

Chapter 2

Strong Correlations and Equation of State of Dense Gases

We summarize the physics and the statistical theory of strongly coupled gases. Starting from the binary correlation functions, we develop systematic expansions with respect to the density, the so-called virial expansions, and also fugacity expansions. Further, we discuss solutions of integral equations (PY and HNC) for dense systems. Quantum effects are treated by the methods of Slater and Beth–Uhlenbeck. Finally, we discuss strongly correlated Fermi–Dirac and Bose–Einstein gases, and Yukawa fluids.

2.1 Classical Molecular Distribution Functions and Density Expansions

2.1.1 Distribution Functions and Ornstein–Zernike Relations

From the classical kinetic theory of gases, we know the equation of state of ideal gases $\beta p = n$ (see Chap. 1). For real gases, the interaction forces lead to corrections to the ideal gas equation of state. We mention the classical theory of van der Waals and the systematic expansions with respect to the density, the so-called virial expansions with respect to density (Hirschfelder et al. 1954). We also mention fugacity expansions, solutions of integral equations and perturbation theories (Barker and Henderson 1967; Croxson 2009; Friedman 1962; Henderson 2009; Ross 1986).

The easiest way to get thermodynamic functions including interaction effects starts from the binary correlation functions. We already pointed out in Chap. 1 that the basic tool of fluid physics is connected with the concept of molecular distribution functions. We define pair distribution functions $g(r)$ for a fluid of average density

n by writing the number of particles in a shell of thickness dr at distance r from a selected particle in the form

$$ng(r)(4\pi r^2)dr . \quad (2.1)$$

Unfortunately, this notation is not unique. Like the French physicist Yvon a decade earlier, Bogoliubov and shortly afterwards also Born, Green, and Kirkwood considered the pair distribution function as the special case of a hierarchy of molecular distribution functions F_s with $s = 1, 2, 3, \dots$, for $s = 2$ (in Bogoliubov's notation). Hence, Bogoliubov denoted the pair distribution by $F_2(r)$. We will use both notations parallel depending on the context.

For two particles of species a and b at locations 1 and 2, the pair distribution is denoted by $F_{ab}(1, 2)$. The pair function converges for uniform systems to unity at large distances where there are no longer any correlations. In the radially symmetric case, we define the correlation function by

$$h(r) = g(r) - 1 = F_2(r) - 1 . \quad (2.2)$$

When there is no radial symmetry, we use a different notation for the function, describing the *total correlation* between molecules 1 and 2 by $h(\mathbf{r}_{12}) = g(\mathbf{r}_{12}) - 1$, which is a measure of the influence of molecule 1 on molecule 2 at a distance $\mathbf{r}_{12}$, with $g(\mathbf{r}_{12})$ the so-called radial distribution function.

An important branch of fluid physics starts with an integral equation introduced by Leonard Ornstein and Frits Zernike in 1914. In statistical mechanics, the Ornstein–Zernike equation is an integral equation defining the so-called *direct correlation function*. It is in fact just another tool for describing the correlation between two molecules, which Ornstein and Zernike proposed to split into two contributions, a direct and an indirect part. The direct contribution is denoted by $c(r_{12})$. The indirect contribution is due to the influence of molecule 1 on a third molecule, labeled 3, which in turn affects molecule 2, directly and indirectly. This indirect effect is weighted by the density and averaged over all possible positions of the particles 3 in the neighborhood.

This decomposition is formulated by

$$h(r_{12}) = c(r_{12}) + \rho \int d\mathbf{r}_3 c(r_{13})h(r_{23}) . \quad (2.3)$$

In the following, we will introduce several integral equations based on additional closure relations between $h(r_{12})$ and $c(r_{12})$. These will be useful for calculating the properties of dense fluids. The mean potential energy is related to the pair correlation function by

$$U_{\text{pot}} = \langle U \rangle = \frac{1}{2}n^2 \int d\mathbf{1} d\mathbf{2} U(12)F_2(12) . \quad (2.4)$$

Another simple relation connecting thermodynamics with the pair function is the *virial formula for the pressure*, valid for simple fluids with radially symmetric potentials:

$$\beta p = n + \frac{2\pi}{3} n^2 \int_0^\infty dr r^3 \frac{dU(r)}{dr} F_2(r) . \quad (2.5)$$

In the simplest possible way, we may approximate the pair function by a Boltzmann factor, whence the mean potential energy becomes

$$U_{\text{pot}} = \langle V \rangle = \frac{1}{2} n^2 \int d1 d2 U(12) \exp[-\beta V(1, 2)] . \quad (2.6)$$

Since the internal energy U and the free energy F are connected by the thermodynamic relation $U = \partial(\beta F)/\partial\beta$, the second virial coefficient is given by integration as

$$B_2^{\text{cl}} = \frac{1}{2} \int d\mathbf{r} \left\{ \exp[-\beta U(\mathbf{r})] - 1 \right\} . \quad (2.7)$$

Bogoliubov–Born–Green–Kirkwood–Yvon Hierarchy

In the 1930s and 1940s, a number of authors, namely, Bogoliubov, Born, Green, Kirkwood, and Yvon, developed a very fruitful method, based on a hierarchy of equations for molecular distribution functions called the BBGKY hierarchy. The authors are not listed chronologically here, but alphabetically. As far as we know, the French physicist Yvon was the first to use this method. We follow here mainly the rather clear and exhaustive work published in 1946 by N.N. Bogoliubov, since it was given in both a classical and a quantum-statistical version (see Bogoliubov 2005–2009).

We start from the classical N -particle density in configuration space, viz.,

$$\rho_N(q_1, \dots, q_N) = \frac{1}{Q_{N,\text{int}}} \exp[-\beta U_N(q_1, \dots, q_N)] . \quad (2.8)$$

We define a series of distribution functions by

$$\begin{aligned} F_s(1, \dots, s) &= V^s \rho_s(1, \dots, s) \\ &= V^s \int d(s+1), \dots, dN \rho_N(1, \dots, N) . \end{aligned} \quad (2.9)$$

For a gas mixture of species $a, b, c, \dots$, the pair distributions F_{ab} and the mean potential energy are given in the classical case by

$$\begin{aligned} F_{ab}(1, 2) &= \exp[-\beta U_{ab}(1, 2)] , \\ U_{\text{pot}} &= \frac{1}{2} \sum_{ab} n_a n_b \int d1 d2 U_{ab}(12) \exp(-\beta U_{ab}) . \end{aligned}$$

For the higher virial coefficients, we may derive corresponding expressions (Bogoliubov 2005–2009; Hirschfelder et al. 1954). The pair correlation functions are only a special case of the set of molecular distribution functions.

2.1.2 Virial Expansions

Since the internal energy U and the free energy F are connected by the thermodynamic relation $U = \partial(\beta F)/\partial\beta$, the free energy is given by integration as

$$F(T, V, N) = F_{\text{id}} + F_{\text{int}} = Nk_{\text{B}}T \left[\ln(n\Lambda^3) - 1 \right] - k_{\text{B}}TV \left[n^2 B_2^{\text{cl}}(T) + n^3 B_3^{\text{cl}}(T) + \dots \right], \quad (2.10)$$

and for the second virial coefficient

$$B_2^{\text{cl}} = \frac{1}{2} \int d\mathbf{r} \left\{ \exp[-\beta V(\mathbf{r})] - 1 \right\}. \quad (2.11)$$

By differentiating with respect to the volume V , i.e., $p = -\partial F/\partial V$, we obtain the equation of state

$$\beta p = -\beta \left(\frac{\partial F}{\partial V} \right)_{T,N} = n \left[1 - n B_2^{\text{cl}}(T) - 2n^2 B_3^{\text{cl}}(T) - \dots \right]. \quad (2.12)$$

2.2 Integral Equation Methods and Prototype Hard Sphere Systems

2.2.1 Percus–Yevick and Hypernetted-Chain Equations

The hard-sphere model for molecular interactions is a rather crude approximation, but it is quite useful as a limiting case (Croxston 2009). The interactions are defined by

$$U(r) = \begin{cases} 0, & r > d, \\ \infty, & r < d. \end{cases} \quad (2.13)$$

We now formulate the PY equation for this system, starting from the Ornstein–Zernike equation. Defining the displacement vector between two molecules to be $\mathbf{r}_{ij} := \mathbf{r}_i - \mathbf{r}_j$, for $i, j = 1, 2, 3, \dots$, the OZ equation can be rewritten using a convolution:

$$\begin{aligned} h(\mathbf{r}_{12}) &= c(\mathbf{r}_{12}) + \rho \int d\mathbf{r}_3 c(\mathbf{r}_{12} - \mathbf{r}_{32}) h(-\mathbf{r}_{32}) \\ &= c(\mathbf{r}_{12}) + \rho \int d\mathbf{r}_{32} c(\mathbf{r}_{12} - \mathbf{r}_{32}) h(\mathbf{r}_{32}) \\ &= c(\mathbf{r}_{12}) + \rho (c * h)(\mathbf{r}_{12}), \end{aligned} \quad (2.14)$$

where $\rho = N/V$ is the number density of molecules. If we then denote the Fourier transforms of $h(\mathbf{r})$ and $c(\mathbf{r})$ by $\hat{H}(\mathbf{k})$ and $\hat{C}(\mathbf{k})$, respectively, and use the convolution theorem, we obtain

$$\hat{H}(\mathbf{k}) = \hat{C}(\mathbf{k}) + \rho \hat{H}(\mathbf{k}) \hat{C}(\mathbf{k}) , \quad (2.15)$$

which yields

$$\hat{C}(\mathbf{k}) = \frac{\hat{H}(\mathbf{k})}{1 + \rho \hat{H}(\mathbf{k})} , \quad \hat{H}(\mathbf{k}) = \frac{\hat{C}(\mathbf{k})}{1 - \rho \hat{C}(\mathbf{k})} . \quad (2.16)$$

One needs to solve for both $h(r)$ and $c(r)$ (or, equivalently, their Fourier transforms). This requires an additional equation, known as a closure relation. The Ornstein–Zernike equation can be seen formally as a definition of the direct correlation function $c(r)$ in terms of the usual correlation function. We may approximate $c(r)$ by

$$c(r) = e^{-\beta w(r)} - e^{-\beta[w(r)-u(r)]} . \quad (2.17)$$

Introducing the function $y(r) = e^{\beta u(r)} g(r)$ into the approximation for $c(r)$, one obtains

$$c(r) = g(r) - y(r) = e^{-\beta u} y(r) - y(r) = f(r) y(r) . \quad (2.18)$$

This is the essence of the Percus–Yevick approximation. If we substitute this result into the Ornstein–Zernike equation, we obtain the Percus–Yevick equation:

$$y(r_{12}) = 1 + \rho \int f(r_{13}) y(r_{13}) h(r_{23}) d\mathbf{r}_3 . \quad (2.19)$$

The approximation was made by Percus and Yevick 1958. For hard spheres, the PY equation has an analytical solution (Henderson 2009).

The hypernetted-chain equation follows from a closure relation to solve the Ornstein–Zernike equation which relates the direct correlation function to the total correlation function. It is commonly used in fluid theory to obtain, e.g., expressions for the radial distribution function. It is given by

$$\begin{aligned} \ln y(r_{12}) &= \ln g(r_{12}) + \beta u(r_{12}) \\ &= \rho \int [h(r_{13}) - \ln g(r_{13}) - \beta u(r_{13})] h(r_{23}) d\mathbf{r}_3 . \end{aligned} \quad (2.20)$$

In the following step we approximate $c(r)$ by w using (2.17). By expanding the indirect part of $g(r)$ in the above equation and introducing the function $y(r) = e^{\beta u(r)} g(r)$, we can approximate $c(r)$ by writing

$$\begin{aligned} c(r) &= e^{-\beta w(r)} - 1 + \beta[w(r) - u(r)] = g(r) - 1 - \ln y(r) \\ &= f(r) y(r) + [y(r) - 1 - \ln y(r)] , \quad f(r) = e^{-\beta u(r)} - 1 . \end{aligned} \quad (2.21)$$

This is the essence of the hypernetted-chain equation. Equivalently, we may write

$$h(r) - c(r) = g(r) - 1 - c(r) = \ln y(r) . \quad (2.22)$$

If we substitute this result into the Ornstein–Zernike equation we obtain the hypernetted-chain equation:

$$\begin{aligned} \ln y(r_{12}) &= \ln g(r_{12}) + \beta u(r_{12}) \\ &= \rho \int [h(r_{13}) - \ln g(r_{13}) - \beta u(r_{13})] h(r_{23}) d\mathbf{r}_3 . \end{aligned} \quad (2.23)$$

2.2.2 *Hard Core Fluids and Fluid Mixtures*

All the electrons in atoms and molecules are subject to the Pauli principle, which stipulates that the same atomic state cannot be occupied by two electrons. As a consequence, other electrons are simply excluded and this appears like a hard core. In the zeroth approximation, atoms and molecules are like hard spheres with well defined radius. Consequently, in the zeroth approximation, dense fluids are like a mixture of hard spheres. For the hard sphere fluid, the correlation functions are known a priori in special distance regions, i.e., for physical reasons we have

$$F_2(r) = 0 , \quad h(r) = -1 , \quad \text{if } r < d . \quad (2.24)$$

With this expression for the binary distribution function, we find the classical second virial coefficient for hard-core potentials. Correspondingly, the EOS for hard sphere gases is

$$\beta p = n \left(1 + \frac{2}{3} \pi n a^3 + \dots \right) .$$

The Percus–Yevick approximation is obtained by completing this exact relation by the approximate relation

$$c(r) = 0 , \quad \text{if } r > d . \quad (2.25)$$

We note also the exact relation for the pressure which follows from (2.5)

$$\beta p = n + \frac{2\pi}{3} n^2 d^3 F_2(d+) . \quad (2.26)$$

In the history of the theory of fluids, much effort went into calculating the higher virial coefficients in the series

$$\beta p = n + \sum_{k=2}^{\infty} B_k n^k . \quad (2.27)$$

Hutchinson and Rushbrook calculated seven coefficients using the PY equation. Their result can be written in the form (see Croxston 2009)

$$B_k = \frac{8}{4^k} (k-4) \left(\frac{2\pi}{3} d^3 \right)^{k-1}. \quad (2.28)$$

Summing these expressions, we find for the pressure and contact value

$$\beta p = n \frac{1 + 2\eta + 3\eta^2}{(1 - \eta)^2}, \quad F_2(d+) = \frac{1 + \eta/2}{(1 - \eta)^2}. \quad (2.29)$$

In this approximation, the pressure may be integrated to give the Helmholtz free energy (Henderson 2009)

$$\beta F = \beta F_{\text{id}} + 2 \ln(1 - \eta) + \frac{6\eta}{1 - \eta}. \quad (2.30)$$

Note that exact solutions of the PY equations for hard spheres were also derived. The essential approximation is due to Wertheim, who assumed for the direct correlation function of hard spheres (Croxston 2009)

$$c(r) = \begin{cases} 0, & \text{if } r > d, \\ -\alpha - \beta(r/d) - \gamma(r/d)^2 - \delta(r/d)^3, & \text{if } r < d. \end{cases} \quad (2.31)$$

Explicit solutions based on these assumptions were given by Thiele and Wertheim using Laplace transforms, and by Baxter using Fourier transforms (Henderson 2009).

