg 1$ the series (2.A1) itself is rapidly convergent, and as $\alpha \to \infty$, $g_n(\alpha) \sim \mathrm{e}^{-\alpha}$ for all n. Some plots of $g_n(\alpha)$ are given in fig. 2.6. Accurate tables have recently been given by Kincaid and Cohen [59]. Also, a table of the zeta functions has been compiled by Gram [60].

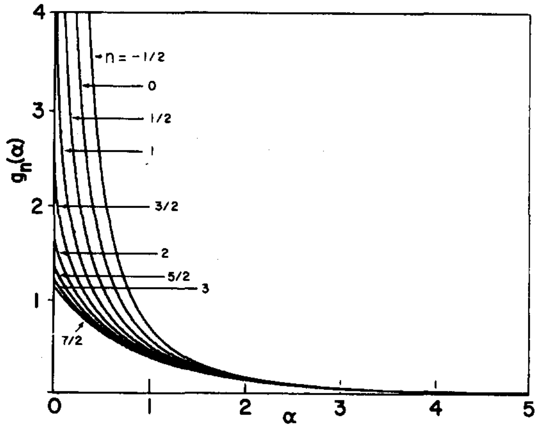

Fig. 2.6. The Bose function $g_n(\alpha)$ for $n = -1/2$ to $7/2$.

3. The thermodynamical properties of an IBG in a finite volume

3.1. Introduction

In this section we study the properties of an IBG in a large but finite volume. The motivation is to show more explicitly how the bulk limit is reached and to discuss the surface properties, especially the surface tension.

To be specific we consider a d-dimensional box (rectangular parallelopiped) with sides $L_1, L_2, \ldots$ $\ldots L_d$. We will *always* assume that the L_i are large compared to the thermal wavelength, so that

$$l_i \equiv L_i/\lambda \gg 1 \tag{3.1}$$

(since λ must be finite this excludes the point $T = 0$) and also for simplicity that the l_i are all of the same order of magnitude. The energy levels are given by

$$\beta \epsilon_{n_1 \ldots n_d} = \frac{\pi}{4} \left\{ \frac{n_1^2}{l_1^2} + \ldots + \frac{n_d^2}{l_d^2} \right\} , \tag{3.2}$$

where

$$n_i = 1, 2, 3, \ldots \quad \text{(Dirichlet boundary conditions, } \psi \to 0) , \tag{3.3}$$

and

$$n_i = 0, 1, 2, \ldots \quad \text{(Neumann boundary conditions, } \partial \psi / \partial n \to 0) . \tag{3.4}$$

We will also consider the case of periodic boundary conditions, for which

$$\beta \epsilon_{n_1 \ldots n_d} = \pi \left\{ \frac{n_1^2}{l_1^2} + \ldots + \frac{n_d^2}{l_d^2} \right\} , \tag{3.5}$$

where

$$n_i = 0, \pm 1, \pm 2, \ldots \quad \text{(periodic boundary conditions)} . \tag{3.6}$$

We will use the ratios

$$\omega_i \equiv l_i/l \equiv L_i/L , \tag{3.7a}$$

where

$$l \equiv L/\lambda , \qquad L \equiv (L_1 L_2 \ldots L_d)^{1/d} . \tag{3.7b}$$

Thus ω_i describe the *shape* (relative dimensions) of the rectangular box and satisfy $\omega_1 \omega_2 \ldots \omega_d = 1$. We will also use the abbreviations

$$N^2 \equiv \frac{n_1^2}{\omega_1^2} + \ldots \frac{n_d^2}{\omega_d^2} , \qquad M^2 \equiv m_1^2 \omega_1^2 + \ldots + m_d^2 \omega_d^2 , \tag{3.8}$$

since these combinations will occur quite often. As in section 2 we will use the dimensionless energy levels e_k defined by

$$\beta \epsilon_k = e_k / l^2 , \qquad e_0 \leqq e_1 \leqq e_2 \ldots . \tag{3.9}$$

We restrict ourselves to the discussion of the thermodynamic properties and start with the grand partition function.

3.2. The grand partition function Z^{gr}

According to the general definition (1.134),

$$\ln Z^{\mathrm{gr}} = \sum_{n_i} - \ln\{1 - \exp(-\alpha - \beta\epsilon_{n_1 \dots n_d})\} \, . \tag{3.10}$$

To discuss the sums over n_i for all values of α, we begin with the case of periodic boundary conditions for which the analysis is most straightforward. Furthermore, as we shall see, the results for the other boundary conditions can be expressed in terms of these results [‡].

a. Periodic boundary conditions, $\alpha l^2 \gg 1$. By expanding the logarithm in (3.10) and using (3.5) and (3.8), one gets

$$\ln Z_0^{\mathrm{gr}}(\alpha, l_1, \dots l_d) = \sum_{n_i=-\infty}^{\infty} \sum_{j=1}^{\infty} j^{-1} \exp\{-j(\alpha + \pi N^2/l^2)\} \, . \tag{3.11}$$

The subscript 0 indicates the periodic boundary conditions, and the sum over n_i means a product of sums for $i = 1, \dots d$. Interchanging the sums and using the identity [‡]

$$\sum_{n=-\infty}^{\infty} \exp(-\pi a n^2) = \frac{1}{\sqrt{a}} \sum_{m=-\infty}^{\infty} \exp(-\pi m^2/a) \, , \tag{3.12}$$

one gets

$$\ln Z_0^{\mathrm{gr}} = l^d \sum_{j=1}^{\infty} j^{-1-d/2} \, \mathrm{e}^{-\alpha j} \sum_{m_i=-\infty}^{\infty} \exp(-\pi l^2 M^2/j) \, . \tag{3.13}$$

Splitting off the $m_i = 0$ term ($m_1 = \dots = m_d = 0$) and approximating the sum over j by an integral (following Greenspoon and Pathria [29–31]) one gets:

$$\ln Z_0^{\mathrm{gr}} \simeq l^d \, g_{1+d/2}(\alpha) + \int_0^{\infty} \mathrm{d}t \; t^{-1-d/2} \exp(-\alpha l^2 t) \sum_{m_i}{}' \exp(-\pi M^2/t) \, , \tag{3.14}$$

where the prime denotes that the single term $m_i = 0$ is omitted from the summation, and where $l^2 t = j$. The $g_n(\alpha)$ are again the Bose functions described in Appendix 2.A. This approximation is justified in Appendix 3.A for large l by showing that the error induced is of order $\mathrm{O}(\mathrm{e}^{-l})$. Note that the second term in (3.14) is a function of just αl^2 and the shape parameters ω_i. Interchanging the sum and the integral and using [‡]

[‡] There has been a long interest in the analysis of Z^{gr} for a box. Indeed some of the expressions in this section have been given (wholly or partially) by Greenspoon and Pathria [29–31], Chaba and Pathria [61], Kruegar [62], and Sonin [63]. See also the related results of Barber and Fisher [64], Carmi [65], Ziman [66], Osbourne [67], Fraser [68,69] and Fowler and Jones [70].

[‡] This is a Jacobi theta transformation and is a simple result of the Poisson summation formula,

$$\sum_{n=-\infty}^{\infty} f(n) = \sum_{m=-\infty}^{\infty} \int_{-\infty}^{\infty} f(x) \exp(2\pi i m x) \, \mathrm{d}x \, ,$$

for $f(n) = \exp(-\pi a n^2)$. (See for example Whittaker and Watson [71].)

[‡] See Erdélyi et al. [72] p. 82, eq. 23.

$$K_\nu(a) = \tfrac{1}{2} a^\nu \int\limits_0^\infty \exp\{-(t + a^2/t)/2\}\, t^{-\nu-1}\, \mathrm{d}t\,, \tag{3.15}$$

where K_ν is the modified Hankel function of order ν, one gets the final result,

$$\ln Z_0^{\mathrm{gr}} \simeq l^d g_{1+d/2}(\alpha) + \sum_{m_i}{}' \; 2\left(\frac{\alpha l^2}{\pi M^2}\right)^{d/4} K_{d/2}(2\sqrt{\pi\alpha}\, lM)\,. \tag{3.16}$$

Since for half integer order the K can be expressed in elementary functions, one gets simple expressions for d odd. Especially one gets for:

$\underline{d = 1}$

$$\ln Z_0^{\mathrm{gr}}(\alpha, l) \simeq l g_{3/2}(\alpha) + 2 \sum_{m=1}^{\infty} \frac{1}{m} \exp(-2\sqrt{\pi\alpha}\, lm)\,, \tag{3.17a}$$

$\underline{d = 2}$

$$\ln Z_0^{\mathrm{gr}}(\alpha, l_1, l_2) \simeq l^2 g_2(\alpha) + \sum_{m_1,}\; \sum_{m_2=-\infty}^{\infty}{}' \frac{2l}{M} \sqrt{\frac{\alpha}{\pi}}\, K_1(2\sqrt{\alpha}\, lM)\,, \tag{3.17b}$$

$$M^2 = m_1^2 \omega_1^2 + m_2^2 \omega_2^2\,,$$

$\underline{d = 3}$

$$\ln Z_0^{\mathrm{gr}}(\alpha, l_1, l_2, l_3) \simeq l^3 g_{5/2}(\alpha) + \sum_{\substack{m_1 m_2 m_3 \\ = -\infty}}^{\infty}\!\!{}' \left(\frac{1}{2\pi M^3} + \frac{l}{M^2}\sqrt{\frac{\alpha}{\pi}}\right) \exp(-2\sqrt{\pi\alpha}\, lM)\,, \tag{3.17c}$$

$$M^2 = m_1^2 \omega_1^2 + m_2^2 \omega_2^2 + m_3^2 \omega_3^2\,.$$

It is not difficult to justify the various interchanges that we have used.

b. Periodic boundary conditions, $0 < \alpha l^2 \ll 1$. Although the expressions (3.17) are valid for all α when $l \gg 1$, it is clear that the series converge quickly only when αl^2 is large compared to 1, so they are only useful in that case. From the discussion in section 2 we expect that in the condensation region, $\alpha \sim \lambda^3/V = 1/l^3$ for $d = 3$ so that αl^2 will be very small. Furthermore from the same discussion one must expect that then $\ln Z^{\mathrm{gr}}$ will become singular as $\ln \alpha$. This singularity must sit in the sums of (3.17). Finally one cannot expand (3.14) or (3.17) in powers of αl^2 because each is singular for $\alpha l^2 = 0$. So one must proceed in a more sophisticated way.

Going back to (3.14) we transform the integral by writing

$$f(\sigma) \equiv \int\limits_0^\infty \mathrm{d}t\, t^{-1-d/2}\, \mathrm{e}^{-\sigma t} \sum_{m_i}{}' \mathrm{e}^{-\pi M^2/t}\,, \tag{3.18}$$

where $\sigma \equiv \alpha l^2$, and introducing the Mellin transform as in Appendix 2.A:

$$F(s) \equiv \int\limits_0^\infty f(\sigma)\, \sigma^{s-1}\, \mathrm{d}\sigma = \Gamma(s)\, \Gamma\left(s + \frac{d}{2}\right) \sum_{m_i}{}' \frac{1}{(\pi M^2)^{s+d/2}}\,, \tag{3.19}$$

since the integrals over σ and t can be evaluated in terms of Γ-functions. Call:

$$C_z(\omega_1,\dots\,\omega_d) \equiv \Gamma(z) \sum_{n_i}{}' \frac{1}{(\pi N^2)^z}\,, \qquad (z > d/2)\,, \tag{3.20}$$

then clearly:

$$F(s) = \Gamma(s)\, C_{s+d/2}\left(\frac{1}{\omega_1}\,,\dots\,\frac{1}{\omega_d}\right). \tag{3.21}$$

Note that in one dimension,

$$C_z = \Gamma(z) \sum_{-\infty}^{+\infty}{}' \frac{1}{(\pi n^2)^z} = 2\pi^{-z}\,\Gamma(z)\,\zeta(2z)\,, \tag{3.22}$$

so that $C_z(\omega_1,\dots\,\omega_d)$ is a kind of generalization of the Riemann ζ-function to d-dimensions. In a way similar to the derivation of Riemann's integral representation of $\zeta(z)$, one can show (see Appendix 3.B for some details):

$$C_z(\omega_1 \dots \omega_d) = \frac{1}{z - d/2} - \frac{1}{z} + \sum_{n_i}{}' E_{1-z}(\pi N^2) + \sum_{m_i}{}' E_{z+1-d/2}(\pi M^2)\,, \tag{3.23}$$

where $E_n(z) = \int_1^\infty \mathrm{d}t\; t^{-n}\,\mathrm{e}^{-zt} = z^{n-1}\,\Gamma(1-n, z)$ is a form of the incomplete Γ-function. From (3.23) also follows the reflection formula:

$$C_z(\omega_1 \dots \omega_d) = C_{d/2-z}\left(\frac{1}{\omega_1} \cdots \frac{1}{\omega_d}\right). \tag{3.24}$$