There exists also a very useful semi-empirical formula which is compatible with the PY solution, but fits the computer simulation data even better. This is the Carnahan–Starling approximation (Ross 1996):

$$\beta F = \beta F_{\text{id}} + \frac{4\eta - 3\eta^2}{(1 - \eta)^2}, \quad p = nk_{\text{B}}T \frac{1 + \eta + \eta^2 + \eta^3}{(1 - \eta)^3}. \quad (2.32)$$

Mixture Rules

Most real fluids are mixtures of several components, and the number of possible combinations is very large. This means that simple rules for calculating the properties of mixtures from those of the pure components are of importance for applications. The linear mixing model (Ross 1996) is a semi-empirical model for calculating thermodynamic functions of a binary system. The assumption is that the pressures p_i , the internal energies ε_i , and the free energies per particle of the two components are known. Defining the mole fractions of the components by

$$x = \frac{N_1}{N_1 + N_2}, \quad (1 - x) = \frac{N_2}{N_1 + N_2}, \quad (2.33)$$

the *linear mixing rule* assumes that the pressure and specific energy have mixing that is linear in the composition x , i.e.,

$$p = xp_1 + (1 - x)p_2, \quad E = xE_1 + (1 - x)E_2. \quad (2.34)$$

For the free energy per particle, we assume the following functional of the composition x :

$$\phi(n, T; x) = x\phi_{\text{pl}} + (1 - x)\phi_{\text{nl}} + 2x \log \frac{2x}{1 + x} + (1 - x) \log \frac{1 - x}{1 + x}. \quad (2.35)$$

Here the last term represents a kind of mixing entropy. The linear mixing functional has a rather simple structure. When the composition is free and chosen by the system by adapting the free energy, we find the actual composition by looking for the minimum corresponding to the composition denoted by γ .

A special mixture of great interest for later studies of partially ionized plasma is the mixture of neutral spheres of density n_0 with diameter d and packing parameter $\eta = \pi d^3 n_0 / 6$ and point charges with density n_1 . These point charges may be considered as a kind of classical neutral ‘electrons’ with radius zero. We assume that the point charges behave like a classical ideal gas, but they are not allowed to penetrate into the interior of the neutral spheres:

$$\beta F = \beta F_{\text{id}} + V n_0 \frac{4\eta - 3\eta^2}{(1 - \eta)^2} - n_1 \ln(1 - \eta). \quad (2.36)$$

The last contribution to the free energy is called the *excluded volume contribution*. It plays an important role for dense plasmas. The presence of point particles in a hard-sphere system greatly increases the free energy, and many point particles may even destroy the hard-sphere subsystem (Ebeling et al. 1976, 2012).

2.3 Quantum Effects

2.3.1 Bose–Einstein and Fermi–Dirac Gases

Virial expansions were originally developed for the classical case, but the same expansion with modified coefficients works for the quantum case. The extension of this classical formula to the quantum case was first given by Uhlenbeck and Beth (1936). Note that, in the classical case, the first term in the expansion is the ideal Boltzmann contribution, but in the quantum case, one has the Fermi–Dirac or Bose–Einstein expressions given in Chap. 3. We see that interactions are not the only source of deviations from the ideal term, i.e., deviations from the simple law $\beta p = n$. Quantum effects also contribute to the virial coefficients. The classical ideal gas law $\beta p = n$ is not valid for quantum gases. We have to distinguish between Bose gases

and Fermi gases. For a *Fermi–Dirac gas*:

$$\beta p = (2s + 1)\Lambda^{-3} f_{5/2}(z) . \quad (2.37)$$

For a *Bose–Einstein gas*:

$$\beta p = \frac{2s + 1}{V} \ln(1 - z) + (2s + 1)\Lambda^{-3} g_{5/2}(z) . \quad (2.38)$$

Here z is the fugacity, related to the density by the relation $n = z\partial(\beta p)/\partial z$. For small densities, we may expand. In the first approximation, we find

$$\beta p = n \left[1 \pm \frac{1}{2^{5/2}} \left(\frac{n\Lambda^3}{2s + 1} \right) + O(n^2) \right] , \quad (2.39)$$

where the upper sign is valid for fermions and the lower sign for bosons. The parameter in the expansion is $n\Lambda^3$. We define $n\Lambda^3 = 1$ as the degeneracy line. On a log-scale we get the line $\log n = (3/2) \log T + \text{const.}$

2.3.2 Density Expansions Including Interaction Effects

The easiest way to get the virial functions including interaction effects starts from the binary correlation functions F_{ab} . In the first classical approximation, the binary correlations are given by a Boltzmann factor and lead to the first order mean potential energy given above. Furthermore, for the second virial coefficient, we find

$$B_2^{\text{cl}} = \frac{1}{2} \int d\mathbf{r} \left\{ \exp[-\beta V(\mathbf{r})] - 1 \right\} . \quad (2.40)$$

For the higher virial coefficients we may derive corresponding expressions (Bogoliubov 2005–2009; Hirschfelder et al. 1954).

In the quantum case, a few changes are needed. The mean potential energy is given by a trace

$$U = \langle V \rangle = \frac{1}{2} \sum_{ab} \text{Tr}[V_{ab}(12)F_{ab}(1, 2)] . \quad (2.41)$$

An easy way to proceed is to use the coordinate representations. The pair probability given classically by a Boltzmann factor is replaced by its quantum-statistical counterpart, the Slater sum of pairs introduced in Chap. 4. In this way, as shown by Beth and Uhlenbeck, the classical expressions remain valid if we just replace the Boltzmann factor by binary Slater sums (Beth and Uhlenbeck 1937; Uhlenbeck and Beth 1936):

$$\exp[-\beta V(\mathbf{r})] \longrightarrow S_2(\mathbf{r}) = C \sum_n \exp[-\beta E_n] \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}) \phi_n(\mathbf{r}) . \quad (2.42)$$

Beth and Uhlenbeck (1937) derived other useful representations. In particular, they studied the role of bound and scattering states and introduced phase shifts.

General Density Expansions

For a more general derivation of virial expansions for gases, we start from the free energy of an N -particle system:

$$\begin{aligned} F(T, V, N) &= -k_B T \ln Q_N(T, V) , \\ Q_N(T, V) &= \text{Trace}_{(1, \dots, N)} [\exp(-\beta \hat{H}_N)] . \end{aligned} \quad (2.43)$$

Using representations in terms of Slater functions (or Slater sums), the quantum-statistical problem may be mapped to a classical form. We use the decomposition

$$Q_N(T, V) = Q_{N, \text{id}} \cdot Q_{N, \text{int}} , \quad Q_{N, \text{id}} = \frac{(2s+1)^N V^N}{N! \Lambda^{3N}} , \quad (2.44)$$

where the ideal part is defined by classical Boltzmann statistics. For the free energy, using Stirling's formula $\ln N! = (N \ln N - N)$, we obtain the representation

$$\begin{aligned} F(T, V, N) &= F_{\text{id}} - k_B T \ln Q_{N, \text{int}} = N k_B T \left[\ln \left(\frac{n \Lambda^3}{2s+1} \right) - 1 \right] \\ &- k_B T \ln \left[\frac{N! \Lambda^{3N}}{(2s+1)^N V^N} \right] \sum_{\sigma_1, \dots, \sigma_N} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \langle \dots | \exp(-\beta \hat{H}_N) | \dots \rangle . \end{aligned}$$

This representation of the free energy already has a classical form and may be treated, e.g., by the well known technique of Mayer expansions (Friedman 1962). Following this route, as proposed by Slater (1939) and Morita (1959), we now introduce the so-called Slater sums or Slater functions.

The N -particle Slater sums are defined by

$$S^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{N! \Lambda^{3N}}{(2s+1)^N} \sum_{\sigma_1, \dots, \sigma_N} \langle \dots | \exp(-\beta \hat{H}_N) | \dots \rangle . \quad (2.45)$$

At small densities we may use a pair approximation

$$S^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \prod_{i < j}^N S^{(2)}(\mathbf{r}_i, \mathbf{r}_j) , \quad (2.46)$$

where, by definition,

$$S^{(2)}(\mathbf{r}_i, \mathbf{r}_j) = \frac{2!\lambda^6}{(2s+1)^2} \sum_{\sigma_1\sigma_2} \langle \mathbf{r}_1\mathbf{r}_2 | \exp(-\beta\hat{H}_2) | \mathbf{r}_1\mathbf{r}_2 \rangle. \quad (2.47)$$

The quantum statistical partition function corresponds directly to the classical form, so the quantum-statistical second virial coefficient is represented by

$$B_2^{qm}(T) = \frac{1}{2V} \int d\mathbf{r}_1 d\mathbf{r}_2 [S^{(2)}(\mathbf{r}_i, \mathbf{r}_j) - 1]. \quad (2.48)$$

For a gas mixture, the expansions for the free energy and the EOS read

$$\begin{aligned} F(T, V, N) &= F_{\text{id}} - k_B T V \left[\sum_{ab} n_a n_b B_{ab}(T) + \sum_{abc} n_a n_b n_c B_{abc}(T) + \dots \right], \\ \beta p &= -\beta \left(\frac{\partial F}{\partial V} \right)_{T,N} = \sum_a n_a \left(1 - \sum_b n_b B_{ab} - 2 \sum_{bc} n_b n_c B_{abc} - \dots \right), \end{aligned} \quad (2.49)$$

where the virial coefficients are expressed by 2-particle and 3-particle Slater functions, etc.

2.4 Pair Correlations and Beth–Uhlenbeck Method

2.4.1 Slater Sums for Pairs and Second Virial Coefficient

In order to calculate the binary Slater sum for two particles of different species a and b and spins s_a and s_b , we write

$$\begin{aligned} S_{ab}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= (1 + \delta_{ab})! \frac{\Lambda_a^3 \Lambda_b^3}{(2s_a + 1)(2s_b + 1)} \\ &\quad \times \sum_{\sigma_1, \sigma_2} \langle \mathbf{r}_1\mathbf{r}_2\sigma_1\sigma_2 | \exp(-\beta\hat{H}_{ab}) | \mathbf{r}_1\mathbf{r}_2\sigma_1\sigma_2 \rangle. \end{aligned} \quad (2.50)$$

Using the properties of energy eigenfunctions and the definitions

$$\lambda_{ab} = \frac{\hbar}{\sqrt{2m_{ab}k_B T}}, \quad m_{ab} = \frac{m_a m_b}{m_a + m_b}, \quad (2.51)$$

we get the final result

$$S_{ab}^{(2)}(r) = 2\pi^{1/2}\lambda_{ab}^3 \left\{ \sum_{l=0}^{\infty} (2l+1) \left[\sum_{s=1}^{l-1} \exp(-\beta E_{sl}) |R_{sl}(r)|^2 \right] + \int dk \exp\left(-\frac{\beta \hbar^2 k^2}{2m_{ab}}\right) |R_{kl}(r)|^2 \frac{dn_l(k)}{dk} \right\}. \quad (2.52)$$

Here we have introduced the density of states $dn_\ell(k)/dk$, which gives the number of states with quantum number ℓ in the interval dk (Beth and Uhlenbeck 1937; Huang 1987; Uhlenbeck and Beth 1936, 2001). Taking symmetry into account, we find the Slater sum with exchange effects:

$$S_{ab}^{(2)}(\mathbf{r}) = (1 + \delta_{ab})! 2\sqrt{\pi}\lambda_{ab}^3 \sum_{l=0}^{\infty} (2l+1) \left[1 \pm \delta_{ab} \frac{(-1)^l}{(2s_a+1)} \right] \times \left[\sum_{s=l+1}^{\infty} e^{-\beta E_{sl}} |R_{sl}(r)|^2 \int_0^{\infty} dk e^{-\lambda_{ab}^2 k^2} \frac{dn_l(k)}{dk} \right] |R_{kl}(r)|^2.$$

Second Virial Coefficient

The second virial coefficient can be expressed by the binary Slater function or Slater sum, as shown in the last section. Using the normalization of the wave functions, we get (Beth and Uhlenbeck 1937; Uhlenbeck and Beth 1936)

$$B_{ab}(T) = (1 + \delta_{ab})! 4\pi^{3/2}\lambda_{ab}^3 \sum_{l=0}^{\infty} (2l+1) \left[1 \pm \frac{(-1)^l}{(2s_a+1)} \right] \times \left\{ \sum_{s=l+1}^{\infty} e^{-\beta E_{sl}} + \int_0^{\infty} dk e^{-\lambda_{ab}^2 k^2} \left[\frac{dn_l(k)}{dk} - \frac{dn_l(k)^0}{dk} \right] \right\}. \quad (2.53)$$

Once again, we have the density of states of pairs $n_\ell(k)$ and the corresponding density $n_\ell(k)^0$ for the noninteracting system, which corresponds to the -1 in the virial formula.

A different and sometimes more convenient way of writing the second virial coefficient may be obtained from a relation between scattering phase shifts and Jost functions (Ebeling et al. 1976; Kraeft et al. 1969; Kremp et al. 1971). We can express the second virial coefficient in terms of the two-particle trace and then use the resolvent representation

$$B_{ab}(T) = \text{const.} \times \text{Tr} \left[\exp(-\beta H_{ab}) - \exp(-\beta H_{ab}^0) \right] \\ = \text{const.} \times \frac{1}{2\pi i} \int_c \exp(-\beta z) \text{Tr} \left(\frac{1}{H_{ab} - z} - \frac{1}{H_{ab}^0 - z} \right). \quad (2.54)$$

In this way we arrive at a representation of the second virial coefficient by a complex integral along a path enclosing the real axis:

$$B_{ab} = \frac{4\pi^{3/2}(1 + \delta_{ab})\lambda_{ab}^3}{(2s_a + 1)(2s_b + 1)} \frac{1}{2\pi i} \int_c \exp(-\beta z) F(z) dz ,$$

$$F(z) = \text{Tr} \left(\frac{1}{H_{ab} - z} - \frac{1}{H_{ab}^0 - z} \right) . \quad (2.55)$$

After some transformations, we arrive at the following complex representation in terms of Jost functions $D_\ell(z)$. To our knowledge this was first obtained in independent work by Kraeft et al. (1969) and Kano and Mishima (1969). The Jost functions $D_\ell(z)$ are analytical functions, well known from scattering theory, with poles at the bound states and a branch cut at the positive real axis defined by the scattering phase shifts. These functions, like other scattering quantities, are exactly known, e.g., for Coulomb systems, and will appear in later calculations. When the attractive well of the interatomic forces is deep enough for bound states to form, the contribution from scattering states may be neglected, at least at low temperatures. Specific problems connected with bound state contributions will be treated later.

2.4.2 Beth–Uhlenbeck Representation for Real Gases

In many cases the attractive van der Waals forces between atoms or molecules in a gas are so weak that the formation of bound states is not possible. As known from quantum mechanics, only deep wells may form bound states. A common example for weak attractive forces are the noble gases. In this case the second virial coefficient contains only scattering contributions. At temperatures below 100 K, classical calculations do not work and we need quantum-statistical calculations based on the density of states (Kilpatrick et al. 1954; Kraeft et al. 1969, 1986; Costa et al. 2013).

In order to find the density of states, we have to analyze the asymptotic of the radial wave functions. For large r , we have

$$\lim_{r \rightarrow \infty} R_{sl}(r) = \frac{\sqrt{2/\pi}}{r} \sin \left[kr - \frac{\pi}{2}l + \delta_l(k) \right] , \quad (2.56)$$

where $\delta_l(k)$ are the scattering phase shifts. Enclosing the system in a sphere with radius R , assuming $R_{sl}(r \geq R) = 0$, the following relation holds:

$$kR - \frac{\pi}{2}l + \delta_l(k) = n_l(k)\pi , \quad n_l(k) = 0, \pm 1, \pm 2, \dots . \quad (2.57)$$

Using the same relation for free particles, we find

$$n_l(k) - n_l^0(k) = \frac{1}{\pi} \delta_l(k) . \quad (2.58)$$

To calculate the second virial coefficient, we need the phase, and we usually have to do numerical calculations (Kilpatrick et al. 1954; Costa et al. 2013). For a few cases such as a hard-sphere, square-well potentials, and Coulomb potentials, exact analytical expressions are available (Beth and Uhlenbeck 1937; Kraeft et al. 1970). The numerical calculation of the phase shifts $\delta_\ell(k)$ requires a precise numerical integration of the radial Schrödinger equation for the case of large distances. Comparing the result with the asymptotic solution

$$\psi_\ell(r) = A \sin \left(kr - \frac{l\pi}{2} + \delta_\ell \right), \quad (2.59)$$

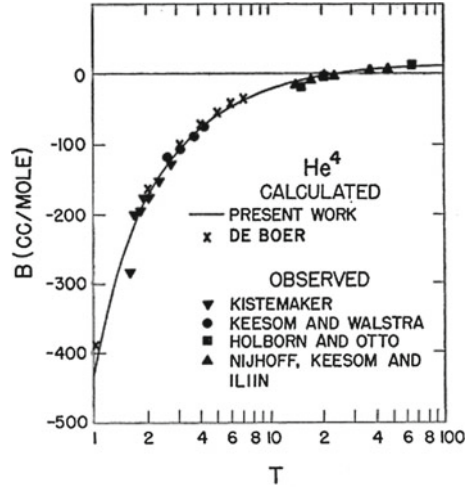
we find the phase shifts as a function of k and l . For example, for He–He interactions the phase shifts with $\ell = 0, 1, 2, 3, 4, \dots$, have been calculated by Kilpatrick et al. (1954). After calculating the phase shifts for the given interaction potential in analytical or numerical form, the virial coefficient may be calculated as a function of temperature (Costa et al. 2013).

At higher temperatures the properties of gases are only weakly influenced by the spins. This is different at lower temperatures, say $T < 100$ K, where the spins of the atoms (or molecules) forming the gas play an essential role. Note that H atoms with spin $s = 0$ and He-4 atoms with spin $s = 1$ are bosons, in contrast to He-3 atoms, which have $s = 1/2$ and are therefore fermions. This leads in particular to essential differences between the properties of the fermionic gas He-3 and the bosonic gas He-4. In an oft-cited paper by Kilpatrick et al. (1954), the second virial coefficients of He-3 and He-4 were calculated at closely spaced temperatures over the range 0.3–60 K using the Lennard-Jones 12-6 potential with parameters given by de Boer and Michels and based on a calculation of the phase shifts. Some results are shown in Fig. 2.1.

A more recent calculation of the virial expansions for He-4 in the region $3 < T < 100$ K was given, e.g., by Costa et al. (2013). According to this study, the ideal quantum term contributes approximately 11 percent at 3 K and less than 1 percent at 100 K. The He-4 diatomic molecule possesses a very weak bound state which contributes less than 0.1 percent at 3 K and much less at higher temperatures. Therefore this contribution may in general be neglected, even in comparison with the ideal Bose contribution.

For most rare gases, such as hard-sphere gases, the virial expansion converges well, since the virial terms decay quickly. In particular, this means we need conditions like $nB_2(T) \ll 1$, $n^2B_3(T) \ll 1$, and so on. For example, for a gas of spheres with diameter d , this gives the condition $nd^3 \ll 1$ or $d \ll n^{-1/3}$. In other words the effective diameter of particles d should be small in comparison to the average distance between particles in the gas. For most rare gases, this is a weak condition which is often satisfied. We have shown that He-4 is well described by the cluster representation, even down to a few degrees kelvin. In all these cases, the second virial coefficient is not too large and is dominated by the scattering contributions. However, there are physical conditions in which the contribution of the second virial coefficient is very large in comparison to the ideal contributions, and even increases

Fig. 2.1 Temperature dependence of the second virial coefficient of helium-4 in the range 1–100 K (Kilpatrick et al. 1954) in comparison with some experimental points



exponentially with the reciprocal temperature $\beta = 1/k_B T$. In this case we have to search for other representations of the pressure.

2.5 Representations in the Grand Canonical Ensemble

2.5.1 Fugacity Expansions

From the theory of ideal quantum gases, we know that the pressure may be represented in terms of the density, but also in terms of expansions with respect to the fugacity z . We shall now derive such fugacity expansions for arbitrary interacting gases. Following the pioneering work of Terrel L. Hill 1960, we will show that fugacity expansions are appropriate tools for gases with deep bound states, showing association and reaction effects (see also Ebeling 1974; Friedman and Ebeling 1979). In order to check the power of these expansions, which have been the appropriate tool since Hill's work, we recall the basic formulae for the grand canonical ensemble.

In this ensemble the basic independent quantity is the chemical potential or the fugacity $z = e^{\beta\mu}$, rather than the density. The density operator is given by

$$\hat{\rho} = \Xi^{-1} \exp \left(\beta \hat{N} \mu - \beta \hat{H}_N \right), \quad (2.60)$$

and the grand canonical partition function is

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} \text{Tr}_{\mathcal{H}_N} e^{-\beta \hat{H}_N}. \quad (2.61)$$

This is a kind of generalized trace, including an N summation, corresponding to a so-called Fock space.

The thermodynamic functions follow from

$$pV = -k_B T \ln \Xi, \quad \langle N \rangle = \frac{\partial}{\partial \mu} (pV) = \beta z \frac{\partial}{\partial z} (pV). \quad (2.62)$$

These formulae provide an expansion of the pressure and the densities with respect to the fugacities. Just for convenience we introduce a new quasi-density $\tilde{z} = \Lambda^{-3} z$, where Λ is again the thermal wavelength. Note that $\tilde{z}$ has the dimension of a density and converges for the classical case to the density n . (In the future we shall sometimes omit the tilde if the meaning is clear from the context.)

The virial function follows by expansion with respect to the quasi-density $\tilde{z}$, which is related to the former density expansion. The virial coefficients follow by comparison of coefficients on both sides of the series expansions. Using the expansion of the log-function, we find

$$\begin{aligned} \beta p = \frac{1}{V} \sum_{j=1}^{\infty} b_j \tilde{z}^j &= \frac{1}{V} \left(\tilde{Q}_1 \tilde{z} + \frac{1}{2!} \tilde{Q}_2 \tilde{z}^2 + \dots \right) \\ &- \frac{1}{2V} \left(\tilde{Q}_1 \tilde{z} + \frac{1}{2!} \tilde{Q}_2 \tilde{z}^2 + \dots \right)^2 + \frac{1}{3V} \left(\tilde{Q}_1 \tilde{z} + \frac{1}{2!} \tilde{Q}_2 \tilde{z}^2 + \dots \right)^3. \end{aligned} \quad (2.63)$$

Comparing the coefficients of equal powers $\tilde{z}^k$, we get

$$\begin{aligned} b_1 &= \frac{1}{V} \tilde{Q}_1, \quad b_2 = \frac{1}{2! V} (\tilde{Q}_2 - \tilde{Q}_1^2), \\ b_3 &= \frac{1}{3! V} (\tilde{Q}_3 - 3\tilde{Q}_1 \tilde{Q}_2 + 2\tilde{Q}_1^3). \end{aligned} \quad (2.64)$$

The general relations follow from Thiele's semi-invariants or equivalent methods of cumulant expansions. For the first terms in the series, we get

$$\beta p V = b_1 \tilde{z} + b_2 \tilde{z}^2 + b_3 \tilde{z}^3 + \dots, \quad (2.65)$$

$$n = \tilde{z} \frac{\partial(\beta p)}{\partial \tilde{z}} = b_1 \tilde{z} + 2b_2 \tilde{z}^2 + 3b_3 \tilde{z}^3 + \dots. \quad (2.66)$$

In principle, this virial expansion is equivalent to the density expansion. However, as we will show, the convergence may differ significantly from case to case. Explicitly, we find

$$b_1(T) = \frac{1}{V} \tilde{Q}_1 = \frac{\Lambda^3}{V} \text{Tr}_1(e^{-\beta \hat{H}_1}) = 1, \quad (2.67)$$

$$b_2(T) = \frac{1}{2V} (\tilde{Q}_2 - \tilde{Q}_1^2) = \frac{1}{V} \Lambda^6 \text{Tr}_{(12)} \left[e^{-\beta \hat{H}_2} - e^{-\beta \hat{H}_2^{(0)}} \right]. \quad (2.68)$$

Comparing with Sect. 5.2, it follows that

$$b_2(T) = B_2(T) . \quad (2.69)$$

For higher orders, the relations are more complicated (Ebeling 1974, 1976).

2.5.2 Fugacity Expansions and the Chemical Picture

From the theory of ideal quantum gases we already know that the pressure may be represented in terms of the density or in terms of expansions with respect to the fugacity z . In the last section we showed that we have these two possibilities for any gas. Let us look first at a hard core system.

Figure 2.2 compares the density expansion for the compressibility coefficient as a function of the dimensionless parameter $y = \pi n d^3/6$ with the Carnahan–Starling expression, which fits well with numerical MC and MD data for hard spheres. The agreement between a first order (second virial approximation) density expansion, viz.,

$$p/nk_B T = 1 + \frac{2}{3}(\pi n d^3) + \dots , \quad (2.70)$$

and the Carnahan–Starling approximation is rather good.

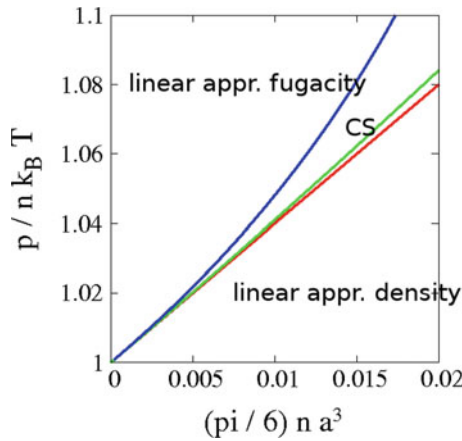


Fig. 2.2 Pressure in relation to ideal pressure for a classical gas of hard spheres. The result of a virial expansion with respect to density as a function of the characteristic hard sphere parameter $(\pi/6)na^3$ is compared with the result of a fugacity expansion. Both expansions are cut off after the second virial coefficients. The results are compared with the Carnahan–Starling formula which is in rather good agreement with the expansion linear in the density

Figure 2.2 also compares, in the second virial approximation, the fugacity expansion (upper curve) with the Carnahan–Starling formula, which is close to the exact EOS for hard sphere systems. As shown already in earlier work (Friedman and Ebeling 1979), we see that, up to $\pi n a^3/6 \sim 0.03$, a density expansion cut off after linear terms in the density is just a bit below the exact curve and describes the real hard-sphere gas quite well. On the other hand, the corresponding fugacity expansion provides too high a pressure and deviates significantly from the exact Carnahan–Starling curve.

Our conclusion is that, for systems with dominating repulsive forces, such as the hard sphere system, the density expansion is much ‘better’ than the fugacity expansion. Here ‘better’ only refers to fast convergence, since in principle the two expansions are equivalent.

In a second example, we consider systems with deep bound states, like a gas of hydrogen atoms which are able to form the bound state H_2 with a binding energy of about 4.7 eV. For systems with deep bound states, we have

$$B_2(T) \approx 8\pi^{3/2}\lambda^3 \sum_{sl} \exp(-E_{sl}/k_B T) . \quad (2.71)$$

When the ground state energy E_{10} has modulus larger than $k_B T$, the exponential function may give a very large contribution. For example, a typical binding energy is 0.1 eV, expressed in 10^3 kelvin. Then temperatures below room temperature may generate such large values of $B_2(T)$ that, in the virial series, the pressure becomes negative and the expansion is no longer physically meaningful.

Hydrogen Gas and the Chemical Picture

We now analyze a hydrogen gas as a simple model case of a gas where the fugacity expansion including only the second virial coefficient yields excellent results. We thus write

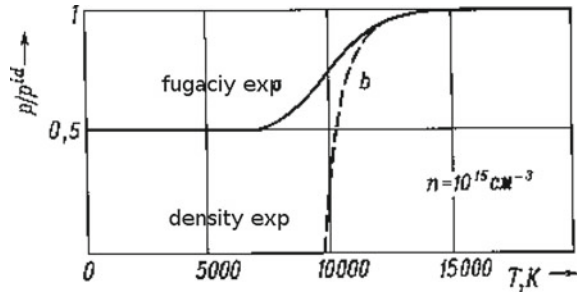
$$\beta p = \tilde{z} + B_2(T)\tilde{z}^2 , \quad n = \tilde{z} + 2B_2(T)\tilde{z}^2 . \quad (2.72)$$

We may consider (2.72) as an implicit EOS and exclude the fugacity by solving the quadratic equation $2B_2(T)\tilde{z}^2 + \tilde{z} - n = 0$. Taking the relevant solution, we thus get the pressure

$$\beta p = \frac{1}{2}n + \frac{1}{2}\tilde{z} = \frac{n}{2} + \frac{1}{8B_2(T)} \left(\sqrt{1 + 8nB_2} - 1 \right) . \quad (2.73)$$

This equation contains only the second virial coefficient. However, in comparison with the density expansion containing only second virial contributions, the new expression for the pressure can never assume negative values, even if $B_2(T)$ assumes very large values. This result suggests that fugacity expansions may be more appropriate for gases with deep bound states than density expansions (Hill 1960; Ebeling 1974, 1976; Friedman and Ebeling 1979).