Inverting the Mellin transform (3.19) and using (3.21, 24), one gets formally:

$$f(\sigma) = \frac{1}{2\pi \mathrm{i}} \int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty} \mathrm{d}s\; \sigma^{-s}\,\Gamma(s)\, C_{-s}(\omega_1 \dots \omega_d)\,, \tag{3.25}$$

where the path must be taken to the right of all singularities. Now it follows from (3.23) that C_{-s} is an analytic function of s except for the two poles at $s = 0$ and $-d/2$. $\Gamma(s)$ has poles at $s = -k$ ($k = 0, 1, 2\dots$) with residues $(-1)^k/k!$. So the integrand of (3.24) has a double pole at $s = 0$, single poles at $s = -k$ and $s = -d/2$ for d odd, or double poles at $s = 0$ and $s = -d/2$ plus the remaining single poles of $\Gamma(s)$ for d even. It is easy to show that the integration path may be deformed to a set of small circles around the poles, and by calculating the residues one gets for:

d odd

$$f(\sigma) = -\ln \sigma - \Gamma(-d/2)\,\sigma^{d/2} + \bar{C}_0(\omega_1 \dots \omega_d) - \gamma + \sum_{k=1}^{\infty} \frac{(-\sigma)^k}{k!}\, C_k(\omega_1 \dots \omega_d)\,. \tag{3.26}$$

d even

$$\begin{aligned} f(\sigma) = {}& -\ln \sigma + \frac{(-\sigma)^{d/2}}{(d/2)!}\left[\ln \sigma + \gamma - \sum_{1}^{d/2} \frac{1}{m} + \bar{C}_{d/2}(\omega_1 \dots \omega_d)\right] \\ & + \bar{C}_0(\omega_1 \dots \omega_d) - \gamma + \sum_{\substack{k=1 \\ \neq d/2}}^{\infty} \frac{(-\sigma)^k}{k!}\, C_k(\omega_1 \dots \omega_d)\,, \end{aligned} \tag{3.27}$$

where

$$\bar{C}_0(\omega_1 \dots \omega_d) \equiv \lim_{z\to 0} \left[C_z(\omega_1 \dots \omega_d) + \frac{1}{z} \right] = -\frac{2}{d} + \sum_{n_i}{}' E_1(\pi N^2) + \sum_{m_i}{}' E_{1-d/2}(\pi M^2) , \tag{3.28a}$$

$$\bar{C}_{d/2}(\omega_1 \dots \omega_d) \equiv \lim_{z\to d/2} \left[C_z(\omega_1 \dots \omega_d) - \frac{1}{z - d/2} \right] = \bar{C}_0 \left(\frac{1}{\omega_1} \dots \frac{1}{\omega_d} \right) , \tag{3.28b}$$

and γ = Euler's constant = -0.572 … . Note that at $\sigma = 0$, $f(\sigma)$ has a logarithmic singularity and also a branch point, apparent in the second term in (3.26) and (3.27). Using these results in (3.14) one finds for:

$\underline{d = 1}$

$$\begin{aligned} &\ln Z_0^{\mathrm{gr}}(\alpha, l) \simeq l\bar{g}_{3/2}(\alpha) - \ln(\alpha l^2) + \sum_{k=0}^{\infty} \frac{(-\alpha l^2)^k}{k!} C_k^0 , \\ &\quad C_0^{\mathrm{o}} \equiv \bar{C}_0 - \gamma , \\ &\quad C_k^{\mathrm{o}} \equiv C_k , \qquad k > 0 . \end{aligned} \tag{3.29a}$$

$\underline{d = 2}$

$$\begin{aligned} &\ln Z_0^{\mathrm{gr}}(\alpha, l_1, l_2) \simeq l^2 g_2(\alpha) - \ln(\alpha l^2) + \alpha l^2 \ln l^2 + \sum_{k=0}^{\infty} \frac{(-\alpha l^2)^k}{k!} C_k^{\mathrm{o}}(\omega_1, \omega_2) , \\ &C_0^{\mathrm{o}}(\omega_1, \omega_2) \equiv \bar{C}_0(\omega_1, \omega_2) - \gamma , \qquad C_1^{\mathrm{o}}(\omega_1, \omega_2) \equiv \bar{C}_1(\omega_1, \omega_2) + \gamma , \\ &C_k^{\mathrm{o}}(\omega_1, \omega_2) \equiv \bar{C}_k(\omega_1, \omega_2) , \qquad k > 1 . \end{aligned} \tag{3.29b}$$

$\underline{d = 3}$ ‡

$$\begin{aligned} &\ln Z_0^{\mathrm{gr}}(\alpha, l_1, l_2, l_3) \simeq l^3 \bar{g}_{5/2}(\alpha) - \ln(\alpha l^2) + \sum_{k=0}^{\infty} \frac{(-\alpha l^2)^k}{k!} C_k^{\mathrm{o}}(\omega_1, \omega_2, \omega_3) , \\ &C_0^{\mathrm{o}}(\omega_1, \omega_2, \omega_3) \equiv \bar{C}_0(\omega_1, \omega_2, \omega_3) - \gamma , \\ &C_k^{\mathrm{o}}(\omega_1, \omega_2, \omega_3) \equiv C_k(\omega_1, \omega_2, \omega_3) , \qquad k > 0 , \end{aligned} \tag{3.29c}$$

where

$$\bar{g}_n(\alpha) \equiv \begin{cases} g_n(\alpha) - \Gamma(1-n)\,\alpha^{n-1} = \displaystyle\sum_{k=0}^{\infty} \zeta(n-k) \frac{(-\alpha)^k}{k!} , & n \neq 1, 2, 3 \dots \\ g_n(\alpha) - \dfrac{(-\alpha)^{n-1}}{(n-1)!} \left[-\ln\alpha + \displaystyle\sum_{m=1}^{n-1} \frac{1}{m} \right] = \displaystyle\sum_{\substack{k=0 \\ \neq n-1}}^{\infty} \zeta(n-k) \frac{(-\alpha)^k}{k!} , & n = 1, 2, 3 \dots . \end{cases} \tag{3.30}$$

In arriving at these final formulas, evidently the branch point terms of $f(\alpha l^2)$ and $l^d g_{1+d/2}(\alpha)$ have exactly cancelled out. Now, these expressions are equivalent to (3.17) but clearly useful when $\alpha l^2 \ll 1$ since then the $(-\alpha l^2)^k$ series are rapidly convergent. In fact, from (3.20) it follows that those series are only convergent for $|\alpha l_1^2| < \pi$, where l_1 is the largest dimension.

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‡ Zasada and Pathria [73] have recently given an expression equivalent to (3.29c), using a different but related derivation. The relationship is discussed by Ziff [74].

The coefficients $C_k(\omega_1 \ldots \omega_d)$ depend only upon the shape parameters and are independent of the volume of the system. For $k > d/2$ they are given by the simple lattice sum (3.20) while for $0 \leqq k \leqq d/2$, (3.23) (which is always valid) must be used. For the particular case of $d = 1$ we have the explicit expressions for C_k in terms of the ζ-functions (3.22) for $k > 0$, and even $\bar{C}_0$ can be written explicitly as follows:

$$\bar{C}_0 = \lim_{z \to 0} \left[2\pi^{-z} \Gamma(z) \zeta(2z) + \frac{1}{z} \right] = \gamma + \ln 4\pi \,. \tag{3.31}$$

Indeed the second term in (3.17a) can be written simply as

$$-2 \ln(1 - \exp(-2\sqrt{\pi\alpha} l)) = 2 g_1 (2\sqrt{\pi\alpha} l) \,, \tag{3.32}$$

and this can be expanded to give (3.22, 29a, 31) directly, using (2.A3).

c. Connection to the Dirichlet and Neumann boundary conditions. The grand partition functions Z_+^{gr} and Z_-^{gr} for the Neumann and Dirichlet boundary conditions on the box respectively can be expressed in terms of the Z_0^{gr} (Pathria [75]). Using the energy levels (3.2–4) one gets for

$d = 1$

$$\begin{aligned} \ln Z_\pm^{\mathrm{gr}}(\alpha, l) &= \sum_{n=\{{0 \atop 1}\}}^{\infty} -\ln(1 - \exp(-\alpha - \pi n^2/4l^2)) \\ &= \tfrac{1}{2} \sum_{n=-\infty}^{\infty} (1 \pm \delta_{n,0})[-\ln(1 - \exp(-\alpha - \pi n^2/4l^2))] = \tfrac{1}{2}[\ln Z_0^{\mathrm{gr}}(\alpha, 2l) \pm g_1(\alpha)] \,. \end{aligned} \tag{3.33a}$$

Quite similarly one gets for

$d = 2$

$$\ln Z_\pm^{\mathrm{gr}}(\alpha, l_1, l_2) = \tfrac{1}{4}[\ln Z_0^{\mathrm{gr}}(\alpha, 2l_1, 2l_2) \pm \ln Z_0^{\mathrm{gr}}(\alpha, 2l_1) \pm \ln Z_0^{\mathrm{gr}}(\alpha, 2l_2) + g_1(\alpha)] \,, \tag{3.33b}$$

$d = 3$

$$\begin{aligned} \ln Z_\pm^{\mathrm{gr}}(\alpha, l_1, l_2, l_3) = \tfrac{1}{8}[&\ln Z_0^{\mathrm{gr}}(\alpha, 2l_1, 2l_2, 2l_3) \pm \ln Z_0^{\mathrm{gr}}(\alpha, 2l_1, 2l_2) \pm \ln Z_0^{\mathrm{gr}}(\alpha, 2l_2, 2l_3) \\ &\pm \ln Z_0^{\mathrm{gr}}(\alpha, 2l_3, 2l_1) + \ln Z_0^{\mathrm{gr}}(\alpha, 2l_1) + \ln Z_0^{\mathrm{gr}}(\alpha, 2l_2) + \ln Z_0^{\mathrm{gr}}(\alpha, 2l_3) \pm g_1(\alpha)] \,. \end{aligned} \tag{3.33c}$$

d. Dirichlet and Neumann boundary conditions, $\alpha l^2 \gg 1$. Using (3.17) and (3.33), one gets for

$d = 1$

$$\ln Z_\pm^{\mathrm{gr}}(\alpha, l) \simeq l g_{3/2}(\alpha) \pm \tfrac{1}{2} g_1(\alpha) + \mathrm{O}(\exp(-2\sqrt{\pi\alpha} l)) \,. \tag{3.34a}$$

$d = 2$

$$\ln Z_\pm^{\mathrm{gr}}(\alpha, l_1, l_2) \simeq l^2 g_2(\alpha) \pm \tfrac{1}{2}(l_1 + l_2) g_{3/2}(\alpha) + \tfrac{1}{4} g_1(\alpha) + \mathrm{O}(\exp(-2\sqrt{\pi\alpha} l)) \,. \tag{3.34b}$$

$d = 3$

$$\begin{aligned} \ln Z_\pm^{\mathrm{gr}}(\alpha, l_1, l_2, l_3) \simeq{}& l^3 g_{5/2}(\alpha) \pm \tfrac{1}{2}(l_1 l_2 + l_2 l_3 + l_3 l_1) g_2(\alpha) + \tfrac{1}{4}(l_1 + l_2 + l_3) g_{3/2}(\alpha) \pm \tfrac{1}{8} g_1(\alpha) \\ &+ \mathrm{O}(\exp(-2\sqrt{\pi\alpha} l)) \,. \end{aligned} \tag{3.34c}$$

Although the explicit form of the $O(\exp(-2\sqrt{\pi\alpha l}))$ term also follows, it is a complicated expression and will not be needed.

e. Dirichlet and Neumann boundary conditions $0 < \alpha l^2 + e_0 \ll 1$. Now one must use (3.29) for Z_0^{gr} in (3.33). For $d = 1$, one gets:

$$\ln Z_\pm^{\mathrm{gr}}(\alpha, l) = l\bar{g}_{3/2}(\alpha) \pm \tfrac{1}{2}\bar{g}_{1/2}(\alpha) - \tfrac{1}{2}(1 \pm 1)\ln\alpha - \tfrac{1}{2}\ln 4l^2 + \tfrac{1}{2}\sum_{k=0}^{\infty} C_k^{\mathrm{o}} \frac{(-4\alpha l^2)^k}{k!}\,. \tag{3.35}$$

Thus for the Neumann case one has for

$d = 1$

$$\ln Z_+^{\mathrm{gr}}(\alpha, l) = l\bar{g}_{3/2}(\alpha) + \tfrac{1}{2}\bar{g}_1(\alpha) - \ln\alpha l^2 + \sum_{k=0}^{\infty} C_k^+ \frac{(-\alpha l^2)^k}{k!} - \tfrac{1}{2}\ln 4l^2\,,$$
$$C_k^+ \equiv \tfrac{1}{2}4^k C_k^{\mathrm{o}}\,. \tag{3.36a}$$

Likewise, one gets for

$d = 2$

$$\ln Z_+^{\mathrm{gr}}(\alpha, l_1, l_2) = l^2\bar{g}_2(\alpha) + \tfrac{1}{2}(l_1 + l_2)\bar{g}_{3/2}(\alpha) + \tfrac{1}{4}\bar{g}_1(\alpha) - \alpha l^2\ln 4l^2 - \ln\alpha l^2$$
$$- \tfrac{1}{4}\ln 4l^2 + \sum_{k=0}^{\infty} C_k^+(\omega_1, \omega_2)\frac{(-\alpha l^2)^k}{k!}\,, \tag{3.36b}$$
$$C_k^+(\omega_1, \omega_2) \equiv 4^{k-1}[C_k^{\mathrm{o}}(\omega_1, \omega_2) + \omega_1^{2k}C_k^{\mathrm{o}} + \omega_2^{2k}C_k^{\mathrm{o}}]\,.$$

$d = 3$

$$\ln Z_+^{\mathrm{gr}}(\alpha, l_1, l_2, l_3) \simeq l^3\bar{g}_{5/2}(\alpha) + \tfrac{1}{2}(l_1l_2, l_2l_3, l_3l_1)\bar{g}_2(\alpha) + \tfrac{1}{4}(l_1 + l_2 + l_3)\bar{g}_{3/2}(\alpha)$$
$$+ \tfrac{1}{8}\bar{g}_1(\alpha) - \ln\alpha l^2 - \tfrac{1}{8}\ln 4l^2 - \tfrac{1}{2}\alpha(l_1l_2\ln l_1l_2 + l_2l_3\ln l_2l_3 + l_3l_1\ln l_3l_1) + \sum_{k=0}^{\infty} C_k^+(\omega_1, \omega_2, \omega_3)\frac{(-\alpha l^2)^k}{k!}\,,$$
$$C_k^+(\omega_1, \omega_2, \omega_3) \equiv \tfrac{1}{8}4^k\left[C_k^{\mathrm{o}}(\omega_1, \omega_2, \omega_3) + \underset{[\times 3]}{(\omega_1\omega_2)^k C_k^{\mathrm{o}}\left(\frac{1}{\sqrt{\omega_1\omega_2}}, \frac{1}{\sqrt{\omega_1\omega_2}}\right)} + \underset{[\times 3]}{\omega_1^{2k}C_k^{\mathrm{o}}}\right]. \tag{3.36c}$$

The [×3] in the definition of C_k^+ indicates the addition of two more terms with the indices cyclically permuted. Also, when $k > d/2$, C_k^+ can be written

$$C_k^+(\omega_1, \ldots \omega_d) = (k-1)!\sum_{n_i}{}' \left(\frac{\pi}{4}N^2\right)^{-k}\,, \tag{3.37}$$

in which the $n_i = 0$ term is omitted.

Now however for the Dirichlet case there is the difficulty (going back to (3.35)) that the expansion is about $\alpha = 0$, while we require an expansion about the first singularity of Z^{gr} which according to (3.11) is at $\alpha = -e_0/l^2 = -\pi/4l^2$ for $d = 1$. Note in (3.35) for the Dirichlet case (−) there is no $\ln\alpha$ term, and also that the $(-\alpha l^2)^k$ series is convergent for $|\alpha l^2| < \pi/4$ only. We want to put that first singularity in evidence.

Using the explicit expression for $C_k^{\mathrm{o}} = C_k$ (3.22) in (3.35), the $(-4\alpha l^2)^k$ series can be summed for $k > 0$:

$$\sum_{k=1}^{\infty} \frac{(-4\alpha l^2)^k}{k!}\,(k-1)!\,2\sum_{n=1}^{\infty} \frac{1}{[\pi n^2]^k} = 2\sum_{n=1}^{\infty} -\ln\left(1+\frac{4\alpha l^2}{\pi n^2}\right), \tag{3.38}$$

and has therefore logarithmic singularities at $\alpha = -\pi n^2/4l^2 = -e_n/l^2$, as does the exact expression for $\ln Z^{\mathrm{gr}}$ (3.11). Splitting off the first singularity above at $\alpha = -\pi/4l^2 = -e_0/l^2$ and expanding the rest about that point, one finds:

$d = 1$

$$\ln Z^{\mathrm{gr}}_{-}(\alpha, l) \simeq l\bar{g}_{3/2}(\alpha) - \tfrac{1}{2}\bar{g}_1(\alpha) - \ln(\alpha l^2 + \pi/4) - \tfrac{1}{2}\ln l^2 + \sum_{k=0}^{\infty} C_k^{-}\,\frac{(-\alpha l^2 - \pi/4)!}{\cancel{k!}}\,,$$

$$C_k^{-} \equiv (k-1)!\,(4/\pi)^k \sum_{n=2}^{\infty} (n^2-1)^{-k}\,, \qquad (k > 0)\,. \tag{3.39a}$$

The expression for the constant C_0^{-} can also be found, but will not be needed for our discussions. Likewise, for $d = 2$ and 3, one finds

$d = 2$

$$\ln Z^{\mathrm{gr}}_{-}(\alpha, l_1, l_2) \simeq l^2\bar{g}_2(\alpha) - \tfrac{1}{2}(l_1+l_2)\bar{g}_{3/2}(\alpha) + \tfrac{1}{4}\bar{g}_1(\alpha) - \alpha l^2 \ln 4l^2 - \tfrac{1}{4}\ln l^2 - \ln(\alpha l^2 + e_0)$$

$$+ \sum_{k=0}^{\infty} C_k^{-}(\omega_1, \omega_2)\,\frac{(-\alpha l^2 - e_0)^k}{k!}\,, \tag{3.39b}$$

$$C_k^{-}(\omega_1, \omega_2) = (k-1)! \sum_{n_1 n_2 = 1}^{\infty}{}' (\pi N^2/4 - e_0)^{-k}\,, \qquad (k > 1)\,,$$

$$e_0 \equiv \frac{\pi}{4}(\omega_1^{-2} + \omega_2^{-2})\,.$$

$d = 3$

$$\ln Z^{\mathrm{gr}}_{-}(\alpha, l_1, l_2, l_3) \simeq l^3\bar{g}_{5/2}(\alpha) - \tfrac{1}{2}(l_1 l_2 + l_2 l_3 + l_3 l_1)\bar{g}_2(\alpha) + \tfrac{1}{4}(l_1 + l_2 + l_3)\bar{g}_{3/2}(\alpha) - \tfrac{1}{8}\bar{g}_1(\alpha)$$

$$- \tfrac{1}{8}\ln l^2 - \ln(\alpha l^2 + e_0) + \frac{\alpha}{2}(l_1 l_2 \ln l_1 l_2 + l_2 l_3 \ln l_2 l_3 + l_3 l_1 \ln l_3 l_1) + \sum_{k=0}^{\infty} C_k^{-}(\omega_1, \omega_2, \omega_3)\,\frac{(-\alpha l^2 - e_0)^k}{k!}\,,$$

$$C_k^{-}(\omega_1, \omega_2, \omega_3) = (k-1)! \sum_{n_1 n_2 n_3 = 1} (\pi N^2/4 - e_0)^{-k}\,, \qquad (k > 1)\,, \tag{3.39c}$$

$$e_0 \equiv \frac{\pi}{4}(\omega_1^{-2} + \omega_2^{-2} + \omega_3^{-2})\,.$$

Again, expressions can also be found for C_0^{-} and C_1^{-}, but they will not be needed here. The important fact is that they depend only upon the shape parameters of the box. The prime on the summations above indicates that the term $n_1 = n_2 = 0$ or $n_1 = n_2 = n_3 = 0$ is skipped.

It is interesting to note that for all boundary conditions and all d, the C_k that we have found for $k > d/2$ can all be written

$$C_k(\omega_1, \dots \omega_d) = (k-1)! \sum_{i=1}^{\infty} (e_i - e_0)^{-k} , \tag{3.40}$$

where e_i are the set of energy levels (dimensionless) representing the system. This suggests that the results may be generalized to a region of any shape by inserting its energy levels above. In fact, all of our expressions (3.29, 36, 39) for the grand partition function satisfy the following relation:

$$\frac{\partial^2}{\partial\alpha^2} \ln Z^{\mathrm{gr}} \simeq \int g(e)\, \mathrm{d}e \left\{ \frac{\exp(\alpha + e/l^2)}{[\exp(\alpha + e/l^2) - 1]^2} - \frac{1}{[\alpha + e/l^2]^2} \right\} + \sum_{k=0}^{\infty} \frac{1}{[\alpha + e_k/l^2]^2} , \tag{3.41}$$

where $g(e)$ is the density of states, taking into account the surface corrections. These expressions were of course derived as approximations of (3.11), which after two differentiations after α is

$$\frac{\partial^2}{\partial\alpha^2} \ln Z^{\mathrm{gr}} = \sum_{k=0}^{\infty} \frac{\exp(\alpha + e/l^2)}{[\exp(\alpha + e_k/l^2) - 1]^2} . \tag{3.42}$$

Comparing this and (3.41) puts the approximation (3.14) in evidence: the "singular part" of this summand is split off before the sum is replaced by an integral. One would expect that (3.41) should apply to any set of energy levels, with the same error of $\mathrm{O}(\mathrm{e}^{-l})$. Later in this section we will give the expression for the density of states $g(e)$ including the surface term, for a general shape, and in section 4 we will make use of (3.41). This method can be applied to Z^{gr} itself, with the addition of a convergence factor and limiting procedure. In this way the results of this section can in fact be generalized to a system of arbitrary shape (see Ziff [74]).

These various results will be discussed in subsection 3.4.

3.3. The canonical partition function

In conformity with our basic postulate that the canonical ensemble describes all equilibrium properties of the system, we now calculate the canonical partition function for the box. This will make use of the results of the previous section, since according to (1.32) the grand partition function is the generating function of the canonical partition function. That relation can be formally inverted as follows:

$$Z(N, \Lambda, T) = \frac{1}{2\pi\mathrm{i}} \int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty} \mathrm{d}\alpha\, \mathrm{e}^{\alpha N} Z^{\mathrm{gr}}(\alpha, \Lambda, T) , \tag{3.43}$$

where the integration path must be to the right of all singularities. We will consider only the three dimensional box, for which $\Lambda \to L_1, L_2, L_3$ with $l_i \equiv L_i/\lambda \gg 1$.

For the discussions of Z^{gr} we have distinguished the two ranges of α, $\alpha l^2 \gg 1$ and $\alpha l^2 + e_0 \ll 1$. As a consequence of that it will turn out that the discussion of $Z(N, \Lambda, T)$ must be divided into two ranges of N, which will correspond to the one phase and condensed regions in the bulk limit.

a. The "one phase" region. The integral in (3.43) can be approximated by means of the well known saddle point method [‡] with the result:

[‡] See Fowler [76], or textbooks such as Huang [43] Ch. 10.

$$Z(N, \Lambda, T) \simeq \frac{1}{2\pi \mathrm{i}} \int_{\alpha_0-\mathrm{i}\infty}^{\alpha_0+\mathrm{i}\infty} \mathrm{d}\alpha \exp\{G(\alpha_0) + (\alpha - \alpha_0)^2 G''(\alpha_0)/2\} = \frac{\mathrm{e}^{\alpha_0 N} Z^{\mathrm{gr}}(\alpha_0, \Lambda, T)}{\sqrt{2\pi G''(\alpha_0)}}, \tag{3.44}$$

where $G(\alpha) \equiv \ln Z^{\mathrm{gr}} + N\alpha$ and the saddle point α_0 is determined by

$$G'(\alpha_0) = N + \frac{\partial}{\partial \alpha_0} \ln Z^{\mathrm{gr}}(\alpha_0, \Lambda, T) = 0\,. \tag{3.45}$$

The relationship between α_0 and N is evidently the same as that between α and N^{gr}.

When $\alpha_0 l^2 \gg 1$, one must use the expressions (3.17c) and (3.34c) for $\ln Z^{\mathrm{gr}}$. To estimate the range of N that corresponds to $\alpha_0 l^2 \gg 1$, and also to estimate $G''(\alpha_0)$, one may use the leading term of $\ln Z^{\mathrm{gr}}$ which is $l^3 g_{5/2}(\alpha)$. Then,

$$N \simeq l^3 g_{3/2}(\alpha_0)\,, \tag{3.46}$$

and if one defines N_c by

$$N_\mathrm{c} \equiv l^3 g_{3/2}(0) = l^3 \zeta(\tfrac{3}{2})\,, \tag{3.47}$$

then this implies that $\alpha l^2 \gg 1$ corresponds to

$$\frac{N_\mathrm{c} - N}{N_\mathrm{c}} \gg \frac{1}{l}\,, \tag{3.48}$$

or essentially that $N < N_\mathrm{c}$ since l is assumed to be large. This follows from the expansion for small α, $g_{3/2}(\alpha) \simeq \zeta(\frac{3}{2}) - 2\sqrt{\pi\alpha}$ (2.A3). We call this the one phase region since this range of N corresponds to $\rho < \rho_\mathrm{c}$ in the bulk limit. Then also $G''(\alpha_0) \simeq l^3 g_{1/2}(\alpha_0)$ and thus

$$\ln Z(N, \Lambda, T) \simeq \ln Z^{\mathrm{gr}}(\alpha_0, \Lambda, T) + N\alpha_0 + \mathrm{O}(\ln l)\,. \tag{3.49}$$

To find $\ln Z(N, \Lambda, T)$ for N satisfying (3.48) it is therefore allowed to use for $\ln Z^{\mathrm{gr}}(\alpha, \Lambda, T)$ the expressions (3.17c) and (3.34c), *including* the terms linear and quadratic in l.

b. The “condensed” region. When $N > N_\mathrm{c}$ the saddle point defined by (3.45) will be at $\alpha_0 + e_0/l^2 \simeq 1/(N - N_\mathrm{c})$, as can be verified directly from (3.29c, 36c, 39c). (Actually, this is true for $(N - N_\mathrm{c})/N_\mathrm{c} \gg 1/l$.) Because the saddle point will be very close to the first singularity of $\ln Z^{\mathrm{gr}}$ at $\alpha_0 = -e_0/l^2$, the use of the saddle point method is problematical‡. This can be seen by carrying out (3.44) to next order:

$$Z(N, \Lambda, T) \simeq \frac{\mathrm{e}^{-\alpha_0 N} Z^{\mathrm{gr}}(\alpha_0, \Lambda, T)}{\sqrt{2G''(\alpha_0)}} \left\{1 - \frac{15}{8} \frac{[G'''(\alpha_0)]^2}{[G''(\alpha_0)]^3} \dots \right\}, \tag{3.50}$$

and for these small values of α_0 it can be shown from (3.29c, 36c, 39c) that G'''^2/G''^3 is of order unity. On the other hand, when α_0 is large compared to $1/l^2$, that term is of order $1/l^3$. We will not try to review the various attempts to improve the saddle point method but instead present a different approach for calculating Z in the particular case of the IBG.