Fig. 2.3 Pressure of hydrogen gas as a function of temperature, calculated from the fugacity expansion (curve *a*) and the density expansion (curve *b*). At lower temperatures the density expansion fails due to the exponential increase from bound state contributions



Let us study us an example an atomic hydrogen gas in the region where molecule formation plays a role. Assuming a bound state energy of molecules (dissociation energy) of $D = 4.7$ eV, we get for the second virial coefficient of the gas

$$B_H^{(2)}(T) \approx \frac{h^3}{\sqrt{2\pi m_H k_B T^3}} \exp\left(\frac{4.7 \text{ eV}}{T [\text{eV}]}\right). \quad (2.74)$$

Figure 2.3 shows the pressure as a function of temperature for a hydrogen gas. Continuous lines show the fugacity expansion and dashed lines the density expansion, including only the second virial coefficient. The curves we obtained show that the fugacity representation describes the physics of a hydrogen gas correctly. There are two limiting cases:

- At low temperatures with $p \rightarrow nk_B T/2$ for $T \rightarrow 0$, the ‘effective particle density’ is just 50% of the density at high temperatures. This is the region where molecules are formed. The number of hydrogen molecules H_2 per cm^3 is half of the total density of atoms.
- At high temperatures there are no molecules present and the ‘effective particle density’ is equal to the total density of atoms.

We see that the fugacity expansion gives a correct physical description of the equilibrium between atoms and molecules in the gas.

So far we have described the system without using any explicit chemical notation, just using physical terms like virial coefficients. So how would a chemist describe the system we are studying here? In a first approximation, the chemist would consider it as a mixture of atoms with density n_A and molecules with density n_M . In the chemical picture, due to the assumption of ideality, we would write for the pressure

$$\beta p = n_A + n_M, \quad n_M/n_A^2 = K(T), \quad (2.75)$$

where the second relation is the mass action law, with a mass action constant $K(T)$ which is proportional to an exponential function of E_0 , the binding energy of formation of a molecule from two atoms. Since the total density of the reacting mixture is given by $n = n_A + 2n_M$, we get the equation of state

$$\beta p = n_A + n_A^2 K(T) , \quad n = n_A + 2n_A^2 K(T) . \quad (2.76)$$

A comparison with the fugacity expansion shows the full equivalence between the physical description given by (2.72) and the chemical description given by the foregoing equations. The two pictures are identical if we use the notation $\tilde{z} = n_A$, $K(T) = B_2(T)$. This means that we may interpret $\tilde{z}$ as the density of free atoms and $B_2(T) \sim \tilde{z}^2$ as the density of free molecules.

This leads us to the insights that for systems with attractive forces and two deep particle bound states, under the condition $\exp(-E_{10}/k_B T) \gg 1$, the method of density expansions is badly convergent and may even lead to negative pressures. On the other hand, fugacity expansions give an excellent description from low to high temperatures. Of course, we may have in reality both strongly repulsive forces with hard sphere core and attractive forces leading to deep bound states in the same system. The way out here is to introduce a description which lies somewhere between fugacity expansions and density expansions. Such ‘mixed expansions’ may be based on a more complicated quasi-particle picture (Hill 1960; Ebeling 1974). A systematic investigation of the thermodynamic formulation of chemical association in statistical mechanics has been given by Fisher and Zuckerman (1998). Several aspects of the relation between the physical and chemical description of plasmas will be investigated in more detail in Chap. 5. In particular, the class of systems with Coulomb interactions which are in part repulsive and in part attractive requires more sophisticated expansions situated somehow between density and fugacity expansions (Ebeling 1974, 1976; Friedman and Ebeling 1979; Kremp et al. 2005).

2.6 Strong Exchange Correlations in Fermi–Dirac Gases

2.6.1 Pair Correlations and Thermodynamics

In classical physics non-ideality means, that the EOS is different from $\beta p = n$. In quantum gases, the situation is more complicated. We already know that Fermi or Bose gases without interactions may develop strong correlations due to exchange effects. For this reason we must look primarily at the correlations between the particles which reflect the degree of coupling.

By definition, we speak about correlations in a fluid if the spatial correlation function $g(1, 2)$ differs from unity. Recall that the pair distribution function of a fluid was defined by $g(1, 2) = 1 + h(1, 2)$. Fermi–Dirac gases show rather strong correlations at high densities due to the Pauli principle. In this sense, they are not ‘ideal’ in the classical meaning of independent particles, but are correlated. In the quantum case, $g(1, 2)$ is the quantum statistical pair distribution function and $h(1, 2)$ the corresponding correlation function of two noninteracting Fermi or Bose particles (Pines and Nozieres 1966; Kremp et al. 2005).

Here we start by investigating Fermi particles (electrons). Then, in the low density limit, we have

$$h(1, 2) = -\frac{1}{2} \exp(-r^2/\lambda^2), \quad \lambda^2 = \frac{\hbar^2}{mk_B T}. \quad (2.77)$$

In the opposite case of high density (strong degeneracy), the correlation function of noninteracting electrons is given by (Pines and Nozieres 1966)

$$h(r) = -\frac{9}{2} \left[\frac{\sin(p_F r) - p_F r \cos(p_F r)}{p_F^3 r^3} \right]^2, \quad p_F^1 = .521 a_{Br_s}. \quad (2.78)$$

Due to the correlations, the EOS is not linear in the density, but increases very fast at higher densities. Our task is now to discuss this function in the full density range. In order to solve this problem we have to express the pressure and other thermodynamic functions explicitly in terms of the densities.

So far we have calculated the thermodynamic functions in the standard way, working in the grand canonical ensemble and considering the fugacities as independent input parameters (see e.g. Huang 2001, Kremp 2005). Only then did we express the pressure in terms of the density for low densities. On the other hand we must consider that the densities are the primary input parameters under normal experimental conditions. Fugacities (chemical potentials) are quantities which are difficult to control directly in experiments in most cases. In order to compare theory with experiment, we need as a rule to represent the thermodynamic functions as an explicit function of the density over a wide range. The implicit representation of the EOS by two equations for p and n depending on the fugacity is not convenient, and in many representations not well convergent. So we have to solve the so-called inversion problem.

In principle it should be enough to get one thermodynamic potential like the free energy $F(T, V, N)$, for example, as a density function and obtain the other potentials in standard way by differentiation from Maxwell relations. In spite of the fact that one thermodynamic potential is enough, because all others could be derived from it, we find it more convenient, to start from two or three explicit thermodynamic functions. This procedure allows us to obtain all other functions just by arithmetic operations such as addition or subtraction, noting that differentiation can introduce inaccuracies.

We thus study the Gibbs potential G_e , free energy F_e , and internal energy U_e , and derive the pressure p_e and the entropy S_e by simple arithmetic relations:

$$p_e V = F_e - G_e, \quad T S_e = U_e - F_e.$$

In the previous chapter, in the framework of the grand canonical ensemble, we expressed the pressure and the thermodynamic functions in terms of the activity z and the chemical potential μ . With the abbreviations $z = \exp(\alpha)$ and $\alpha = \mu/k_B T$, for the density of a Fermi–Dirac gas, we find (Huang 1987; Landau and Lifshits 1980, 2001)

$$\frac{n\Lambda^3}{2s+1} = \frac{4}{\sqrt{\pi}} \int_0^\infty dx \frac{x^2 z}{e^{-x^2} + z} \equiv f_{3/2}(z) . \quad (2.79)$$

The function $f_{3/2}(z)$ is analogous to the g -function for a Bose gas and may also be represented by expansions in z (in the region of convergence):

$$f_\lambda(z) = \sum_{l=1}^{\infty} (-1)^{l+1} \frac{z^l}{l^\lambda} . \quad (2.80)$$

Besides this definition of Fermi functions, we will use also another definition (DeWitt 1961; Kraeft et al. 1986):

$$I_\nu(y) = \frac{1}{\Gamma(\nu+1)} \int_0^\infty dx \frac{x^\nu}{\exp(x-y) + 1} . \quad (2.81)$$

There is an extensive mathematical literature on the properties of this class of functions (see, e.g., Wasserman et al. 1970, Zimmermann 1987, Lether 2000, Fukushima 2015). In the first approximation, for the corrections to the Boltzmann expressions for the chemical potential, we find the series

$$\frac{\mu}{k_B T} = \ln z = \ln \frac{n\Lambda^3}{2s+1} + \frac{1}{2\sqrt{2}} \frac{n\Lambda^3}{2s+1} + \dots . \quad (2.82)$$

Similar expressions follow for the pressure, viz.,

$$\begin{aligned} p &= k_B T \left(\frac{2s+1}{\Lambda^3} \right) f_{5/2}(z) = \frac{k_B T (2s+1)}{\Lambda^3} \left(z - \frac{z^2}{2^{2/5}} + \dots \right) \\ &\approx nk_B T \left[1 + \frac{1}{4\sqrt{2}} \left(\frac{n\Lambda^3}{2s+1} \right) \right] . \end{aligned} \quad (2.83)$$

In general, for applications, we must express the pressure and the chemical potential in terms of densities and temperatures. The task of excluding the activities and expressing them in terms of densities is called the *inversion problem*.

As mentioned above, we find it most convenient to start with the chemical potential of the electrons (which is the Gibbs potential per electron) and the free energy per electron, both measured in $k_B T$ (or possibly in Rydberg) as primary quantities:

$$\alpha_e = \frac{\beta G_e}{N_e}, \quad \phi_e = \frac{\beta F_e}{N_e} . \quad (2.84)$$

The main contribution to these functions comes from the ideal terms which were already considered in detail on a rather elementary basis. The extension to the region of weak correlations requires greater accuracy and more precise studies of the series

with respect to the degeneracy parameter. Note that there is a long list of mathematical studies of the Fermi integrals (see, e.g., Wasserman et al. 1970, Lether 2000). The problem of inversion from the variable α to n is non-trivial (Zimmermann 1987). Note that the known limiting cases have to be respected:

$$\alpha_e = \ln y, \quad \text{if } y \ll 1, \quad \alpha \longrightarrow \left(\frac{3\sqrt{\pi}}{4} \right)^{2/3} y^{2/3}, \quad \text{if } y \gg 1. \quad (2.85)$$

We use a convenient formula proposed by Zimmermann (1988), consisting of two different analytical expressions for low and high densities, and given in dimensionless units $y = n_e \Lambda_e^3 / 2$ which are smoothly interpolated:

$$\begin{aligned} \varphi_e^{\text{FD}}(y) = w_1(y - 5.5) \left[\ln(y) - 1 + 0.1768y - 0.0165y^2 + 0.000031y^3 \right] \\ + w_2(y - 5.5) \left(0.7254y^{2/3} - 2.040y^{-2/3} - 0.45y^{-2} \right), \end{aligned} \quad (2.86)$$

$$\begin{aligned} \alpha_e^{\text{FD}} = w_1(y - 2.5) \left[\ln(y) + .3536y - 0.00198y^2 + 0.000124y^3 \right] \\ + w_2(y - 2.5) \left(1.209y^{2/3} - .6803y^{-2/3} + 0.45y^{-2} \right), \end{aligned} \quad (2.87)$$

where the interpolating weight factors are defined by

$$w_1(x) = [1 + \exp(+bx)]^{-1}, \quad w_2(x) = [1 + \exp(-bx)]^{-1}, \quad (2.88)$$

with $b \approx 10$. These expressions turn out to be very convenient for practical calculations of the thermodynamic functions, including the equation of state:

$$\pi = \beta n p^{\text{FD}} = \varphi_e^{\text{FD}}(y) - \alpha_e^{\text{FD}}(y). \quad (2.89)$$

Finally, we note once again that the ideal properties of a Fermi gas change in the presence of an external magnetic field B , since the particles, e.g., electrons have a finite Larmor radius $\omega_c = eB/m_e$. The field effect may be estimated by the replacement (Steinberg et al. 1998)

$$n_e \Lambda_e^3 \longrightarrow n_e \Lambda_e^3 \frac{\tanh x_e}{x_e}, \quad x_e = \frac{\hbar \omega_c}{2k_B T}. \quad (2.90)$$

Note that this effect leads to an effective decrease in the degeneracy of light charged particles such as electrons.

2.6.2 Hartree–Fock Contributions

In order to demonstrate the role of physical interactions we consider the prototype system referred to as a ‘Yukawa gas’ and closely related models. Here only weak interactions will be taken into account and in a linear approximation, i.e., in the Hartree–Fock approximation. Our basic assumption about the potential is that it has a Fourier transform. The Coulomb case is excluded so far, because of the specific singularities.

As a standard example of a gas with weak interactions with Fourier transform, we consider a quantum gas with Yukawa or related exponential interactions:

$$V_{ab}^Y(r, \eta) = g_{ab} \frac{\exp(-\eta r)}{r}, \quad V^E = -\frac{\partial V^Y(r, \eta)}{\partial \eta}. \quad (2.91)$$

The first potential was developed by Hideki Yukawa in 1935 to describe strong forces in elementary particle physics, mediated by the exchange of massive particles. This potential now plays a paradigmatic role in statistical physics, since it has found applications in many fields (Fortov et al. 2005; Langin et al. 2016; Ott et al. 2014). The Coulomb case appears here as a limit of very small η , so the limit $\eta \rightarrow 0$ will be mostly excluded. As already discussed in Chap. 1, the Yukawa potential has a singularity at $r = 0$ which may lead to difficulties at higher orders of perturbation expansions. A regularization at $r = 0$ is possible by adding a term of the same form as the one used by Kramers in electrolyte theory, Heller in quantum chemistry, and Kelbg, Deutsch, and others in the quantum statistics of plasmas:

$$V_{ab}^{\text{KD}}(r) = g_{ab} \left[\frac{\exp(-\eta r)}{r} - \frac{\exp(-\alpha r)}{r} \right]. \quad (2.92)$$

At small distances, the so-called Kelbg–Deutsch potential has a finite value. We assume in the following that $\alpha \gg \eta$ has a sufficiently large value and serves only to avoid divergencies in higher orders of perturbation theory due to singularities at $e = 0$.

There are different ways to calculate the Hartree–Fock approximation (HFA). The first and simplest is to begin by calculating the correlation functions of the free Fermi gas in coordinate space, and then obtain the thermodynamic functions by averaging the interaction energy

$$\langle U_{\text{int}} \rangle = \frac{1}{2} N \left\langle V^Y(1, 2) [1 + h^{\text{FD}}(1, 2)] \right\rangle, \quad (2.93)$$

where $h^{\text{FD}}(1, 2)$ is the quantum statistical pair correlation function of an ideal Fermi–Dirac system. In the low density limit, we have the standard result for fermions given in the last section. Averaging the Yukawa potential just with the first term ‘1’ for the pair distribution function gives the Hartree contribution

$$E^H = F^H = 2\pi k_B T V g \lambda^2 \frac{1}{6\eta^2} . \quad (2.94)$$

For the Coulomb limit $\eta = 0$, the Hartree term is formally infinite, but this term cancels with the contribution from the background of counter charges (Kremp et al. 2005). Note that this term does not appear at all in regularized models (Pines and Nozieres 1967; Bobrov et al. 2015). The second term coming from averaging with the term $\exp(-r^2/\lambda^2)$ is the so-called Hartree–Fock term. This term is convergent and, in the Coulomb case $\eta = 0$, after elementary integration, yields the known Hartree–Fock contribution to the interaction energy and free energy:

$$E^{\text{HF}} = F^{\text{HF}} = -V n g \pi \int_0^\infty dr r \exp(-r^2/\lambda^2) = -\frac{V}{2} \pi n g \lambda^2 . \quad (2.95)$$

Including the contribution from $\eta > 0$, we get

$$E^{\text{HF}} = F^{\text{HF}} = -\pi n g \left\{ -\frac{\lambda^2}{4} + \frac{\sqrt{\pi}}{8} \exp(\eta^2 \lambda^2 / 4) [1 - \Phi(\eta \lambda / 2)] \right\} . \quad (2.96)$$

In the opposite case of high density (strong degeneracy), the correlation function of noninteracting electrons is given by (Pines and Nozieres 1966)

$$h^{\text{FD}}(r) = -\frac{9}{2} \left[\frac{\sin(p_F r) - p_F r \cos(p_F r)}{p_F^3 r^3} \right]^2 , \quad p_F^1 = .521 a_B r_s . \quad (2.97)$$

By integration, for the Coulomb case, we obtain the ground state energy

$$E^{\text{HF}} = -N_e \frac{3}{5} \frac{p_F^2}{2m} . \quad (2.98)$$

In order to get the full expression for the Hartree–Fock contributions for any degree of degeneracy, representations in the momentum space are more convenient (Kraeft et al. 1986; Kremp et al. 2005):

$$\langle U_c \rangle = V \int \frac{d\mathbf{p}_1 d\mathbf{p}_2}{(2\pi)^6} V^Y(\mathbf{p}_1 \mathbf{p}_2) f(\mathbf{p}_1) f(\mathbf{p}_2) . \quad (2.99)$$

These analytic expressions depend on the full Fermi functions f taken as functions of the momenta. The result of this integration is known only for the Coulomb limit $\eta = 0$. After some transformations of the integral, we derive (De Witt 1996; Kraeft et al. 1986; Wasserman et al. 1970)

$$\langle U_c \rangle = 2V \frac{g}{\Lambda^4} \int_{-\infty}^{\alpha} dy I_{-1/2}^2(y) . \quad (2.100)$$

The Hartree–Fock contribution to the free energy follows by charging (integration with respect to e^2), and by derivation with respect to α , we find a particularly simple expression for the chemical potentials at any degeneracy:

$$\alpha^{\text{HF}} = -\frac{g}{k_{\text{B}}T\Lambda} I_{-1/2}(\alpha) . \quad (2.101)$$

Note that density and ideal chemical potential are connected by the implicit equations

$$\frac{1}{2}n_e\Lambda_e^3 = I_{1/2}(\alpha_e) , \quad \alpha = \beta\mu_e^{\text{FD}} . \quad (2.102)$$

The Hartree–Fock approximations given here were derived as the first corrections to ideality in the grand canonical ensemble. If we are interested in the corrections in an ensemble with given density and temperature, we have to introduce the canonical ideal chemical potentials from the Fermi expressions, which have to be inverted (Kraeft et al. 1986). The task of excluding the activities and expressing them in terms of the densities is another *inversion problem*, similar to the one for the ideal Fermi gas. As pointed out above, for the ideal case, we find it most convenient to take as primary quantities the Gibbs potential per electron, which is the chemical potential of the electrons, and the free energy per particle measured in $k_{\text{B}}T$:

$$\alpha^{\text{HF}} = \frac{\beta G^{\text{HF}}}{N} , \quad \varphi = \frac{\beta F^{\text{HF}}}{N} . \quad (2.103)$$

After obtaining these two thermodynamic functions in the Hartree–Fock approximation, all others, e.g., the pressure, follow just by algebraic operations.

First we find α^{HF} as a function of the dimensionless electron density $y = n\Lambda^3/2$, where the limiting cases of small or large density have to be respected. As for the Fermi–Dirac case, we use the method of piecewise representations and interpolations developed for the ideal Fermi contributions by Zimmermann (1987):

$$\begin{aligned} \varphi^{\text{HF}}(y) = & -\frac{g}{k_{\text{B}}T\Lambda_e} \left[w_1(y-1.8)(0.5y - 0.3540y^2 + 0.1825y^3) \right. \\ & \left. + w_2(y-1.8)(0.9307y^{1/3} - 0.6976y^{-1} + 0.7635y^{-7/3}) \right] , \end{aligned} \quad (2.104)$$

$$\begin{aligned} \alpha^{\text{HF}}(y) = & -\frac{g}{k_{\text{B}}T\Lambda_e} \left[w_1(y-0.8)(y - 1.0612y^2 + 0.7299y^3) \right. \\ & \left. + w_2(y-0.8)(1.241y^{1/3} - .6981y^{-1} + 1.018y^{-7/3}) \right] . \end{aligned} \quad (2.105)$$

Here the interpolating weight factors are the same as in the previous section. By construction of the interpolating procedure these expressions are compatible with the known approximations for low or high degeneracy. For alternative representations

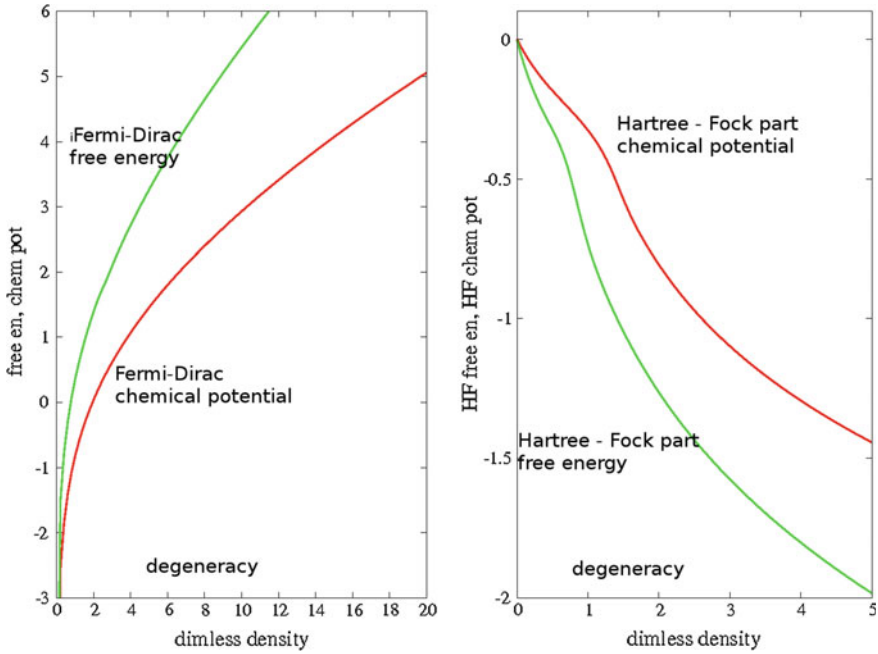


Fig. 2.4 Free energy per electron (*green*) and chemical potential (*red*) of an ideal electron gas in the Fermi–Dirac model (*left*) and the (additional) Hartree–Fock contribution (*right*). The EOS is found as the difference between the two curves. The density is given in the dimensionless units $y = n_e \Lambda_e^3/2$. Deviations from the thermodynamics of a classical gas increase significantly with the density

including the higher order terms and covering the full range, see Perrot and Dharma-Wardana (1984) and Kraeft et al. (1986).

The dependence of the Hartree–Fock functions on the density is shown in Fig. 2.4 (right panel). We observe here a smooth transition between the two regions of the expansions, in the region of intermediate degeneracy. For the intermediate region $E_F < T < 12E_F$, a parametrization of the Hartree–Fock contributions was given by Perrot and Dharma-Wardana (1984). This approximation, which is considered as rather appropriate, will be given explicitly in Chap. 6, along with other, simpler but less precise approximations. The expressions for the Hartree–Fock term are also useful for calculations of the Hartree–Fock contribution to the equation of state

$$\beta p^{\text{HF}}(y) = \alpha_e^{\text{HF}}(y) - \varphi_e^{\text{HF}}(y) . \quad (2.106)$$

The Hartree–Fock contributions increase strongly with the density, changing their analytical shape at certain value of the degeneracy parameter, where non-degenerate behavior goes more or less abruptly over into degenerate behavior.

In certain regions of the density and temperature, roughly speaking the region with $r_s > 1$ and $\Gamma > 1$, the Hartree–Fock contribution (shown in Fig. 2.4 right panel) is not small, and gives a substantial correction to the thermodynamic properties of the ideal Fermi gas. As mentioned, the Hartree–Fock contribution increases strongly with the density and changes its analytical shape to a $n^{1/3}$ law at the transition to strong degeneracy. We have found here full expressions for a Yukawa gas only in the nondegenerate case, and closed expressions for all degrees of degeneracy only for small η , which is the Coulomb limit.

The region where Hartree–Fock approximations work is a relatively large part of the density–temperature plane, covering a region near the boundary of the ideal region. Here correlations due to interactions are still very weak, but nevertheless strongly influence the behavior. A characteristic property of Fermi particles is that they occupy (in the isotropic case) all energy states in momentum space inside the Fermi sphere with the Fermi momentum p_F as radius. We note that the first careful studies of the Green’s functions for electrons and other Fermi particles at low T were presented in key papers by Gellman and Brueckner 1957, Galitskii et al. 1958a, Galitskii (1958), Montroll and Ward (1958), and Vedenov and Larkin (1959). It has been shown in particular that the pole of the Green’s functions defines the energy spectrum of the Fermi quasi-particles, information that is critical for the low temperature thermodynamics. The microscopic derivation of the Fermi liquid theory using the diagrammatic methods of quantum field theory for very low T was carried out by Landau in 1959 and in 1960. Applications to the theory of superconductivity were developed by Gorkov in 1958. For a summary, see the monograph by Abrikosov, Gorkov and Dzyaloshinsky (1965). Several results for applications to plasmas will be given in Chaps. 5 and 6.

2.7 Quantum Statistics of Prototype Yukawa Gases

2.7.1 *Perturbation Theory for Pair Density Operators*

In the previous section we considered Hartree–Fock approximations (HFA) for a quantum gas with interactions having a Fourier transform. On this basis, we studied the region of weak correlations for any degree of degeneracy. The HFA is valid in the border region near to the region of ideal Fermi or Bose gases. Here the interactions are weak and may be taken into account in a linear approximation with respect to the interaction parameter, i.e., in the HFA. We shall now study Yukawa gases as a particular example of interacting quantum gases, still in the region of weak correlations and low density. Then we will study higher order approximations in the interaction parameter, including the role of bound states and assuming weak degeneracy.

We consider the Yukawa gas as a prototype of interactions having a Fourier transform, which is here rather simple $4\pi g_{ab}/(t^2 + \eta^2)$, but may be replaced by other

interactions of same type. The Coulomb case appears as a limiting case and there are many other interesting applications (Fortov et al. 2005). We will then go beyond the HFA and include large values of the interaction parameter. In some sense the prototype Yukawa gas is just opposite to the prototype hard-sphere gas. As before, we use the virial expansion (Beth and Uhlenbeck 1937) and develop a systematic perturbation theory with respect to the interaction parameter g_{ab} for the Fermi and the Bose cases, including strong interactions. Generalizing the previous result, we include mixtures of gases with arbitrary spin, but restrict the calculations to weak degeneracy here.

Since the Slater function of a pair is the diagonal element of the pair density operator, we can take advantage of the general expansion technique for density operators. Using g for the interaction parameter and following Abrikosov et al. (1965) we get the expansion

$$\rho_2(\beta, g) = \exp(-\beta H_0) \sum_{n=0}^{\infty} (-1)^n g^n \int_0^\beta d\tau_n V^Y(\tau_n) \cdots \int_0^{\tau_2} d\tau_1 V^Y(\tau_1) ,$$

with

$$V^Y(\tau) = \exp(\tau H_0) V^Y \exp(-\tau H_0) . \quad (2.107)$$

We may now proceed to the region of weak correlations by systematic expansions of the Slater sums (Slater functions) with respect to the interaction parameter, and calculate the contributions term by term (Kelbg and Hoffmann 1964).