First rewrite (3.43) in terms of $z \equiv \mathrm{e}^{-\alpha}$:

$$Z(N, \Lambda, T) = \frac{1}{2\pi\mathrm{i}} \oint \frac{Z^{\mathrm{gr}}(-\ln z, \Lambda, T)}{z^{N+1}} \mathrm{d}z = \frac{1}{2\pi\mathrm{i}} \oint \frac{1}{z^{N+1} \prod_k (1 - z\exp(-e_k/l^2))}\,, \tag{3.51}$$

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‡ This point has been studied in detail by Schubert [77, 78], Dingle [79], and especially Dingle [80] pp. 267–271.

where we have used (1.134) for Z^{gr} and the dimensionless energy levels $e_k \equiv \beta\epsilon_k l^2$. The contour must encircle the origin and exclude the singularities of Z^{gr} at $z = \exp(e_k/l^2)$. Replacing z by $1/t$, the integral can be performed by evaluating the residues at $t = \exp(-e_k/l^2)$. Assuming for simplicity that all levels are non-degenerate, this leads to the identity ‡

$$Z(N, \Lambda, T) = \sum_{k=0}^{\infty} \frac{\exp(-Ne_k/l^2)}{\prod\limits_{j \neq k} [1 - \exp -(e_j - e_k)/l^2]} \equiv \sum_{k=0}^{\infty} Z^{(k)}(N, \Lambda, T) . \tag{3.52}$$

For Dirichlet and Neumann boundary conditions the states e_k are nondegenerate if the dimensions L_1, L_2, L_3 are incommensurate, while for the periodic boundary conditions there are always degeneracies in the excited states. The ground state is *always* non-degenerate and as we shall see the corrections required if some of the higher states are degenerate are of minor importance.

This result allows one to express $Z(N, \Lambda, T)$ successively in terms of Z^{gr}. Consider first $Z^{(0)}$; comparing the definition (3.52) with $Z^{\mathrm{gr}}(\alpha, \Lambda, T)$ of (1.134), one concludes,

$$\ln Z^{(0)}(N, \Lambda, T) = -Ne_0/l^2 + \lim_{\alpha \to -e_0/l^2} [\ln Z^{\mathrm{gr}}(\alpha, \Lambda, T) + \ln(1 - \exp(-\alpha - e_0/l^2))] . \tag{3.53}$$

For $\ln Z^{\mathrm{gr}}$ one just use (3.29c, 36c, 39c) since they give the behavior about $\alpha = -e_0/l^2$. By a straightforward calculation one obtains therefore for $(N - N_{\mathrm{c}})/N_{\mathrm{c}} \gg 1/l$,

$$\ln Z_0^{(0)}(N, \Lambda, T) \simeq l^3 \zeta(\tfrac{5}{2}) + C_0^{\mathrm{o}}(\omega_1, \omega_2, \omega_3) - \ln l^2 , \tag{3.54a}$$

$$\ln Z_+^{(0)}(N, \Lambda, T) \simeq l^3 \zeta(\tfrac{5}{2}) + \tfrac{1}{2}(l_1 l_2 + l_2 l_3 + l_3 l_1)\zeta(2) + \tfrac{1}{4}(l_1 + l_2 + l_3)\zeta(\tfrac{3}{2}) - \ln l^2 + C_0^{+}(\omega_1, \omega_2, \omega_3) , \tag{3.54b}$$

$$\begin{aligned} \ln Z_-^{(0)}(N, \Lambda, T) &\simeq -Ne_0/l^2 + l^3 \bar{g}_{5/2}(-e_0/l^2) - \tfrac{1}{2}(l_1 l_2 + l_2 l_3 + l_3 l_1)\bar{g}_2(-e_0/l^2) \\ &\quad + \tfrac{1}{4}(l_1 + l_2 + l_3)\bar{g}_{3/2}(-e_0/l^2) - \tfrac{1}{8}\bar{g}_1(-e_0/l^2) - \ln l^2 + C_0^{-}(\omega_1, \omega_2, \omega_3) \\ &\simeq l^3 \zeta(\tfrac{5}{2}) - \tfrac{1}{2}(l_1 l_2 + l_2 l_3 + l_3 l_1)\zeta(2) - (N - N_{\mathrm{c}})e_0/l^2 + \mathrm{O}(l) . \end{aligned} \tag{3.54c}$$

Note that $\ln Z^{(0)}$ depends only upon N by $-Ne_0/l^2$, and therefore for Neumann and periodic boundary conditions it is independent of N. Turning now to $Z^{(1)}$, which is clearly negative, one can express it in terms of Z^{gr} as follows

$$\begin{aligned} \ln(-Z^{(1)}) = -Ne_1/l^2 - \ln(\exp\{-(e_0 - e_1)/l^2\} - 1) + \lim_{\alpha \to -e_1/l^2} [&\ln Z^{\mathrm{gr}}(\alpha, \Lambda, T) \\ + \ln(1 - \exp(-\alpha - e_0/l^2)) + \ln(1 - \exp(-\alpha - e_1/l^2))] &. \end{aligned} \tag{3.55}$$

Again a direct calculation can be carried out using (3.29c, 36, 39c) after resumming the $(-\alpha l^2)^k$ series to put the $\alpha = -e_1/l^2$ singularity in evidence. In all cases one finds that $\ln(-Z^{(1)})$ is smaller than $\ln Z^{(0)}$ by the term $(N - N_{\mathrm{c}})(e_1 - e_0)/l^2$, where N_{c} is again defined by (3.47). Therefore, if

$$\frac{(N - N_{\mathrm{c}})(e_1 - e_0)}{l^2} \simeq \frac{N - N_{\mathrm{c}}}{N_{\mathrm{c}}} l \gg 1 , \tag{3.56}$$

then $-Z^{(1)}$ is much smaller than $Z^{(0)}$. This is essentially $N > N_{\mathrm{c}}$ if l is large. Likewise, one can show that the $k > 1$ terms of (3.52) are even smaller, so that for N satisfying (3.56), we have

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‡ This identity has also been derived by Dingle [81] by means of a partial fraction expansion of the denominator of (3.51).

$$Z(N, \Lambda, T) = Z^{(0)}(N, \Lambda, T)\{1 - \mathrm{O}(\exp\{-(N - N_c)/l^2\})\} , \tag{3.57}$$

or

$$\ln Z(N, \Lambda, T) = \ln Z^{(0)}(N, \Lambda, T) - \mathrm{O}(\exp\{-(N - N_c)/l^2\}) , \tag{3.58}$$

with $Z^{(0)}$ given by (3.54). In the same way one can show that the eventual degeneracies of the states e_k for $k > 0$ do not affect this conclusion[‡].

Thus with the results (3.49) and (3.54–58) the discussion of the properties of the canonical partition function has been related to the previous discussion of the grand partition function for all values of N except in a small region about N_c,

$$|N - N_c|/N_c \lesssim 1/l , \tag{3.59}$$

which vanishes in the bulk limit.

3.4. Discussion

a. Proof of the bulk properties. In the last two sections we have derived expansions of the grand partition function $Z^{gr}(\alpha, L_1, L_2, L_3, T)$ and of the canonical partition function $Z(N, L_1, L_2, L_3, T)$ for the two ranges of α and N. We called these two ranges already the "one phase" and "condensed" regions, and our first task must therefore be to show that in the bulk limit these expansions actually lead to the equation of state and the thermodynamic properties of the IBG in the one phase and condensed regions as discussed in section 2. We must also show that we get the *same* results for both ensembles and for all boundary conditions.

The proof is simple and can essentially be read off the equations. Consider first the expansions (3.17c, 34c) and (3.29c, 36c, 39c) of the grand partition function in the two ranges of α. For large $l_i \equiv L_i/\lambda$ the leading term in *all* these expansions are proportional to $l^3 = (L_1L_2L_3)/\lambda^3$. Next observe that the parameters $a_1, a_2, \ldots$ introduced in section 1.3 to describe the outside force field become in our case the lengths L_1, L_2, L_3 and that the corresponding generalized forces $X_1, X_2, \ldots$ become $p_1L_2L_3, p_2L_3L_1, p_3L_1L_2$, where p_1, p_2, p_3 are the pressures on the three pairs of sides of the box. From the general thermodynamic relation (1.34):

$$p_i^{gr} = \frac{kT}{L_1L_2L_3} L_i \left(\frac{\partial \ln Z^{gr}}{\partial L_i}\right)_\alpha , \tag{3.60}$$

it follows therefore immediately that asymptotically for large L_i, the pressures p_1, p_2, p_3 become equal and the common value p^{gr} is given in this limit by:

$$p^{gr} = kT\left(\frac{\partial}{\partial V} \ln Z^{gr}\right)_\alpha = \frac{kT}{V} \ln Z^{gr} . \tag{3.61}$$

Finally note (1.35), which can also be written as

$$N^{gr} = -\frac{\partial}{\partial \alpha} \ln Z^{gr} . \tag{3.62}$$

From (3.17c) and (3.34c) one thus reads off that in the range $\alpha > 0$ in the bulk limit $L_i \to \infty$ (using $g'_{5/2}(\alpha) = -g_{3/2}(\alpha)$):

[‡] Compare Dingle [81] Appendix.

$$p^{\mathrm{gr}} = \frac{kT}{\lambda^3}\, g_{5/2}(\alpha)\,, \tag{3.63a}$$

$$\rho^{\mathrm{gr}} = \frac{N^{\mathrm{gr}}}{V} = \frac{1}{\lambda^3}\, g_{3/2}(\alpha)\,, \tag{3.63b}$$

for all three boundary conditions. On the other hand from (3.29c, 36c, 39c) one reads off that in the bulk limit for $\alpha + e_0/l^2 \to 0$ as $1/V$, one gets for all three boundary conditions

$$p^{\mathrm{gr}} = \frac{kT}{\lambda^3}\, \zeta(\tfrac{5}{2})\,, \tag{3.64}$$

using (3.61), while from (3.62) one concludes that in this range

$$\rho^{\mathrm{gr}} \simeq \frac{1}{\lambda^3}\, \zeta(\tfrac{3}{2}) + \frac{1}{V(\alpha + e_0/l^2)}\,, \tag{3.65}$$

which implies that (3.64) holds asymptotically in V for all $\rho > \rho_{\mathrm{c}}$, where as before $\rho_{\mathrm{c}} \equiv \zeta(\frac{3}{2})/\lambda^3$. These are just the results of section 2.3, demonstrated for the case of the box.

It is also easy to show that one gets the *same* results from the expansions of the canonical partition function (3.45, 49, 54) in the two ranges $(N_{\mathrm{c}} - N)/N_{\mathrm{c}} \gg 1/l$ and $(N - N_{\mathrm{c}})/N_{\mathrm{c}} \ll 1/l$. The asymptotic equality of the three pressures p_1, p_2, and p_3 follows from the same argument as before, except that now

$$p_i = \frac{kT}{L_1 L_2 L_3}\, L_i \left(\frac{\partial}{\partial L_i}\right)_N kT \ln Z\,, \tag{3.66}$$

so that instead of (3.61) the common value of p is given by

$$p = kT \left(\frac{\partial \ln Z}{\partial V}\right)_N\,. \tag{3.67}$$

In the "one phase region" one gets therefore from (3.49)

$$\frac{p}{kT} = \frac{\partial}{\partial V} \ln Z^{\mathrm{gr}}(\alpha_0, \Lambda, T) + \left(\frac{\partial \alpha_0}{\partial V}\right)_N \left[N + \frac{\partial}{\partial \alpha_0} \ln Z^{\mathrm{gr}}(\alpha_0, \Lambda, T)\right]. \tag{3.68}$$

But from (3.45) it follows that the last term is zero, so that one gets again (3.61) with $p = p^{\mathrm{gr}}$ while (3.45) becomes (3.62) with $N = N^{\mathrm{gr}}$. One obtains therefore the same equation of state (3.63) except that α is now called α_0. In the "condensed region" one sees from (3.54) directly that in the bulk limit the pressure is given by (3.64) and that then the pressure is independent of N and therefore of the density. Note especially that for Dirichlet boundary conditions the term $\propto (N - N_{\mathrm{c}})$ disappears.