We denote the expansion of the binary Slater function with respect to the g -parameter by

$$S_{ab} = S_{ab}^{(0)} + S_{ab}^{(1)} + S_{ab}^{(2)} + \cdots .$$

It is useful to introduce representations of the Slater sums by plane waves. This scheme was also used in the original papers by Uhlenbeck and Beth (Uhlenbeck and Beth 1936, 1937). Following here the early work of the Kelbg school, we shall systematically use this representation by plane wave eigenfunctions (see Ebeling et al. 1967):

$$S_{ab}(r) = A \int d\mathbf{k} \exp(-\mathbf{k} \cdot \mathbf{r}) \exp(-\beta \hat{H}_{ab}) \exp(+i\mathbf{k} \cdot \mathbf{r}) , \quad (2.108)$$

$$\hat{H}_{ab} = -\frac{\hbar^2}{2m_{ab}} \Delta + V_{ab} , \quad (2.109)$$

where m_{ab} is the relative mass. The Fourier representation in the distance coordinate space reads

$$\tilde{S}_{ab}^{(n)}(\mathbf{t}) = \int d\mathbf{r} S_{ab}^{(n)}(\mathbf{r}) \exp(i\mathbf{t} \cdot \mathbf{r}) . \quad (2.110)$$

In order to find the virial coefficient, we only need an integral over the Slater sum, and it is sufficient to get the Fourier transforms at the zero point $t = 0$. To calculate the Fourier transforms of the Slater function, we define

$$v_{ab}(r) = \exp(-i\mathbf{k} \cdot \mathbf{r}) \exp(-\beta \hat{H}_{ab}) \exp(i\mathbf{k} \cdot \mathbf{r}) ,$$

and the Fourier transform

$$v_{ab}(\mathbf{k}, \mathbf{t}) = \int d\mathbf{r} \exp(i\mathbf{t} \cdot \mathbf{r}) v_{ab}(\mathbf{k}, \mathbf{r}) . \quad (2.111)$$

With these definitions we can use our general perturbation scheme by transforming to the functions v_{ab} . For the first two iterations, we find

$$v_{ab}^{(1)}(\mathbf{k}, \mathbf{t}) = -\beta \int_0^\beta d\beta' \tilde{V}_{ab}(\mathbf{t}) \exp \left[-\lambda_{ab}^2 (\mathbf{t}^2 - 2\mathbf{k} \cdot \mathbf{t}) \left(1 - \frac{\beta'}{\beta} \right) \right] , \quad (2.112)$$

$$v_{ab}^{(2)}(\mathbf{k}, \mathbf{t}) = \frac{1}{8\pi^3} \int_0^\beta d\beta' \int_0^{\beta'} d\beta'' \int d\mathbf{t}' \tilde{V}_{ab}(\mathbf{t} - \mathbf{t}') \tilde{V}_{ab}(\mathbf{t}') \exp \left\{ -\lambda_{ab}^2 \left[(\mathbf{t}^2 - 2\mathbf{k} \cdot \mathbf{t}) \left(1 - \frac{\beta'}{\beta} \right) + (\mathbf{t}'^2 - 2\mathbf{k} \cdot \mathbf{t}') \left(\frac{\beta'}{\beta} - \frac{\beta''}{\beta} \right) \right] \right\} . \quad (2.113)$$

On the basis of these approximations for the Bloch functions, we find the free energy up to second order in the coupling g . In the same way, we may go to any order.

2.7.2 Perturbation Expansion for the Free Energy

Introducing the first two iterations of the functions v_{ab} given before into the formula for the Slater functions, the corresponding Fourier transforms can be written

$$\tilde{S}_{ab}(\mathbf{t}) = \frac{\lambda_{ab}^3}{\pi^{3/2}} \int d\mathbf{k} \exp(-\lambda^2 \mathbf{k}^2) \times \left[v_{ab}(\mathbf{k}, \mathbf{t}, \beta) + \frac{(-1)^{2s_a}}{(2s_a + 1)} \delta_{ab} v_{ab}(\mathbf{k}, \mathbf{t} + 2\mathbf{k}, \beta) \right] . \quad (2.114)$$

In Chaps. 4–6, we will use similar expressions for plasmas. For Yukawa gases, we get the first (linear) approximation of the Slater function in the Fourier representation:

$$\tilde{S}_{ab}^{(1)}(\mathbf{t}) = -\beta \frac{4\pi g_{ab}}{t^2 + \eta^2} \exp \left(-\frac{1}{2} \lambda_{ab}^2 t^2 \right) M \left(\frac{1}{2}, \frac{3}{2}; -\frac{1}{4} \lambda_{ab}^2 t^2 \right) + \frac{(-1)^{2s_a}}{(2s_a + 1)} 4\pi \delta_{ab} \beta g_{ab} \int d\alpha \int \frac{d\mathbf{k}}{\eta^2 + (2\mathbf{k} + \mathbf{t})^2} \exp \left\{ -\lambda_{ab}^2 [k^2 + \alpha \mathbf{t} \cdot (\mathbf{t} + 2\mathbf{k})] \right\} , \quad (2.115)$$

where M is the Kummer function (or confluent hypergeometric function). We get the second virial function and the free energy as deviations from the Boltzmann term in the form of an expansion with respect to the interaction parameter:

$$F = F^B - \frac{1}{2}V \sum_a n_a \sum_b n_b \cdot \sum_{p \geq 1} [\tilde{S}_{ab}^{(p)}(\mathbf{t} = 0)] + \dots \quad (2.116)$$

Summarizing these calculations, we find the free energy by carrying out the integrations. For the pressure we get

$$\beta p = \sum_a n_a + \sum_a n_a \sum_b n_b \cdot \sum_{p \geq 1} [\tilde{S}_{ab}^{(p)}(\mathbf{t} = 0)] + \dots \quad (2.117)$$

For the exponential potential, we do not have any divergence problems when carrying out the integrals in the series, neither at $r \rightarrow 0$, nor at $r \rightarrow \infty$. For Yukawa potentials, there are no divergencies up to second order. However, beginning at the third order, we have to include regularization, e.g., a finite α parameter, in order to avoid divergencies in the classical limit at $r = 0$.

In the classical limit $\hbar = 0$, all integrations are elementary. A well known approximation for the excess pressure and the corresponding sound velocity used, e.g., in the theory of the Bose gas by Bogoliubov, is

$$\beta p_{\text{ex}} = +n^2 \tilde{V}(\mathbf{t} = 0) , \quad c_v = \sqrt{n \tilde{V}(\mathbf{t} = 0)} . \quad (2.118)$$

For the free energy of the classical Yukawa gas, we get

$$F = F^B - V k_B T \sum_a n_a \sum_b n_b \left(-4\pi \frac{\beta g_{ab}}{\eta^2} + 2\pi \frac{\beta^2 g_{ab}^2}{\eta} \right) . \quad (2.119)$$

Including quantum effects leads to more complicated integrals. For the free energy, the result for the first order which provides the Fock and the Hartree–Fock contributions of a mixture with arbitrary spins is

$$F^{\text{HF}} = 2\pi k_B T V \sum_{ab} \left\{ g_{ab} \lambda_{ab}^2 \frac{1}{6\eta^2} + \frac{\delta_{ab}}{2(2s_a + 1)} \pi g \lambda_{ab}^2 \left[1 - \frac{1}{2} \eta \lambda_{ab} \exp\left(\frac{1}{4} \eta^2 \lambda_{ab}^2\right) [1 - \Phi(\eta \lambda_{ab}/2)] \right] \right\} , \quad (2.120)$$

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x dt \exp(-t^2/2) . \quad (2.121)$$

For the case $g \rightarrow e_a e_b$, $\eta \rightarrow 0$, (2.121) reduces to a relation which will be used for plasmas. In the second order of perturbation theory, we find

$$\tilde{S}_{ab}^{(2)}(\mathbf{t} = 0) = \frac{\pi}{\eta} \beta^2 g_{ab}^2 - \frac{\pi \sqrt{\pi}}{2} \lambda_{ab} \beta^2 g_{ab}^2 + \frac{\pi}{\eta} \beta^2 g_{ab}^2 f_2(\zeta) . \quad (2.122)$$

The first term is purely classical and the second is a quantum contribution. The third is a mixed contribution, given by an integral f_2 that cannot be solved. An estimate may be found by a median value approximation, viz.,

$$f_2(y) \approx \left(1 + \frac{1}{2}y^2\right) \left[\exp(y^2) \operatorname{erfc}(y/2) - 1 \right] , \quad (2.123)$$

where

$$\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty dt \exp(-t^2) .$$

Putting together these results we arrive at the following expressions for the free energy of Yukawa gases containing the first two orders in the coupling g_{ab} in the direct and the exchange contributions. The ‘virial functions’ Q for the direct Heisenberg term and E for the exchange term are in principle infinite series in the coupling g :

$$F = F^{\text{id}} - V k_B T \sum_{ab} n_a n_b 2\pi \lambda_{ab}^3 \left[Q(\gamma_{ab}, \zeta) \pm \frac{(-1)^{2s_a}}{(2s_a + 1)} E(\gamma_{ab}, \zeta) \right] . \quad (2.124)$$

The coupling parameter γ and the decay parameter ζ are defined by

$$\gamma_{ab} = \beta \frac{g_{ab}}{\lambda_{ab}} , \quad \zeta = \eta \lambda_{ab} . \quad (2.125)$$

For the Yukawa case, the first expansion terms of the virial functions read

$$Q(\gamma, \zeta) = \frac{2\gamma}{\zeta^2} + \frac{1}{2} \pi^{3/2} \gamma^2 + \frac{\gamma^2}{\zeta} [1 + f_2(\zeta)] , \quad (2.126)$$

$$E(\gamma, \zeta) = \frac{\sqrt{\pi}}{4} + \frac{\gamma}{2} \left[1 - \frac{\zeta}{2} \operatorname{erfc}(\zeta/2) \right] . \quad (2.127)$$

The other limit $\eta \rightarrow 0$ does not exist, but we will show in Chap. 6 that, for small η , a known result for Coulomb plasmas [we mean the second term in (2.122)] arises, which was first obtained for Coulomb systems (Ebeling et al. 1967, 1976).

2.8 Analytical Properties of Thermodynamic Functions of Yukawa Systems

2.8.1 Bound States and Analytical Properties

This section investigates the general structure of the thermodynamic functions of fermion systems with interactions possessing a Fourier transform. Extending the perturbation theories now to arbitrary order, we will also be able to include bound state situations where the coupling is strong and where bound states may play an important role. The first model to be treated is a one-component Yukawa gas. In contrast to the previous section, we use here the notation λ for the strength of the interaction. This is the main parameter determining the analytical properties of the gas. The one-component Yukawa gas plasma (OCP) is used nowadays as an idealized model in which particles interact through a Coulomb potential going as r^{-1} with an additional exponential decay with length $1/\eta$. The model is considered as paradigmatic and is used to approximately describe a wide range of physical systems, especially strongly coupled plasmas of charged particles on a background, such as dusty plasmas (Fortov et al. 2005; Langin et al. 2016; Ott et al. 2014). Note that all physical properties of Yukawa OCPs are expected to be universal in η when expressed in appropriate scaled units (Langin et al. 2016). Most of the existing calculations of thermodynamic functions are purely classical, and indeed for many applications, such as dusty plasmas, quantum effects are not relevant. Nevertheless, we will continue here with the quantum-statistical approach used in the previous section, in order to close an existing gap for Yukawa systems.

This section is mainly dedicated to two-component electro-neutral gaseous systems and is heavily based on the analytic properties of the system with respect to the λ -parameter. The first terms of Taylor expansions in λ were obtained in the previous section. We will show here that a two-component symmetrical Yukawa system is paradigmatic for a whole class of systems with bound states, such as hydrogen plasmas.

We begin with the analytical properties of one-component systems with respect to the interaction parameter λ and then go to a model of a ‘two-component plasma’ in which the two components have opposite ‘charges’. The basic assumption is that the partition function of the system, namely,

$$Tr \left\{ \exp \left[-\beta H_0 - \beta \lambda V(r) \right] \right\}, \quad (2.128)$$

is analytic with respect to the interaction parameter. In spite of the fact that we do not have exact theorems giving the conditions of validity, we are convinced that the class of potentials for which analyticity holds is sufficiently big. At least for the second virial coefficient, which is a partition function for $N = 2$, a proof of analyticity exists for special potentials (Ebeling et al. 1976; Kremp et al. 2005, 1971). This proof is relevant to integrable interaction potentials with the property

$$\int_0^\infty dr \, r |V(r)| < \infty, \quad \int_0^\infty dr \, r^2 |V(r)| < \infty. \quad (2.129)$$

This condition is in particular satisfied by our Yukawa-type interaction potentials.

We assume that the interaction strength λ may have positive or negative values, and study first one-component systems, changing λ from positive to negative values, with special interest in the bound state effects for $\lambda < 0$. Note that the bound state energies of Yukawa systems are not analytic functions of λ . They have been studied in great detail analytically as well as numerically (Rogers et al. 1970; Bessis et al. 1975; Kilimann and Ebeling 1990; Lehmann and Ebeling 1991). For small η , the potential may be approximated by an expansion in η :

$$V(r) = \lambda \frac{1}{r} - \lambda \eta + \frac{1}{2} \lambda \eta^2 r + \dots. \quad (2.130)$$

A linear perturbation theory taking into account the negative sign of the bound state energies leads to the simple estimate

$$E_{sl} = \begin{cases} -\frac{\lambda^2 \mu}{\hbar^2 s^2} + |\lambda| \eta, & \text{if } s^2 < \frac{|\lambda| \mu}{\hbar^2 \eta}, \\ 0, & \text{otherwise.} \end{cases}$$

In the first approximation, the shifts relative to the Coulomb levels are positive and level-independent. At the point where they cross zero, the bound states disappear. Note that details of the bound states have been carefully investigated numerically and by perturbation methods (Rogers et al. 1970; Kilimann and Ebeling 1990; Lehmann et al. 1996).

A useful formula for approximating the s -states has been given by Dutt and Mukherjee (1981):

$$E_{s0} = -\frac{\lambda^2 \mu}{\hbar^2} \left(\frac{1}{s} - \frac{s \eta}{2} \right)^2 + \eta \left[0.61 \exp(-s^2 \eta) - 0.11 \right]. \quad (2.131)$$

A special and quite relevant property is that the number of bound states is always finite for finite η . For the ground state and the excited states, the shifts may be estimated by perturbation expansion with respect to η (Kilimann and Ebeling 1990). According to Mott's estimate (Mott 1961), the ground state disappears for $\eta^{-1} > 2a_B$, where a_B is the Bohr radius. Rogers et al. (1970) found $\eta a_B = 1.19$ numerically for the critical value.

Variational methods are also quite effective using test wave functions (Rogers et al. 1970) of the form

$$\psi(r, \alpha) = (\pi \alpha^3)^{-1/2} \exp(-r/\alpha). \quad (2.132)$$

With simple analytical calculations one may obtain results which agree sufficiently well with Rogers et al. (1970) (see Rogers et al. 1970). Introducing the dimensionless parameter $X = e^2\eta$, several authors have shown that, at certain value X_{sl} , the level with quantum numbers s, l disappears and merges with the continuum (Rogers et al. 1970), Bessis et al. (1975). Following Rogers et al. (1970) we get, for example

$$\begin{aligned} X_{10} &= 1.19 , \\ X_{20} &= 0.3103 , \quad X_{21} = 0.2202 , \\ X_{30} &= 0.1394 , \quad X_{31} = 0.1127 , \quad X_{32} = 0.0913 , \\ X_{40} &= 0.0788 , \quad X_{41} = 0.0679 , \quad X_{42} = 0.0581 , \quad X_{43} = 0.0498 . \end{aligned}$$

Note that several other approximate representations of the levels are known (Kilimann and Ebeling 1990; Rogers et al. 1970). For example Kilimann and Ebeling (1990) use a fourth order polynomial in X to represent the levels. Here we use a more convenient (less precise) approximation by means of a second order polynomial with $a_B = \hbar^2/\mu|\lambda|$ and $X = \eta a_B$:

$$E_{sl}(X) = -\frac{\lambda^2}{2\hbar^2 s^2} \left[1 - 2s^2 X + (2s^2/X_{sl})X^2 - X^2/X_{sl}^2 \right] , \quad (2.133)$$

with $E_{sl} = 0$ if $X > X_{sl}$. For later applications it may be useful to realize that $X \sim |\lambda|$ and that the X_{sl} are just numbers, which are tabulated.

Let us assume from now on that the bound state levels are known with sufficient accuracy. We will study first one-component systems and then symmetric pseudo-plasmas, bearing in mind the postulated analyticity with respect to λ . Note that we define $B_2(T)$ here in such a way that Bose and Fermi correlations are included, not in the ideal part, but in the second virial coefficient. The two main ways to split the second virial coefficient into two parts are:

- Decomposition into a symmetric and an antisymmetric contribution:

$$B_2(T, \lambda) = B_2^{\text{sy}}(T, \lambda) + B_2^{\text{as}}(T, \lambda) . \quad (2.134)$$

with

$$\begin{aligned} B_2^{\text{sy}}[T, \lambda] &= \frac{1}{2}(B_2(T, \lambda) + B_2(T, -\lambda)) , \\ B_2^{\text{as}}[T, \lambda] &= \frac{1}{2}(B_2(T, \lambda) - B_2(T, -\lambda)) . \end{aligned} \quad (2.135)$$

Under the assumption that $B_2(\lambda)$ is an analytic function with the expansion

$$B_2(\lambda) = a_1\lambda + a_2\lambda^2 + a_3\lambda^3 + \dots , \quad (2.136)$$

the even part is given by the sum of the even terms

$$B_2^{\text{sy}}(\lambda) = a_2\lambda^2 + a_4\lambda^4 + \dots . \quad (2.137)$$

The method of decomposition of second virial coefficients into even and odd parts is well known from classical statistical thermodynamics (Falkenhagen 1971). It has been shown that, for strong interactions, the asymptotic is determined only by the symmetric part. This important property will play a role in the following decomposition.

- The second virial coefficient is split into a bound state and a scattering state contribution (Beth and Uhlenbeck 1937):

$$B_2(T, \lambda) = B_2^{\text{bs}} + B_2^{\text{sc}} . \quad (2.138)$$

This decomposition is sometimes complicated. The two constituents are in general nonanalytic functions. From the whole structure of the virial coefficient, it is evident that the bound state part determines the asymptotic for strong coupling. In the Coulomb case, the two methods of decomposition are identical. This is connected with the property $E_s \sim \lambda^2$ mentioned above. For a Yukawa system, the bound states are less simple. In our approximation for the bound states, we get

$$B_2^{\text{bs}}(T; \lambda) = \frac{2}{\sqrt{\pi}} \Lambda^{3/2} \exp(-\eta\beta|\lambda|) \sum_{k=1}^{\infty} \frac{1}{\Gamma(k+1)} \left(\frac{\beta\lambda^2}{\hbar^2} \right)^k \zeta^*(2k-2, \eta) ,$$

where we have introduced a modified zeta-function. For $\eta \rightarrow 0$, this is the original Riemann zeta function. We see that for Yukawa potentials the bound state part and the symmetrical part are not equal, but they agree for the Coulomb case $\eta \rightarrow 0$. For finite values of η , the symmetric part and the bound state part agree only with respect to the low temperature asymptotic. In the Coulomb case, the two representations are identical. This case will be important in the following.

2.8.2 Exact Virial Coefficient and Thermodynamic Functions

We first investigate the one-component Yukawa gas and write for the second virial coefficient

$$B_2(T; \lambda) = \frac{2}{\sqrt{\pi}} \Lambda^{3/2} \sum_{\ell=0}^{\infty} (2\ell+1) \left[1 \pm \frac{(-1)^\ell}{2s+1} \right] B_\ell(T, \lambda) , \quad (2.139)$$

with $\Lambda = h/\sqrt{2\mu k_B T}$ (μ -reduced mass) and

$$\begin{aligned} B_l &= B_l^{\text{bs}} + B_l^{\text{sc}} , & B_l^{\text{bs}} &= \sum_{s>l} \left[\exp(-\beta E_{sl}) - 1 \right] , \\ B_l^{\text{sc}} &= \frac{\beta}{\pi} \int_0^\infty dE \delta_l(E) \exp(-\beta E) . \end{aligned} \quad (2.140)$$

Here the (-1) under the sum stems from a partial integration and use of Levinson's theorem (Kraeft et al. 1969; Kremp and Kraeft 1972; Kremp et al. 1971, 2005). With this definition, we define the bound state part in such a way that free particles do not have a bound state part. In the Coulomb limit, this function of λ has the analytical form

$$B_l(\lambda) = \Theta(-\lambda) f^b(|\lambda|) + \text{sign}(\lambda) f^f(|\lambda|), \quad (2.141)$$

and correspondingly the l-terms have the expansions

$$B_l(\lambda) = \tilde{a}_{1l}\lambda + \tilde{a}_{2l}\lambda^2 + \tilde{a}_{3l}\lambda^3 + \dots. \quad (2.142)$$

If the system possesses bound states $\lambda < 0$, it follows that the bound state contribution is even in the interaction parameter λ :

$$f^b(|\lambda|) = 2a_2\lambda^2 + 2a_4\lambda^4 + \dots. \quad (2.143)$$

This is the special case we mentioned above. At lower temperatures, the bound states give the dominant contribution to the total virial coefficient, i.e., we have the asymptotic

$$B_2 \sim B_2^{\text{bs}} = 2a_2\lambda^2 + 2a_4\lambda^4 + \dots. \quad (2.144)$$

In other words, the low temperature behavior of a gas with bound states is dominated by the even coefficients. We will see that, under certain conditions, the asymptotic is even exact. This result is typical and of great value for Coulomb systems. Note that, for Coulomb systems with $\lambda \sim e^2$, the bound state energies are of order $\lambda^2 \sim e^4$. Accordingly, the bound state contributions to the virial functions are even in λ^2 .

The analytical properties of the second virial coefficient as a function of the interaction parameter have rather deep consequences. In order to understand some of these consequences, let us study the pseudo-plasma consisting of two Yukawa gases with opposite 'charges' defined by (2.145). We assume a mixture of two types of 'charges' with opposite sign and the same concentration. This defines a kind of binary plasma model which has 50% positive interactions $\lambda > 0$ of charges with the same sign and 50% negative interactions $\lambda < 0$ of charges with opposite sign. We refer to this artificial system, which is a caricature of a Coulomb plasma, as a Yukawa gas plasma:

$$V_{ee} = V_{ii} = \frac{e^2}{r} \exp(-\eta r), \quad V_{i.e.} = -\frac{e^2}{r} \exp(-\eta r). \quad (2.145)$$

Up to the second virial coefficient, the free energy is given by

$$\delta F = -k_B T V \left(n_e^2 B_{ee} + 2n_e n_i B_{ei} + n_i^2 B_{ii} \right). \quad (2.146)$$

Introducing $\lambda = e^2$, we expand with respect to this parameter and get

$$\delta F = -k_B T V \left[n_e^2 (a_1 e^2 + a_2 e^4 + \dots) + 2n_e n_i (-a_1 e^2 + a_2 e^4 + \dots) + n_i^2 n (a_1 e^2 + a_2 e^4 + \dots) \right]. \quad (2.147)$$

With $n_e = n_i = n_0$, it follows that

$$\delta F = -k_B T V 4n_0^2 (a_2 e^4 + a_4 e^8 + \dots) = -V k_B T 2n_0^2 B_2^{bs}. \quad (2.148)$$

After adding the prefactors and the l -summations we get explicit

$$\delta F = -k_B T V 2n_0^2 \frac{\Lambda^{3/2}}{\sqrt{\pi}} \sum_{l=0}^{\infty} (2l+1) \sum_{s>l} [\exp(-\beta E_{sl}) - 1]. \quad (2.149)$$

This result is exact. No approximations were made, except that we omitted the exchange terms.

Let us now estimate the exchange contributions to the second virial coefficient. This contribution exists only for pairs of identical species, i.e., for positive coupling parameters corresponding to repulsion. Note that there is no compensation with respect to exchange, since exchange contributions are missing for the $\pm$ interactions. We write this symmetry-dependent term in a form which we borrow from known results for Coulomb systems (Kraeft et al. 1986):

$$B_{ab}^S = \delta_{ab} \frac{(-1)^{2s_a} \delta_{ab}}{2(2s_a + 1)} E(\tilde{\xi}_{ab}; \eta), \quad \tilde{\xi}_{ab} = -\frac{g_{ab}}{\lambda_{ab}}. \quad (2.150)$$

For Coulomb systems, this function may be calculated using the exact scattering phases. This will be shown in Chap. 4. The result is a function which decays quickly with increasing (negative) coupling. For Yukawa plasmas, we know only the linear term

$$E(g, \eta) = E(\tilde{\xi}) = \frac{\sqrt{\pi}}{4} + \frac{\tilde{\xi}}{2} + \dots \approx 0.1768 \exp(-2.828|\tilde{\xi}|). \quad (2.151)$$

This surprising result tells us that the exchange effects disappear exponentially with increasing coupling, and may be neglected in a certain temperature range where $|\tilde{\xi}| \gg 1$.

To sum up we may say that the direct terms are strongly determined by compensation effects and that exchange terms are (presumably) exponentially small. This result is not influenced by drastic approximations. However, we should stress that we have assumed here without comment that the masses of all particles are equal, i.e., all thermal wavelengths are equal, otherwise the cancelation would not be complete and our final result would not be exact. (Note also that we should not confuse the

thermal wavelength Λ with the interaction parameter λ .) This surprising exact result tells us the following things about our model plasma:

- The free energy is determined by the bound state contributions alone.
- All contributions from scattering states cancel out completely.
- Only the even powers $g^4, g^8, \dots$, contribute.
- Exchange effects give exponentially small contributions.

In spite of the fact that these statements cannot be directly transferred to the more complicated Coulomb systems, we will see later that the basic features remain valid for the Coulomb case (Ebeling et al. 1976).

The result we got for the free energy may be obtained in an equivalent way for the pressure in the grand canonical ensemble for ‘electrons and positrons’ interacting via Yukawa forces. As shown by the above considerations, a regularized partition function arises, which is similar to the PBL partition function discussed in Chap. 1. This choice is not an arbitrary invention, but deeply connected with the analyticity of the functions with respect to the interaction parameter. In later chapters, we will see that the choice of the Brillouin–Planck–Larkin partition for Coulomb systems has some deep roots in the analytical properties of thermodynamical and partition functions.

2.9 Strongly Correlated Bose Gases at Low Temperatures

2.9.1 Noninteracting Bose Gases

Here we use a well known method to find expressions for the pressure and the density of noninteracting Bose gases (Huang 1987; Landau and Lifshits 1980, 2001). We consider the total system as a conjunction of subsystems in quantum state k . The energy E , total particle number N , and pressure p are additive:

$$E = \sum_k E_k, \quad N = \sum_k N_k, \quad p = \sum_k p_k. \quad (2.152)$$

Note that here the summation index k runs over all the microscopic states and not only over the different energy states. Here the spin states are to be counted as extra quantum states. The partial pressures p_k of subsystems are like partial pressures in a mixture of ideal gases and are therefore additive according to (2.152). We apply the laws of grand canonical ensembles to the subsystem k , where N_k is the particle number in state k . For the partial pressure p_k and the mean particle number $\bar{N}_k$ of the subsystem in state k , we thus get the following expressions (Huang 1987; Landau and Lifshits 1980, 2001):

$$p_k = -\frac{k_B T}{V} \ln(1 - q) = -\frac{k_B T}{V} \ln \left[1 - \exp \left(\frac{\mu - \epsilon_k}{k_B T} \right) \right], \quad (2.153)$$

$$\bar{N}_k = \frac{\partial}{\partial \mu} (p_k V) = \frac{\exp\left(\frac{\mu - \epsilon_k}{k_B T}\right)}{1 - \exp\left(\frac{\mu - \epsilon_k}{k_B T}\right)} = \frac{1}{\exp\left(\frac{\epsilon_k - \mu}{k_B T}\right) - 1} . \quad (2.154)$$

This is the Bose–Einstein distribution for the mean occupation number of the one-particle state k . The condition $N = \sum_k \bar{N}_k$ provides the chemical potential μ and the internal energy follows by summing the energies over all states k .

In order to specify the formula for the energy we need to specify the concrete species with definite spin. We proceed as before, concentrating on the problem of phase transitions and Einstein condensation. However, we have to consider that, for bosons, the same state may be occupied by many particles. In particular, this is true for the lowest state, the ground state of the gas $p_x = p_y = p_z = 0$. We denote the mean occupation of the ground state by $\bar{N}_0$. Following Einstein, a macroscopic occupation of this state is possible. Therefore it is useful to separate the ground state occupation:

$$\bar{N}_0 = \frac{2s + 1}{\exp(-\mu/k_B T) - 1} = \frac{(2s + 1)z}{z - 1} . \quad (2.155)$$

Here $z = \exp(\beta\mu)$ is the fugacity. By integration in spherical coordinates and using the substitution $p = x\sqrt{2mk_B T}$, it follows that

$$N = \bar{N}_0 + \frac{2s + 1}{\Lambda^3} V \frac{4}{\sqrt{\pi}} \int_{0^+}^{\infty} dx x^2 \frac{z}{e^{x^2} - z} \quad (2.156)$$

$$= \bar{N}_0 + \frac{2s + 1}{\Lambda^3} V g_{3/2}(z) , \quad (2.157)$$

with the thermal wavelength

$$\Lambda = h/\sqrt{2\pi m k_B T} . \quad (2.158)$$

We have introduced here the Bose function

$$g_{3/2}(z) \equiv \frac{4}{\sqrt{\pi}} \int_0^{\infty} dx x^2 \frac{z}{e^{x^2} - z} = \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}} . \quad (2.159)$$

The series expansion is valid only within the radius of convergence. Since the signs of the contributions do not alternate as for Fermi gases, the convergence is restricted to $0 \leq z \leq 1$, whence the chemical potential of Bose gases is always negative. For the case $z = 1$, we may express the series in terms of Riemann's zeta-function. According to Riemann's definition we have

$$\zeta(z) = \sum_{\ell=1}^{\infty} \frac{1}{\ell^z}, \quad g_{3/2}(1) = \sum_{\ell=1}^{\infty} \frac{1}{\ell^{3/2}} = \zeta(3/2) \approx 2.612.$$

For the pressure, we get in a similar way,

$$pV = -Tk_B(2s+1) \ln(1-z) + \frac{2s+1}{\Lambda^3} g_{5/2}(z) Tk_B V, \quad (2.160)$$

$$g_{5/2}(z) = \int_0^{\infty} dx x^2 \ln(1 - ze^{-x^2}) = \sum_{l=1}^{\infty} \frac{z^l}{l^{5/2}}. \quad (2.161)$$

We see once again that the series (2.161) converges only for $0 \leq z \leq 1$, which means that, due to $z = \exp(\mu/k_B T)$, we always have $\mu < 0$. Bose–Einstein gases cannot have positive chemical potentials. Only photons, which are the limiting case, have zero chemical potential $\mu = 0$, and $z = 1$.