We will not spell out the proof that besides the equation of state also all other thermodynamic properties derived in section 2 follow from the leading terms in our expansions, since this is almost obvious. One can say therefore that at least for the box we have given a more rigorous derivation of the results of section 2, and have shown explicitly the independence of these results from the choice of ensemble and of boundary conditions. The question remains of course to show that all thermodynamic properties are in the bulk limit *also* independent of the shape of the container. To show this the argument of section 2 is still needed.

b. Surface properties. Just like the bulk thermodynamic properties one can read off from our expansions the surface corrections by looking at the terms which are proportional to the area $A = 2(L_1L_2 + L_2L_3 + L_3L_1)$ of the box. Consider again first the expansions of the grand partition function. From the equation for the grand canonical surface tension (1.72)

$$\gamma^{\mathrm{gr}} = \left(\frac{\partial}{\partial A}\right)_{\alpha,V,T} [-kT \ln Z^{\mathrm{gr}}(\alpha, T, V, A)] , \tag{3.69}$$

and from (3.17c, 29c) one concludes that for periodic boundary conditions $\gamma^{\mathrm{gr}} = 0$, while for Neumann and Dirichlet boundary conditions one gets in the "one phase" region from (3.34c)

$$\gamma^{\mathrm{gr}} = \mp \frac{kT}{4\lambda^2} g_2(\alpha) , \tag{3.70}$$

where to be consistent *asymptotically* for large L_i, α must be determined from (3.63b). The same result follows from the equation (1.71) for the canonical surface tension

$$\gamma = \left(\frac{\partial}{\partial A}\right)_{N,V,T} [-kT \ln Z(N, T, V, A)] , \tag{3.71}$$

and from (3.45, 49) by using exactly the same argument by which we showed that $p^{\mathrm{gr}} = p$. In the "one phase region" the surface tension is therefore (just like p) a function of ρ and T. It is positive for Dirichlet boundary conditions and negative for Neumann boundary conditions. Note also that in these two cases one can speak of a volume and a surface contribution to the total number of particles N, since from (3.62) one gets by using the first two terms in our expansions:

$$N = \frac{V}{\lambda^3} g_{3/2}(\alpha) \pm \frac{A}{4\lambda^2} g_1(\alpha) . \tag{3.72}$$

Interpreting $g_{3/2}(\alpha)/\lambda^3$ as the contribution per unit volume, then the surface contribution per unit area becomes:

$$\rho' = \pm \frac{1}{4\lambda^2} g_1(\alpha) \tag{3.73}$$

(positive for the Neumann case and negative for Dirichlet). For the periodic boundary conditions there is no surface term.

Turning now to the "condensed region" one reads from (3.36c, 39c, 54b,c) that for both ensembles ‡

$$\gamma = \mp \frac{kT}{4\lambda^2} \zeta(2) , \tag{3.74}$$

and is therefore a function of the temperature alone (just like the bulk thermodynamical properties in the condensed region). We have plotted $|\gamma|$ as a function of T/T_c at constant ρ, and as a function of ρ_c/ρ at constant T, in figures 3.1 and 3.2.

Thus the behavior of γ is exactly like the behavior of the pressure, and just as in that case we may interpret its independence of the density for $\rho > \rho_c$ by saying that the condensed particles

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‡ This expression has been given by Singh [82]. Note also that the surface contributions to C_v have been calculated by Barber and Fisher [64].

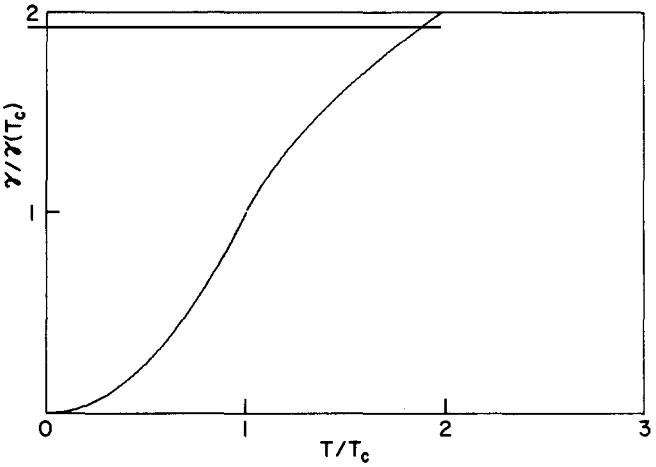

Fig. 3.1. The surface tension γ as a function of the temperature T at constant density, scaled by $\gamma(T_c) \equiv \mp kT_c\zeta(2)/4\lambda_c^2$ and T_c.

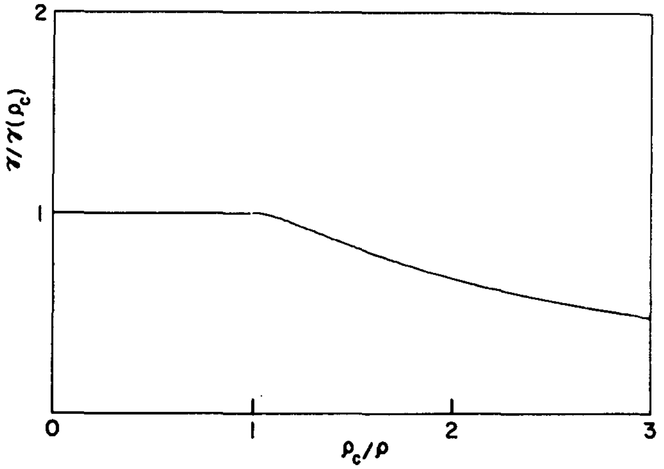

Fig. 3.2. The surface tension γ as a function of the specific volume $1/\rho$, at constant T, scaled by $\gamma(\rho_c) \equiv \mp kT\zeta(2)/4\lambda^2$ and $1/\rho_c$.

do not contribute to the surface tension as well as not to the bulk thermodynamical properties. Note in particular that this is true in the Dirichlet case since the ground state gives a contribution only of order l (when $N - N_c = O(l^3)$) in (3.39c) and (3.54c).

With respect to the surface density, there is the apparent difficulty that in N^{gr} as given by (3.62, 36c, 39c) there are no terms proportional to the area (in the condensed region) since $\bar{g}_1(0) = 0$, and furthermore as the condensed region is approached and $\alpha \to 0$ the surface density given by (3.73) diverges according to (2.A3). As we will discuss in more detail in section 5, the reason is that in the condensed region the transition from the density at the wall to the density inside goes so slowly that it is not integrable and cannot be replaced by a "surface density".

Note that ρ' and γ satisfy the thermodynamic relation

$$\rho' = -(\partial\gamma/\partial\mu)_T\,, \tag{3.75}$$

with $\mu = -\alpha kT$ according to (1.58). This is only applicable in the one phase region since α is constant when $\rho > \rho_{\mathrm{c}}$. Furthermore, (1.58) implies that the surface entropy is

$$s' = -\left(\frac{\partial\gamma}{\partial T}\right)_{\mu} = \begin{cases} -2\gamma/T + k\alpha\rho' , & \rho < \rho_{\mathrm{c}} , \\ -2\gamma/T , & \rho > \rho_{\mathrm{c}} , \end{cases} \tag{3.76}$$

and from (1.60) it follows that the surface energy is $u' = \gamma + Ts' + \mu\rho' = -\gamma$.

Finally we must discuss the question whether the results (3.70, 73, 74) are *independent of the shape* of the vessel (just like the bulk properties). To do this we must generalize the argument of section 2 by taking into account a refinement of the Weyl theorem (2.49) to include the surface corrections, namely that [‡]

$$g(e) \sim \frac{\sqrt{e}}{\Gamma(\frac{3}{2})} \pm \frac{1}{4}\frac{a}{\Gamma(1)} , \tag{3.77}$$

as $e \to \infty$, for Neumann (+) and Dirichlet (−) boundary conditions, where a is the surface area of the (unit) volume Λ_0, so that $A = aL^2$. In the grand canonical ensemble, the surface tension follows as the area part of the asymptotic form of Ω^{gr}:

$$\Omega^{\mathrm{gr}} = -kT \ln Z^{\mathrm{gr}} \sim -p^{\mathrm{gr}} V + \gamma^{\mathrm{gr}} A , \tag{3.78}$$

according to (1.70). First of all note that the first term of (3.77) implies p^{gr} equivalent to (2.52) since

$$\begin{aligned} \Omega^{\mathrm{gr}} &= kT \sum_{k=0}^{\infty} \ln[1 - \exp(-\alpha - \lambda^2 e_k/L^2)] \sim kT \frac{L^3}{\lambda^3} \int_0^{\infty} \frac{2}{\sqrt{\pi}}\sqrt{x}\, \mathrm{d}x \ln[1 - \mathrm{e}^{-\alpha - x}] \\ &= -\frac{kT}{\lambda^3}\frac{2}{\sqrt{\pi}}\frac{2}{3}L^3 \int_0^{\infty} \frac{x^{3/2}\,\mathrm{d}x}{\mathrm{e}^{\alpha + x} - 1} = -p^{\mathrm{gr}} L^3 \end{aligned} \tag{3.79}$$

(by partial integration), and that when $\alpha + e_0/l^2 \sim 1/[L^3(\rho - \rho_{\mathrm{c}})]$ the $k = 0$ term gives an insignificant contribution which vanishes when $V \to \infty$ and again (2.55) follows for $\rho > \rho_{\mathrm{c}}$. Likewise, including the second term of (3.77), one finds $\Omega^{\mathrm{gr}} = -p^{\mathrm{gr}} L^3 + \gamma^{\mathrm{gr}} a L^2$ with the same γ^{gr} as before, (3.70). Then it also follows that the canonical surface tension is identical to γ^{gr}, according to (2.41, 63, 64).

Appendix 3.A. Justification of (3.14)

An application of the Poisson sum formula gives the identity

$$\tfrac{1}{2} f(0) + \sum_{j=1}^{\infty} f(j) = \sum_{s=-\infty}^{+\infty} \int_0^{\infty} f(x)\, \mathrm{e}^{2\pi i s x}\, \mathrm{d}x = \int_0^{\infty} f(x)\, \mathrm{d}x + 2 \sum_{s=1}^{\infty} \int_0^{\infty} f(x) \cos(2\pi s x)\, \mathrm{d}x , \tag{3.A1}$$

for any $f(x)$. This can be used to discuss the sum over j in (3.13), as the Fourier integral above can be done according to (3.15). For example, for $d = 1$ one gets

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[‡] See Kac [49], also McKean and Singer [50].

$$
\begin{aligned}
l \sum_{j=1}^{\infty} j^{-3/2} \exp(-\alpha j - \pi l^2 m^2/j) &= \sum_{s=-\infty}^{+\infty} \frac{1}{m} \exp\{-2\sqrt{\pi(\alpha + 2\pi i s)}\, lm\} \\
&= \frac{1}{m} \exp(-2\sqrt{\pi\alpha}\, lm) + 2 \sum_{s=1}^{\infty} \frac{1}{m} \exp(-A^{+} ml) \cos A^{-} ml \,, \qquad (3.\mathrm{A2}) \\
A^{\pm} &\equiv \sqrt{2\pi}\, (\alpha^2 + 4\pi^2 s^2)^{1/4} \sqrt{1 \pm \frac{\alpha}{\sqrt{\alpha^2 + 4\pi^2 s^2}}} \,.
\end{aligned}
$$

The first term gives (3.17a). (Note that $f(0) = 0$.) No matter how small or large α is, the $s = 1$, $m = 1$ term is at least as small as $e^{-2\pi l} \simeq O(e^{-l})$, and the higher s and m terms are much smaller. Without discussing the convergence of these series, we argue that *asymptotically* in l the error induced by going from (3.13) to (3.14) is of this order.

Appendix 3.B. Proof of (3.23)

$C_z(\omega_1, \dots \omega_d)$ as defined by (3.20) only converges for $z \geq d/2$. To get a representation valid for all values of z, use the integral representation of the Γ function:

$$
\begin{aligned}
C_z &\equiv \sum_{n_i}{}' \frac{\Gamma(z)}{[\pi N^2]^k} = \sum_{n_i}{}' \int_0^{\infty} \mathrm{d}x\, x^{z-1} \exp(-\pi N^2 x) \\
&= \sum_{n_i}{}' \int_0^{1} \mathrm{d}x\, x^{z-1} \exp(-\pi N^2 x) + \sum_{n_i}{}' \int_1^{\infty} \mathrm{d}x\, x^{z-1} \exp(-\pi N^2 x) \,. \qquad (3.\mathrm{B1})
\end{aligned}
$$

The second integral converges for all z. In the first integral the transform (3.12) can be used after adding and subtracting the $n_i = 0$ term:

$$
\begin{aligned}
&\sum_{n_i}{}' \int_0^{1} \mathrm{d}x\, x^{z-1} \exp(-\pi N^2 x) = \sum_{n_i} \int_0^{1} \mathrm{d}x\, x^{z-1} \exp(-\pi N^2 x) - \frac{1}{z} \qquad (3.\mathrm{B2}) \\
&= \sum_{m_i} \int_0^{1} \mathrm{d}x\, x^{z-d/2-1} \exp(-\pi M^2/x) - \frac{1}{z} = \sum_{m_i}{}' \int_1^{\infty} \mathrm{d}t\, t^{d/2-z-1} \exp(-\pi M^2 t) + \frac{1}{z - d/2} - \frac{1}{z} \,,
\end{aligned}
$$

where M is defined in (3.9), and in the last line we have split off the $m_i = 0$ term. The exchanges of the sum and integral can be justified for all d, as for the case $d = 1$ when this is Riemann's integral representation of the zeta function [‡].

It should be noted that the lattice sums C_z have appeared in connection with perturbative expansions of the hard sphere gas. (See for example Huang, Yang and Luttinger [83], and Wu [84].) In fact there has recently been renewed interest in the mathematical theory of the Madelung constant and related sums, and in this connection the sums C_z have also been introduced. Especially in the most recent of these (Zucker [85]) the identity (3.23) has also been given.

[‡] See Whittaker and Watson [71].

4. The fluctuation problem for the finite IBG

4.1. Introduction

In section 2 we found that the canonical and grand canonical ensembles differ in some of their predictions of the *bulk* properties for the condensed IBG, such as the fluctuations in the overall density of particles in the ground state, and that the macroscopic fluctuations in the grand canonical ensemble indicated the unphysical nature of that ensemble. Now one might wonder whether for large but finite systems these differences also occur, or whether they depend sensitively on the size of the system and are a result only of the infinite volume limit. In the last section we discussed the partition functions for the IBG in finite boxes, but since we were only concerned with the thermodynamical properties, whose behavior in the infinite system is the same in the two ensembles, we did not address this point. In this subsection we will show how the expressions for the partition functions can also be used to discuss these fluctuations. In fact we will find that the large system acts qualitatively like the bulk system; namely, in the "condensed region" when $(N - N_c)/N_c \gg 1/l$ the fluctuations in the density of particles in the ground state in the canonical ensemble goes to zero as

$$\frac{\langle(\Delta n_0)^2\rangle}{V^2} \sim \frac{1}{V^{2/3}\lambda^4} \sum_{k\neq 0} \frac{1}{(e_k - e_0)^2}\,, \tag{4.1}$$

where e_k are the dimensionless energy levels given by (3.10), so that the coefficient of $V^{-2/3}\lambda^{-4}$ is a constant that depends only upon the shape of the system. In the grand canonical the fluctuations are "macroscopic":

$$\frac{\langle(\Delta n_0)^2\rangle^{\mathrm{gr}}}{V^2} \sim \left(\frac{N^{\mathrm{gr}} - N_c}{V}\right)^2 . \tag{4.2}$$

When $V \to \infty$ these give (2.16) and (2.67).

We will also show how the occupations and their fluctuations can be used to calculate the one and two particle density matrices. We only consider a three dimensional box, and always assume that $l_i \gg 1$.

4.2. Proof of (4.1–2)

In the grand canonical ensemble we have according to (1.138–9) that for all k,

$$\frac{\langle n_k^2\rangle^{\mathrm{gr}} - (\langle n_k\rangle^{\mathrm{gr}})^2}{V^2} = \frac{(\langle n_k\rangle^{\mathrm{gr}})^2 + \langle n_k\rangle^{\mathrm{gr}}}{V^2} \tag{4.3}$$

(exactly), where

$$\langle n_k\rangle^{\mathrm{gr}} \equiv \frac{1}{\exp(\alpha + e_k/l^2) - 1} \tag{4.4}$$

are the occupations in terms of the dimensionless e_k. From these the well known result (4.2) follows directly, since when $(N^{\mathrm{gr}} - N_c)/N_c \gg 1/l$ then $\alpha + e_0/l^2 \sim 1/(N^{\mathrm{gr}} - N_c)$ and therefore

$$\langle n_0\rangle^{\mathrm{gr}} \sim N^{\mathrm{gr}} - N_c\,. \tag{4.5}$$

For the excited states $k > 0$ we can take $\alpha = 0$ and therefore

$$\langle n_k\rangle^{\mathrm{gr}} \simeq \frac{1}{\exp(e_k - e_0)/l^2 - 1} \lesssim \frac{l^2}{(e_k - e_0)}\,, \tag{4.6}$$

so that $\langle n_k\rangle^{\mathrm{gr}}/V \to 0$ as $V^{-1/3}$, and their fluctuations (4.3) go to zero as $V^{-2/3}$, as $V \to \infty$.

In the canonical ensemble, we have found that when $(N - N_{\mathrm{c}})/N_{\mathrm{c}} \gg 1/l$, then

$$\ln Z(N, \Lambda, T) \simeq -Ne_0/l^2 - \sum_{k\neq 0} \ln(1 - \exp\{-(e_k - e_0)/l^2\}) + \mathrm{O}(\exp\{-(N - N_{\mathrm{c}})/l^2\})\,. \tag{4.7}$$

Evidently the average occupations of the states and their fluctuations (1.28–29) can be found by considering Z to be a function of the energy levels and differentiating with respect to them:

$$\langle n_k\rangle \equiv \frac{1}{Z} \sum_{\{n_j\}} n_k \exp(-\textstyle\sum_j n_j e_j/l^2) = -l^2 \dfrac{\partial}{\partial e_k} \ln Z\,, \tag{4.8}$$

$$\langle n_k^2\rangle - \langle n_k\rangle^2 = \left(-l^2 \frac{\partial}{\partial e_k}\right)^2 \ln Z\,. \tag{4.9}$$

Then (4.7) can be used for $\ln Z$ when $(N - N_{\mathrm{c}})/N_{\mathrm{c}} \gg 1/l$, and one finds [‡]:

$$\langle n_k\rangle \simeq \begin{cases} \dfrac{1}{\exp(e_k - e_0)/l^2 - 1}\,, & k > 0\,, \\ N - \displaystyle\sum_{j>0} \langle n_j\rangle\,, & k = 0\,, \end{cases} \tag{4.10}$$

$$\langle n_k^2\rangle - \langle n_k\rangle^2 \simeq \begin{cases} \langle n_k\rangle^2 + \langle n_k\rangle\,, & k > 0\,, \\ \displaystyle\sum_{j>0} [\langle n_j\rangle^2 + \langle n_j\rangle]\,, & k = 0\,. \end{cases} \tag{4.11}$$

Clearly for the excited states $k > 0$ this gives the same results as the grand canonical ensemble (4.6). For the ground state there is evidently the following formal relation between these expressions and the grand partition function:

$$\begin{aligned} \langle n_0\rangle &\simeq N - \lim_{\alpha\to -e_0/l^2} \{(-\partial/\partial\alpha) \ln Z^{\mathrm{gr}} - [\exp(\alpha + e_0/l^2) - 1]^{-1}\}\,, \\ \langle n_0^2\rangle - \langle n_0\rangle^2 &\simeq \lim_{\alpha\to -e_0/l^2} \{(\partial/\partial\alpha)^2 \ln Z^{\mathrm{gr}} - [\exp(\alpha + e_0/l^2) - 1]^{-1} - [\exp(\alpha + e_0/l^2) - 1]^{-2}\}\,. \end{aligned} \tag{4.12}$$

These are similar to (3.53). Specializing now to the box these can be evaluated using the explicit expansions of Z^{gr} about $\alpha = -e_0/l^2$, (3.29, 36, 39). One finds:

$$\langle n_0\rangle = N - N_{\mathrm{c}} + \begin{cases} \mathrm{O}(l^2) & \text{periodic b.c.} \\ \mathrm{O}(l^2 \ln l^2) & \text{Neumann and Dirichlet b.c.} \end{cases} \tag{4.14}$$

[‡] These expressions have been found by Dingle [79–81] (in a similar way) and Fraser [69]. Reif [86] and Hauge [32] also arrived at these results, using however the saddle point method.

and for the fluctuations one finds that the leading term is given by:

$$\langle n_0^2\rangle - \langle n_0\rangle^2 \simeq l^4 C_2^{\mathrm{o},\pm}(\omega_1, \omega_2, \omega_3)\,, \tag{4.15}$$

for all three boundary conditions. Writing these in terms of e_k according to (3.40), the result (4.1) follows. This expression has also been given by Hauge [32]. Now it is immediately suggested that (4.1) might hold for an arbitrary shape of the boundary, not just a box, whose single particle energy spectrum is given by e_k. In fact (4.1) also follows directly from (3.41) and (3.77), which represent a system of arbitrary shape. Alternatively, one can use the fact that (4.1) is true for a box to prove it for an arbitrary shape, by inscribing and surrounding the region by a box and using the Hilbert inequality of the ordered eigenvalues, but we will omit the details here.

Note that the relative fluctuations in the occupation of the ground state have also been calculated by Fujiwara, ter Haar, and Wergeland [87], for a large system in the canonical ensemble. They also found that they vanish when $V \to \infty$ in the condensed region (as well as the non-condensed region), but that they approach this value as $V^{-1/3}$. This contradicts our result of $V^{-2/3}$ as given by (4.15) (divided by V^2).

4.3. Further comments

The "cross fluctuation" $\langle n_j n_k\rangle$ ($j \neq k$) can also be found by differentiation:

$$\langle n_j n_k\rangle = \frac{1}{Z}\left(-l^2 \frac{\partial}{\partial e_j}\right)\left(-l^2 \frac{\partial}{\partial e_k}\right) Z = \langle n_j\rangle\langle n_k\rangle + \left(-l^2 \frac{\partial}{\partial e_j}\right)\left(-l^2 \frac{\partial}{\partial e_k}\right) \ln Z\,. \tag{4.16}$$

Using (4.7) for ln Z one finds that in the "condensed region":

$$\langle n_j n_k\rangle = \begin{cases} \langle n_j\rangle\langle n_k\rangle\,, & j \neq k\,; \quad j, k \neq 0\,, \\ \langle n_j\rangle\langle n_0\rangle - \langle n_j\rangle^2 - \langle n_j\rangle\,, & j \neq 0\,; \quad k = 0\,. \end{cases} \tag{4.17}$$

With this result, along with (4.10) and (4.11), the one and two particle density matrices can be calculated, since according to (1.133):

$$\rho_1(\boldsymbol{r}', \boldsymbol{r}''; N, \Lambda, T) = \sum_{k=0} \langle n_k\rangle\, \psi_k^*(\boldsymbol{r}_1'')\, \psi_k(\boldsymbol{r}_1')\,, \tag{4.18}$$

while the result (1.132) for ρ_2 can be written in the form:

$$\begin{gathered} \rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{r}_1, \boldsymbol{r}_2; N, \Lambda, T) = \sum_{j,k} \Psi_{jk}^*(\boldsymbol{r}_1'', \boldsymbol{r}_2'')\, \Psi_{jk}(\boldsymbol{r}_1', \boldsymbol{r}_2')\, C_{jk}\,, \\ \Psi_{jk}(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv \tfrac{1}{2}(\psi_j(\boldsymbol{r}_1)\, \psi_k(\boldsymbol{r}_2) + \psi_k(\boldsymbol{r}_1)\, \psi_j(\boldsymbol{r}_2))\,, \\ C_{jk} \equiv \begin{cases} 2\langle n_j n_k\rangle\,, & j \neq k\,, \\ \langle n_j^2\rangle - \langle n_j\rangle\,, & j = k\,. \end{cases} \end{gathered} \tag{4.19}$$

To see this one must replace the restricted sums over the occupation numbers by the unrestricted sums over the energy states. Then one can show that when $l \to \infty$ the bulk canonical density matrices in the condensed region (2.22, 25b) follow. The result in the one phase region also follows from (4.18–19); then the saddle point method is valid and one has from (3.49):

$$\langle n_k\rangle = \frac{1}{\exp(\alpha_0 + e_k/l^2) - 1}\,, \tag{4.20a}$$

$$\langle n_k^2\rangle = 2\langle n_k\rangle^2 + \langle n_k\rangle\,, \tag{4.20b}$$

$$\langle n_j n_k\rangle = \langle n_j\rangle\langle n_k\rangle\,, \qquad j \neq k\,, \tag{4.20c}$$

where α_0 is determined by (3.45).

In this way, London [16] first calculated the two particle distribution function (= the diagonal element of ρ_2) for all densities. Note however that he *assumed* that $\langle n_j n_k\rangle = \langle n_j\rangle\langle n_k\rangle$ for all $j \neq k$, even for j or k equal to zero. One can see from (4.17) that this is essentially true, since the contribution of the $\langle n_j\rangle^2 + \langle n_j\rangle$ term (when $k = 0$) vanishes in the limit $l \to \infty$. Thus we have verified London's method.

5. Local properties of an IBG near a wall

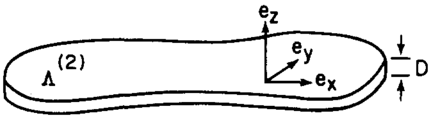
5.1. Introduction

Near the boundary of a region, there will be variations in the local density, pressure, and energy, as well as in the distribution functions and density matrices. These variations are responsible for the finite volume corrections that we have discussed in the last two sections, but they also occur at the boundary of an infinite system, or more accurately a half-infinite system. Up till now we have not discussed the local structure of a finite IBG as described by the density matrices, which we had emphasized in the description of the bulk properties in section 2. In this section we return to the density matrices, calculating them for a half-infinite system, and discuss the local properties that derive from them. The advantage of using the half-infinite system is that there are no complications from curved boundaries, edges, finite size, or finite number. The results should also describe the surface characteristics of large finite systems in an asymptotic sense.

5.2. The density matrices of a half-infinite system

We proceed as in section 2.3, using the grand canonical density matrices as generating functions of the canonical ones.

Consider a region Λ in the shape of a flat slab of constant thickness D, whose face is the two-dimensional region $\Lambda^{(2)}$ in the x–y plane of area L^2, as shown below:



The walls are assumed to be perpendicular to $\Lambda^{(2)}$, so that the states factor into a product of states $\psi_k^{(2)}(x, y)$ on $\Lambda^{(2)}$ and one dimensional states $\psi_k^{(1)}(z)$ of the segment D, which we call the region $\Lambda^{(1)}$. Then the grand canonical one particle density matrix (1.141) becomes

$$\rho_1^{\mathrm{gr}}(\boldsymbol{r}', \boldsymbol{r}''; N, \Lambda^{(1)}, \Lambda^{(2)}, T) = \sum_{j=1}^{\infty} \mathrm{e}^{-\alpha j} W^{(1)} W^{(2)} , \tag{5.1a}$$

$$W^{(2)} \equiv \sum_{k=0}^{\infty} \frac{1}{L^2} y_k^{(2)*}\left(\frac{x''}{L}, \frac{y''}{L}\right) y_k^{(2)}\left(\frac{x'}{L}, \frac{y'}{L}\right) \exp(-je_n^{(2)}\lambda^2/L^2) , \tag{5.1b}$$

$$W^{(1)} \equiv \sum_{n=0}^{\infty} \frac{1}{D} y_n^{(1)*}\left(\frac{z''}{D}\right) y_n^{(1)}\left(\frac{z'}{D}\right) \exp(-je_n^{(1)}\lambda^2/D^2) . \tag{5.1c}$$

We have written this in terms of the dimensionless states and energy levels on both $\Lambda^{(1)}$ and $\Lambda^{(2)}$, as in section 2.3. The origin of the coordinate system is chosen so that the plane $z = 0$ corresponds to the lower face – in other words, the endpoint of the segment $\Lambda^{(1)}$ – and falls within the boundary of $\Lambda^{(2)}$. As $L \to \infty$,

$$W^{(2)} \sim \frac{1}{j\lambda^2} \exp[-\pi\{(x' - x'')^2 + (y' - y'')^2\}/j\lambda^2] , \tag{5.2}$$

analogous to (2.74), for all boundary conditions. On $\Lambda^{(1)}$ the dimensionless states and energy levels for the various boundary conditions are given by:

periodic b. c:

$$y_n^{(1)}\left(\frac{z}{D}\right) = \mathrm{e}^{-2\pi i n z/D} , \qquad e_n^{(1)} = \pi n^2 , \qquad n = 0, 1, 2, \ldots \tag{5.3a}$$

Dirichlet b. c:

$$y_n^{(1)}\left(\frac{z}{D}\right) = \sqrt{2}\sin(n\pi z/D) , \qquad e_n^{(1)} = \pi n^2/4 , \qquad n = 1, 2, 3, \ldots \tag{5.3b}$$

Neumann b. c:

$$y_n^{(1)}\left(\frac{z}{D}\right) = \begin{cases} 1 , & e_0^{(1)} = 0 , \qquad n = 0 , \\ \sqrt{2}\cos(n\pi z/D) , & e_n^{(1)} = \pi n^2/4 , \qquad n = 1, 2, 3, \ldots . \end{cases} \tag{5.3c}$$

Then, for periodic boundary conditions:

$$W^{(1)} = \frac{1}{D} \sum_{n=-\infty}^{+\infty} \exp\{-j\pi n^2\lambda^2/D^2 + 2\pi i n(z' - z'')/D\} \sim \frac{1}{j^{1/2}\lambda} \exp\{-\pi(z' - z'')^2/j\lambda^2\} , \tag{5.4}$$

as $D \to \infty$, while for Dirichlet (–) and Neumann (+), one gets:

$$\begin{aligned} W^{(1)} &= \frac{1}{D}\frac{1}{2} \sum_{n=-\infty}^{+\infty} \exp\{-j\pi n^2\lambda^2/4D^2\} \left(\cos\frac{n\pi(z' - z'')}{D} \pm \cos\frac{n\pi(z' - z'')}{D}\right) \\ &\sim \frac{1}{j^{1/2}\lambda} (\exp\{-\pi(z' - z'')^2/j\lambda^2\} \pm \exp\{-\pi(z' + z'')^2/j\lambda^2\}) \\ &= \frac{1}{j^{1/2}\lambda} \exp\{-\pi(z' - z'')^2/j\lambda^2\} (1 \pm \exp\{-4\pi z'z''/j\lambda^2\}) . \end{aligned} \tag{5.5}$$

In the periodic case there is no effect from the presence of the boundaries, except that z' and z'' are restricted to $z > 0$, while in the Neumann and Dirichlet cases there is an extra term that is only important when both z' and z'' are near the surface $z = 0$.

Using the results (5.2, 4, 5) the expression of ρ_1^{gr} in the limit of $D \to \infty$ and $L \to \infty$ *together* such that $N^{\mathrm{gr}}/L^2D = \rho$ can be found. Again α as a function of ρ is determined by (2.40). As before, when $\rho < \rho_c$, α will limit to a value greater than zero given by (2.3), and ρ_1^{gr} will be given by

$$\rho_1^{\mathrm{o,gr}}(\boldsymbol{r}', \boldsymbol{r}''; \rho, T) = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} j^{-3/2} \exp\{-\alpha j - \pi |\boldsymbol{r}' - \boldsymbol{r}''|^2/j\lambda^2\}\ , \tag{5.6a}$$

$$\rho_1^{\pm,\mathrm{gr}}(\boldsymbol{r}', \boldsymbol{r}''; \rho, T) = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} j^{-3/2} \exp\{-\alpha j - \pi |\boldsymbol{r}' - \boldsymbol{r}''|^2/j\lambda^2\}\,(1 \pm \exp\{-4\pi z'z''/j\lambda^2\})\ , \tag{5.6b}$$

for periodic (o), Neumann (+) and Dirichlet (−) boundary conditions.

In the condensed region, one must take for α:

$$\alpha + \frac{e_0^{(1)}\lambda^2}{D^2} + \frac{e_0^{(2)}\lambda^2}{L^2} \sim \frac{1}{L^2D(\rho - \rho_c)}\ , \tag{5.7}$$

so that the occupation of the lowest state $\sim L^2D(\rho - \rho_c)$ as L and $D \to \infty$. Then it follows simply as before that the density matrices are given by:

$$\rho_1^{\mathrm{o,gr}}(\boldsymbol{r}', \boldsymbol{r}''; \rho, T) = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} j^{-3/2} \exp\{-\pi |\boldsymbol{r}' - \boldsymbol{r}''|^2/j\lambda^2\} + \rho - \rho_c\ , \tag{5.8a}$$

$$\rho_1^{+,\mathrm{gr}}(\boldsymbol{r}', \boldsymbol{r}''; \rho, T) = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} j^{-3/2} \exp\{-\pi |\boldsymbol{r}' - \boldsymbol{r}''|^2/j\lambda^2\}(1 + \exp\{-4\pi z'z''/j\lambda^2\}) + \rho - \rho_c\ , \tag{5.8b}$$

$$\rho_1^{-,\mathrm{gr}}(\boldsymbol{r}', \boldsymbol{r}''; \rho, T) = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} j^{-3/2} \exp\{-\pi |\boldsymbol{r}' - \boldsymbol{r}''|^2/j\lambda^2\}(1 - \exp\{-4\pi z'z''/j\lambda^2\})\ , \tag{5.8c}$$

for $\rho > \rho_c$. In the periodic and Neumann cases the ODLRO is $\rho - \rho_c$ because the contribution of the lowest state is constant and equal to unity. However in the Dirichlet case there is no ODLRO because $y_0(0) = 0$, or namely that when D is made infinite, the ground state remains zero any finite distance from the plane $z = 0$. We will discuss this more in the next subsection.

The s-particle grand canonical density matrices are just symmetrized products of these one particle matrices, according to (2.71). The canonical reduced density matrices follow by the inversion technique of section 2. Since the density distribution $\nu(x, \rho)$ is clearly the same as in the bulk case, one has again that $\rho_s = \rho_s^{\mathrm{gr}}$ for $\rho < \rho_c$, and for $\rho > \rho_c$ one must use (2.66). This implies first of all that $\rho_1 = \rho_1^{\mathrm{gr}}$ (for all boundary conditions). Note that for the Dirichlet case $\rho_s = \rho_s^{\mathrm{gr}}$ for all s since (5.8c) does not depend upon the density. Now we will discuss the properties that follow from the density matrices, especially the one particle density matrix.

5.3. The local density and the pressure-stress tensor

The basic characteristics of the one-particle density matrix are the diagonal element $\boldsymbol{r}' = \boldsymbol{r}''$ and the "curvature" about that point. These are related to the two local properties, the density and the pressure-stress tensor.

The diagonal element is just the local density. Thus, from (5.8a) it follows that for periodic boundary conditions the local density is constant and equal to the average density:

$$n_1^{\mathrm{o}} \equiv \rho_1^{\mathrm{o}}(\boldsymbol{r}, \boldsymbol{r}) = \rho \,, \tag{5.9}$$

while for the Neumann and Dirichlet cases it follows from (5.8b, c) that the density varies near the boundary at $z = 0$:

$\rho < \rho_{\mathrm{c}}$

$$n_1^{\pm}(z) = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} j^{-3/2}\, \mathrm{e}^{-\alpha j}(1 \pm \exp\{-4\pi z^2/j\lambda^2\}) = \rho \pm F(2z, \alpha, T) \,, \tag{5.10a}$$

$\rho > \rho_{\mathrm{c}}$

$$n_1^{+}(z) = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} j^{-3/2} (1 \pm \exp\{-4\pi z^2/j\lambda^2\}) + \rho - \rho_{\mathrm{c}} = \rho + F(2z, 0, T) \,, \tag{5.10b}$$

$$n_1^{-}(z) = \frac{1}{\lambda^3} \sum_{j=1}^{\infty} j^{-3/2} (1 - \exp\{-4\pi z^2/j\lambda^2\}) = \rho_{\mathrm{c}} - F(2z, 0, T) \,. \tag{5.10c}$$

We have written these in terms of the function $F(r, \alpha, T)$ defined in (2.18). Some plots of $n_1(z)$ are given in fig. 5.1. The limiting behavior at $z = 0$ and ∞ is summarized below:

$$n_1^{+}(0) = \begin{cases} 2\rho \,, & \rho < \rho_{\mathrm{c}} \\ \rho + \rho_{\mathrm{c}} \,, & \rho > \rho_{\mathrm{c}} \end{cases} \qquad n_1^{+}(\infty) = \rho \tag{5.11a}$$

$$n_1^{-}(0) = 0 \qquad\qquad n_1^{-}(\infty) = \begin{cases} \rho \,, & \rho < \rho_{\mathrm{c}} \,, \\ \rho_{\mathrm{c}} \,, & \rho > \rho_{\mathrm{c}} \,. \end{cases} \tag{5.11b}$$

Note that when $\rho > \rho_{\mathrm{c}}$, the value $n_1(\infty)$ is reached as $1/z$ according to the discussion of the properties of $F(r, 0, T)$ of (2.24). In the Dirichlet case in the condensed region the density approaches ρ_{c} and not ρ as $z \to \infty$. This is because the ground state $y_0(z/D)$ varies over the thickness D, and when $D \to \infty$ it is flat and zero any finite distance from the boundary. This is why there is no ODLRO term in (5.8c).

In the one phase region it is possible to integrate the difference of $n_1(z)$ from the bulk value $n_1(z) = \rho$:

$$\int_0^{\infty} [n_1(z) - \rho]\, \mathrm{d}z = \pm \int_0^{\infty} \frac{1}{\lambda^3} \sum j^{-3/2} \exp\{-\alpha j - 4\pi z^2/j\lambda^2\}\, \mathrm{d}z = \pm \frac{1}{4\lambda^2}\, g_1(\alpha) \,. \tag{5.12}$$

It can be interpreted as the surface density ρ' and agrees with the expression found in the third

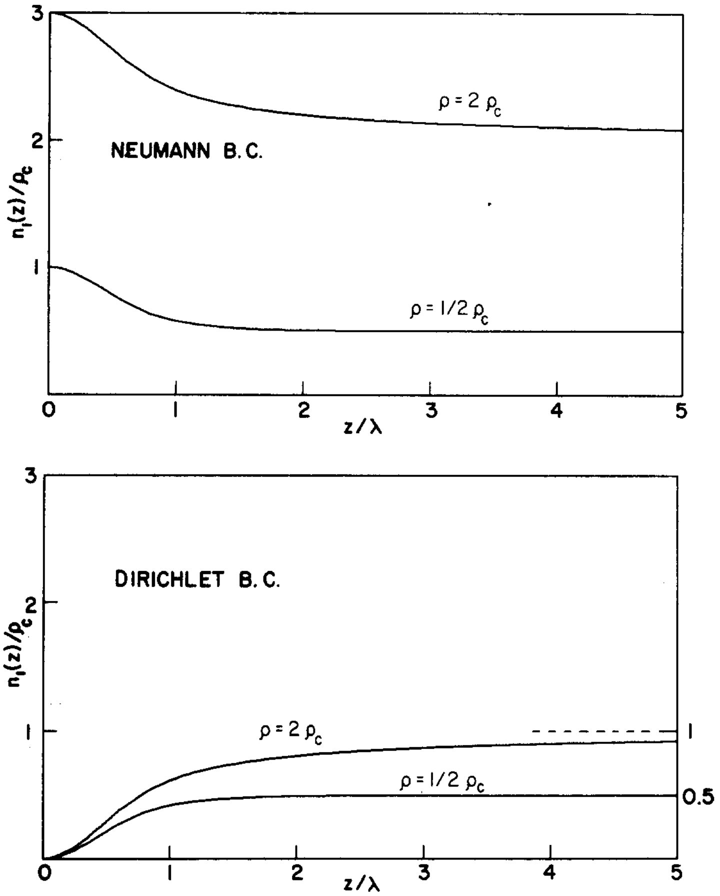


Fig. 5.1. The local density $n_1(z)/\rho_c$ near a wall (at $z = 0$) in a half-infinite IBG for the average density ρ equal to 0.5 ρ_c and $2\rho_c$, for the Dirichlet and Neumann boundary conditions on the wavefunctions at the wall.

section (3.73). In the condensed region $\alpha = 0$ and this integral doesn't exist; in fact the integrand ($= F(2z, 0, T)$) $\sim 1/z$ as $z \to \infty$. Thus the concept of a "surface density" as defined by the integral above is not valid in the condensed region. This explains why we failed to find such a function in section 3. Note that this behavior is due to the long range behavior in $F(2z, 0, T)$ but is *not* due to either the ODLRO or the variation of the Dirichlet ground state.

The pressure-stress tensor follows from the one-particle density matrix according to (1.93):

$$P_{ij}(\boldsymbol{r}) = -\frac{\hbar^2}{m}\left[\frac{\partial}{\partial \xi_i}\frac{\partial}{\partial \xi_j}\rho_1\left(\boldsymbol{r}+\frac{\xi}{2}, \boldsymbol{r}-\frac{\xi}{2}\right)\right]_{\xi=0}, \tag{5.13}$$

assuming that the local velocity $\boldsymbol{v}$ defined by (1.82) is zero, which is the case here as can easily be verified. Then it follows from (5.6) and (5.8) that the off diagonal elements P_{xy}, P_{yz}, and P_{zx} are zero always, and that for periodic boundary conditions,

$$P^{\circ}_{xx} = P^{\circ}_{yy} = P^{\circ}_{zz} = \left\{ \begin{array}{ll} \dfrac{kT}{\lambda^3} g_{5/2}(\alpha) , & \rho < \rho_c \\ \\ \dfrac{kT}{\lambda^3} \zeta(5/2) , & \rho > \rho_c \end{array} \right\} = p , \tag{5.14}$$

while for Dirichlet (–) and Neumann (+),

$$P^{\pm}_{zz} = \left\{ \begin{array}{ll} \dfrac{kT}{\lambda^3} g_{5/2}(\alpha) , & \rho < \rho_c \\ \\ \dfrac{kT}{\lambda^3} \zeta(5/2) , & \rho > \rho_c \end{array} \right\} = p , \tag{5.15a}$$

$$P^{\pm}_{xx}(z) = P^{\pm}_{yy}(z) = \left\{ \begin{array}{ll} \dfrac{kT}{\lambda^3} \sum j^{-5/2}\, \mathrm{e}^{-\alpha j}(1 \pm \exp\{-4\pi z^2/j\lambda^2\}) , & \rho < \rho_c , \\ \\ \dfrac{kT}{\lambda^3} \sum j^{-5/2}(1 \pm \exp\{-4\pi z^2/j\lambda^2\}) , & \rho > \rho_c . \end{array} \right. \tag{5.15b}$$

The normal pressure (5.15a) is constant and equal to p, as is necessary for the maintenance of hydrostatic equilibrium (1.114):

$$\sum_{i=1}^{3} \frac{\partial P_{ij}}{\partial r_i} = 0 . \tag{5.16}$$

The tangential pressure (5.15b) is only equal to p (and the pressure is only isotropic) when $z \to \infty$. Near the wall it is increased for the Neumann case and decreased for the Dirichlet. In fact the integral of the difference is equal to the surface tension, since according to the *mechanical* definition the surface tension γ is (minus) the extra force per length (tension) along a cut in the surface due to a decrease of the tangential pressure P_{xx} from its bulk value ‡. For $\rho < \rho_c$ one gets:

$$\gamma = -\int_0^{\infty} (P_{xx}(z) - p)\, \mathrm{d}z = \mp \frac{kT}{\lambda^3} \int_0^{\infty} \sum j^{-5/2} \exp\{-\alpha j - 4\pi z^2/j\lambda^2\}\, \mathrm{d}z = \mp \frac{kT}{4\lambda^2}\, g_2(\alpha) , \tag{5.17a}$$

and similarly for $\rho > \rho_c$:

$$\gamma = \mp \frac{kT}{4\lambda^2}\, \zeta(2) . \tag{5.17b}$$

This agrees with our previous result (3.70, 73) and demonstrates therefore the equivalence of the thermodynamical and mechanical definitions of the surface tension for the IBG.

The integral for γ (5.17a) is quite similar to that for ρ' (5.12), as indeed ρ' and γ are related by the thermodynamical expression (3.75). Note however that γ exists in the condensed region since

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‡ This is the so-called Bakker relation [88]. See also Ono and Kondo [35].

$P_{xx} \to p$ as $1/z^3$ as $z \to \infty$, which is integrable. Note also that the condensed phase contributes neither to P_{ij} nor to γ.

The negative ρ' and positive γ of the Dirichlet case are what would be expected for a fluid that is repelled from a wall, and the positive ρ' and negative γ of the Neumann case is what would be expected for a fluid that is attracted to a wall. The behavior of attraction and repulsion can be seen quite clearly in the plots of the local density in fig. 5.1. In fact the Dirichlet boundary condition represents an infinite hard wall and therefore a repulsion. However, the Neumann boundary condition has no direct physical connection.

The values of n_1, $P_{xx} = P_{yy}$ and P_{zz} can be used to illustrate the behavior of the density matrices themselves. Consider

$$\tilde{\rho}_1(\boldsymbol{r}, \boldsymbol{\xi}) \equiv \rho_1(\boldsymbol{r} + \tfrac{1}{2}\boldsymbol{\xi}, \boldsymbol{r} - \tfrac{1}{2}\boldsymbol{\xi}) \,, \tag{5.18}$$

and expand for small $\boldsymbol{\xi}$ about $\boldsymbol{\xi} = 0$. One finds:

$$\tilde{\rho}_1(\boldsymbol{r}, \boldsymbol{\xi}) = n_1(\boldsymbol{r}) + \pi \frac{\xi_x^2}{\lambda^2} \frac{P_{xx}(\boldsymbol{r})}{kT} + \pi \frac{\xi_y^2}{\lambda^2} \frac{P_{yy}(\boldsymbol{r})}{kT} + \pi \frac{\xi_z^2}{\lambda^2} \frac{P_{zz}(\boldsymbol{r})}{kT} + \ldots \,, \tag{5.19}$$

using that $\boldsymbol{v} = 0$ and $P_{ij} = 0$ $(i \neq j)$. In the $\boldsymbol{\xi} \equiv \boldsymbol{r}' - \boldsymbol{r}''$ space, a surface of constant $\tilde{\rho}_1$ (for small ξ) is an ellipsoid whose axes are proportional to $1/\sqrt{P_{xx}}$, $1/\sqrt{P_{yy}}$, and $1/\sqrt{P_{zz}}$. When all of these are equal, as is the case for large z, the surface is a sphere. However near the wall the surface is flattened for the Dirichlet case, while for the Neumann case it is an ellipsoid with its long axis perpendicular to the wall – that is, stretched toward the wall.

Note that the local energy density $mn_1 \epsilon^k$ is related to P_{ij} according to (1.93) and (1.95):

$$mn_1 \epsilon^k = \tfrac{1}{2}(P_{xx} + P_{yy} + P_{zz}) = P_{xx}(z) + p/2 \,, \tag{5.20}$$

and evidently varies near the wall according to the behavior of $P_{xx}(z)$. It is always positive and approaches the bulk value $\frac{3}{2}p$ far from the wall.

5.4. The two-particle distribution function

This also follows from ρ_1^{gr}. First of all the (canonical) density matrices can be found as in section 2, according to (2.41, 61, 71). When $\rho < \rho_{\mathrm{c}}$, the density matrices are symmetrized products of the ρ_1^{gr}, and in particular taking the diagonal element $\boldsymbol{r}_1' = \boldsymbol{r}_1''$, $\boldsymbol{r}_2' = \boldsymbol{r}_2''$ of ρ_2 one gets the two-particle distribution function:

$$n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = n_1(z_1) n_1(z_2) + [\rho_1(\boldsymbol{r}_1, \boldsymbol{r}_2)]^2 \tag{5.21}$$

for all boundary conditions, using the appropriate expressions for $n_1(z)$ and ρ_1. Transforming to the coordinates $\boldsymbol{r} \equiv (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2$, $\boldsymbol{\xi} = \boldsymbol{r}_1 - \boldsymbol{r}_2$ and expanding to lowest order in $\boldsymbol{\xi}$ for a fixed $\boldsymbol{r}$, one gets

$$n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) \simeq (n_1(z))^2 + (F(\xi, \alpha, T) + F(2z, \alpha, T))^2 \,. \tag{5.22}$$

This exhibits clearly the departure from the bulk behavior $\rho^2 + F(\xi, \alpha, T)^2$ for finite z.

In the condensed region (5.21) also holds, with the appropriate n_1 and ρ_1, except for the case of Neumann boundary conditions where the constant $(\rho - \rho_{\mathrm{c}})^2$ must be subtracted. Essentially the behavior is like in the one phase region.

Concluding remarks

This survey of the properties of the IBG does not pretend to be in any sense complete. We will list here a number of topics which have attracted attention recently and which need we believe further clarification.

a) The two dimensional film of an IBG of thickness D. The interest lies in the question how the transition from two to three dimensions occurs as D increases from zero to infinity, and especially how the condensed phase and the ODLRO develops when $D \to \infty$. Because of the paradigmatic quality of the IBG this may throw light on the question when a liquid He II film becomes superfluid. For a flat IBG film one can discuss the thermodynamic properties in a way similar to the treatment in section 3 for a finite box. (In fact, there is a direct relation to the properties in a *one* dimensional segment.) Many aspects of the film have been studied in detail, especially by Greenspoon and Pathria [29–31] and Barber and Fisher [64] (whose motivation was also to determine the scaling of the critical exponents of a finite system). But so far the local properties and the density matrices have not been discussed in detail.

There is a peculiarity of this system with regard to the bulk limit which should be mentioned. When $D \to \infty$ the bulk thermodynamical properties are obtained, but the density matrices differ from the bulk ones: there is never any ODLRO in the lateral direction, and also the large fluctuations in the grand canonical ensemble never develop. This is a result of the double limiting process, since first the lateral extent of the film is made infinite, and then $D \to \infty$. For each finite D the volume and number is infinite, there is no phase transition, and the ensembles are identical. To find the asymptotic properties of large but finite systems (in all dimensions), i.e. physical systems, it seems more appropriate to take the limit D and $L \to \infty$ all at once (L being the lateral extent of the film), equivalent to the bulk limit of section 2.

b) A half infinite IBG in an outside constant gravitational field. This has attracted attention (Nordsieck and Lamb [89], Widom [90], Becker [91], and Uhlenbeck [92]) because of the question whether for a strong field the condensed phase will appear somehow at the bottom of the vessel, and how the hydrostatic equilibrium is maintained. In fact one finds that there is no separation of the phases although most of the condensed particles stay within the short distance $(\hbar^2/m^2g)^{1/3}$ of the bottom (where there must be a hard wall boundary) and are held up by the zero point motion or the quantum pressure, while the non-condensed particles extend over the characteristic length kT/mg and are held up by the hydrodynamical pressure. A precise discussion requires the elucidation of the notion of local equilibrium and the calculation of the density matrices, the distribution functions, and the stress tensor. A similar system that can be studied is an IBG in a "harmonic oscillator" external field $V = m\omega^2 z^2/2$ in one dimension and free in the other two [‡]. The advantage is that with known identities of the Hermite polynomials the density matrices in the finite system can be written explicitly. But in either case, because the extent of the fields is infinite, there is a difficulty in the *concept* of the infinite volume limit which in our opinion needs further examination. Intriguing is the question in which sense one still can speak of the ODLRO.

c) An IBG in a rotating vessel. This was first considered by Blatt and Butler [94]. The special interest lies in the fact that there are cirtical angular velocities ω_1, ω_2,... which can be interpreted as due to the appearance of a quantized vortex at the center of the bucket with vorticity $\hbar/m$, $2\hbar/m$,... as pointed out by Putterman, Kac and Uhlenbeck [95]. This shows that the condensate has some superfluid properties. As in the case of the external fields there is a problem of the definition of the bulk limit. Again a more thorough discussion is needed, making use of the density matrices (which have been given by Putterman [19]) and also for finite buckets and finally non-cylindrical vessels.

[‡] The IBG in a *three* dimensional harmonic oscillator "vessel" has been studied by de Groot, Hooyman and ten Seldam [93].

d) The approach to the canonical equilibrium state of the IBG. This is a completely open problem! As we mentioned in the introduction it requires some kind of interaction between the particles which may be in some sense very small, as for instance a hard sphere repulsion with a small radius $a \ll \lambda$ and $\ll n^{-1/3}$. In the one phase region and especially close to the classical limit it is possible to discuss the approach to the Bose distribution by the Uehling–Uhlenbeck equation, which is a generalization of the Boltzmann equation. This fails however in the condensed region. Putterman [19] has tried to adapt the notion of local equilibrium as used in the Chapman–Enskog theory of a classical gas to the IBG. In this way he obtains a version of the two-fluid equations of Landau, just as in the classical theory one obtains the Euler hydrodynamical equations. It remains to be seen whether these interesting ideas can be substantiated.

Note added in proof: It has come to our attention that the function $C_Z(\omega_1 \ldots \omega_d)$ introduced on p. 221, along with more general forms of Riemann's zeta function, has been exhaustively treated by Epstein [96]. Especially the representation (3.23), which is derived in Appendix 3.B, is also contained in his work.

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