Referring to (2.157), we can draw some conclusions about occupation of the ground state. The function $g_{3/2}(z)$ has a vertical tangent at the point $z = 1$, but remains finite there. We can show that $g_{3/2}(1) \approx 2.612$ and find the relation

$$n = n_0 + \frac{2s+1}{\Lambda^3} g_{3/2}(z), \quad (2.162)$$

$$n_0 = \frac{\bar{N}_0}{V} = \frac{2s+1}{V} \frac{z}{1-z}. \quad (2.163)$$

We see that, if $n\Lambda^3/(2s+1) > g_{3/2}(1)$ holds, the occupation $(\Lambda^3/V)z/(1-z)$ must have a finite positive value. This means that one value of the momentum $\mathbf{p} = \mathbf{0}$ is occupied by a finite macroscopic part of the bosons which are in the ground state.

This effect was first detected in 1925 by Einstein, after extending Bose’s statistics to gases. We call this effect *Bose–Einstein condensation*. Very often the term ‘Bose condensation’ is used, but as a matter of fact, in Bose’s work, we cannot find a single remark about the possibility of a condensation effect. For temperatures and densities outside the region of Bose–Einstein condensation, the ground state is occupied by only an infinitesimal fraction of the particles, whence

$$n = 0 + \frac{2s+1}{\Lambda^3} g_{3/2}(z). \quad (2.164)$$

From these relations, we may deduce the phase diagram.

So how can one observe Bose–Einstein condensation? If we increase the density in a Bose–Einstein gas, we expect the phase transition at the point where

$$n = \frac{(2s+1)}{\Lambda^3} g_{3/2}(1)$$

is satisfied. Then occupation of the ground state begins with a finite number of gas particles, since from now on n_0 must have a positive value. At this point, the equation of state changes qualitatively. Below the phase transition we have

$$p = k_B T \frac{2s+1}{\Lambda^3} g_{5/2}(z) , \quad (2.165)$$

and after condensation has begun

$$pV = -k_B T (2s+1) \ln(1-z) . \quad (2.166)$$

Let us now calculate the relative occupation of the ground state $\bar{N}_0/N$ as a function of temperature. For the critical density as function of temperature, we obtain

$$n_{\text{cr}} = \frac{(2s+1)}{\Lambda^3} g_{3/2}(1) , \quad (2.167)$$

where $\Lambda = \Lambda(T)$. In this way, for the critical temperature and density, we find

$$T_{\text{cr}} = \frac{h^2 n^{2/3}}{2\pi m k_B [(2s+1)g_{3/2}(1)]^{2/3}} , \quad \frac{\bar{N}_0}{N} = 1 - \left(\frac{T}{T_{\text{cr}}} \right)^{3/2} . \quad (2.168)$$

2.9.2 Interacting Bose Gases and Phase Transitions

As we have shown for non-interacting Bose particles, these systems may condense at $T = 0$ into a single quantum state with the minimal energy. For the homogeneous system, all particles then go into the quantum state with $\mathbf{p} = 0$. For interacting Bose gases which we discuss here, the situation is more complicated and we have to distinguish between the region far above the Bose condensation temperature and the region near to it and below it.

In previous sections, we have shown that, at not too low temperatures and not too high densities, boson gases including interactions are well described by virial expansions and the Beth–Uhlenbeck method. We have seen in detail how the thermodynamics of the He gas at $T < 100$ K is determined by the spin of the atoms forming the gas. For He-4 atoms, the spin is $s = 1$, i.e., the atoms are bosons, in contrast to He-3 atoms which have $s = 1/2$ and are therefore fermions. The role of the spins leads in particular to essential differences between the properties of the fermion gas He-3 and the boson gas He-4.

In an oft-cited paper by Kilpatrick et al. (1954), the second virial coefficients of He-3 and He-4 are calculated at closely spaced temperatures over the range

0.3–60 K using the Lennard-Jones 12-6 potential with parameters given by de Boer and Michels and based on a calculation of the phase shifts. A more recent calculation of the virial expansions for an He-4 gas in the region $5 < T < 100$ K was given by Costa et al. (2013). According to Costa et al. (2013), the ideal quantum term contributes approximately 11 percent at 3 K and less than 1 percent at 100 K. The He-4 diatomic molecule possesses a very weak bound state which contributes less than 0.1 percent at 5 K and much less at higher temperatures. To sum up, we may say that the properties of rare He-4 gases may be well described by a density expansion and the Beth–Uhlenbeck representation of the second virial coefficient. However, at still lower temperatures, below 3 K, and higher densities, the properties of He-4 gas can no longer be described by a density expansion and the Beth–Uhlenbeck representation of the second virial coefficient. This is characteristic for nearly all interacting Bose gases. Going down to even lower temperatures and up to higher densities, we reach regions where completely different methods have to be developed (Landau et al. 1980; Huang 2001).

Note that the problems connected with Bose–Einstein condensation and other low-temperature phenomena like superfluidity and superconductivity are of great interest to modern physics. In his pioneering work in 1925, Albert Einstein already pointed out that there could be links to phenomena like superfluidity and superconductivity.

Since cluster expansions were unable to describe the influence of interaction on phenomena near zero temperatures, several alternative methods applicable to that region were developed, e.g., by N.N. Bogoliubov, starting with his pioneering work in 1947 (see Bogoliubov 1947, 1952, 2005–2009). We may also mention beautiful work by Feynman (1954) and Brueckner and Sawada (1957) not forgetting the methods developed by Landau and his school (Landau et al. 1976, 1980).

Bogoliubov and other workers started from the model of a gas having a weakly repulsive potential with Fourier transform $\tilde{V}(p)$ and the idea that weak excitations may be modeled as a nearly ideal gas of bosonic quasi-particles. The ansatz for the Hamiltonian is

$$H = E_0 + \sum_p E(p) n_p, \quad (2.169)$$

where the n_p are the occupation numbers of the quasi-particles in momentum space and the $E(p)$ are the energies of elementary excitations, represented by

$$E(p) = \sqrt{\frac{N_0}{V} \frac{p^2}{2m} \tilde{V}(p) + \frac{p^4}{4m^2}}. \quad (2.170)$$

In a later paper by Belyaev (1958) the diagrammatic methods of field theory were applied to calculate several first order corrections to the particle spectrum and the ground state energy. The microscopic foundation of the Bogoliubov model is the momentum representation of the Hamiltonian, viz.,

$$\hat{H} = \frac{p^2}{2m} \hat{a}_p^\dagger \hat{a}_p + \frac{1}{2V} \sum \tilde{V}(|p_1 - p'_1|) \hat{a}_{p_1}^\dagger \hat{a}_{p'_1}^\dagger \hat{a}_{p'_2} \hat{a}_{p_2}, \quad (2.171)$$

where $p_1 + p_2 = p'_1 + p'_2$ is stipulated. According to Bogoliubov's fundamental idea, due to the macroscopic occupation of the ground state, the operators a_0 are standard c-numbers and $(a_0)^2 = (a_0^\dagger)^2 = N_0$ is the macroscopic occupation of the ground state. After diagonalization of the Hamiltonian, Bogoliubov and also Brueckner and Sawada get the form

$$E(p) = \sqrt{\frac{N^2}{2V} \tilde{V}(0) + \frac{N_0}{2V} \sum_p \tilde{V}(p) + A_p} . \quad (2.172)$$

In the Bogoliubov theory, for small momenta, we get

$$E(p) = v_s p , \quad (2.173)$$

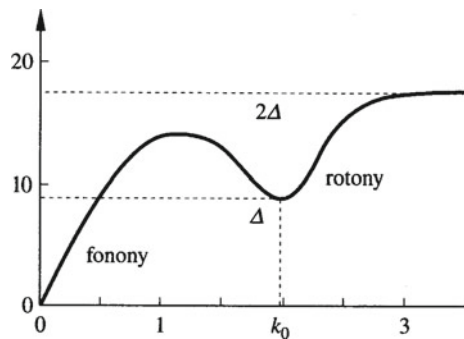
where v_s is the speed of sound given by

$$v_s^2 = \rho \tilde{V}(0)/2m . \quad (2.174)$$

The linear increase is determined by the speed of sound v_s , so that the corresponding excitations may be interpreted as phonons. Several theories, and in particular Landau's model, then provide a region of excitations corresponding to a minimum which Landau associates with 'rotons'.

Phonon–roton excitations, predicted by Landau and measured experimentally by neutron scattering, result in the critical velocity exceeding the observed values of superfluid flow breakdown by an order of magnitude. The Landau arguments associating the minimum in the energy of excitations with 'rotons' are notoriously difficult to understand. However, what seems to be evident from several theoretical approaches and experimental observations (Bobrov and Trigger 2013) is the existence of a minimum in the characteristic curve $E(p)$ which corresponds in Fig. 2.5 to a characteristic wave number $k_0 \sim 2 \text{ \AA}^{-1}$. We notice in this connection that similar excitation curves are also observed in completely different systems consisting of active Brownian particles and dusty plasmas (Trigger and Zagorodny 2004; Trigger et al. 2015).

Fig. 2.5 Phonon and roton excitations in Landau's model for the dispersion curve of He-4 according to Huang (1987, 2001). The energy (in kelvin) is represented over the wave number k (in $\text{\AA}^{-1}$)



Phase Transitions in Low-Temperature Bose Gases

We consider again the noninteracting Bose–Einstein gas. For temperatures below the critical value $T < T_{\text{cr}}$, the system consists of particles in the ground state and particles in states with finite momentum $|\mathbf{p}| > 0$. Therefore the momentum distribution is also a mixture of two parts, where the first is proportional to $\delta(\mathbf{p})$. The specific heat is shown in Fig. 2.6 as a function of temperature. The peak at $T = T_{\text{cr}}$ is an edge, not a pole, and looks like the Greek letter λ . Therefore the transition is sometimes called the λ -transition.

Later we will discuss the fact that in experiments He-4 gases show a phase transition with a transition temperature $T_c \approx 2.17$ K. Assuming a density $\rho \sim 0.15$ g/cm³ for liquid He, we find a transition temperature around 3.2 K. This is sufficiently close to the experimental value. However, the experimentally observed transition in He-4 is not an ‘Einstein condensation’. Analyzing the experiments (Fig. 2.7), we see a typically non-symmetric λ which is not similar to the ‘edge’ in Fig. 2.6. We may conclude that He-4 does not undergo a proper Einstein condensation, so we may ask which physical systems are the right candidates to manifest the condensation which Einstein predicted in 1925.

The Einstein condition

$$n \frac{h^3}{\sqrt{2\pi m k_B T}^3} \approx 2.612(2s + 1) \quad (2.175)$$

shows that we need low temperatures, high densities, small masses, and weak interactions. These conditions as formulated by Einstein are extremely difficult to fulfil. One needs very low temperatures in the range of milli- or even micro-kelvins and relatively high densities. Due to the enormous experimental difficulties, a convincing

Fig. 2.6 Specific heat of a Bose–Einstein gas as function of temperature, showing a phase transition at $T \approx 3.2$ K

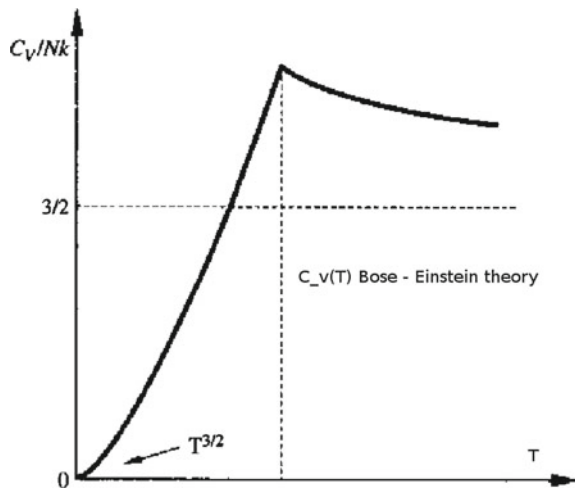
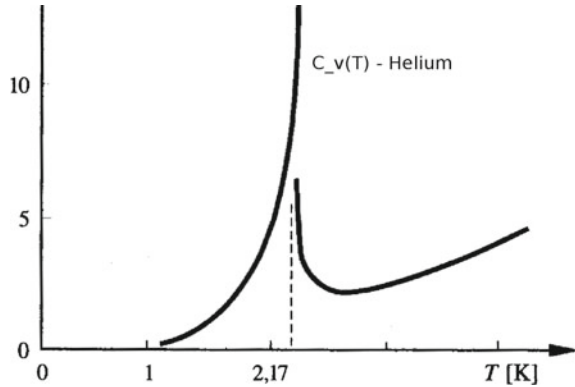


Fig. 2.7 Specific heat of helium-4 (in J/g K) against temperature (in degrees kelvin), with a so-called λ -point at $T \approx 2.17$ K



experimental verification of Einstein's prediction of a condensation of atomic gases at low temperature was confirmed only 70 years after the prediction.

Nowadays many groups around the world work in that field, and several Nobel Prizes have already been attributed. For gases of alkali atoms or atoms of other elements in magnetic traps, Eric Cornell reported in 1995 at the *International Conference of Laser Spectroscopy* on experiments at the University of Boulder which confirmed Einstein's prediction, as well as parallel experiments in the group run by Wolfgang Ketterle at MIT (Davis et al. 1995). For theoretical developments, see, e.g., Pethick and Smith (2001), and also Pitaevskii and Stringari (2003).

We note that Bose–Einstein condensation is related to two remarkable low-temperature phenomena (Greenberger et al. 2009):

- superfluidity, in which a liquid flows with zero friction, and
- superconductivity, in which electrons move through a material with zero electrical resistance.

A hypothetical system of special interest which we will discuss in Chap 10 is excitonic systems. In highly excited semiconductor systems, a Boson gas of electron–hole atoms may be created. These so-called excitons have a very small mass and are ideal candidates for Einstein condensates. A problem is, however, the existence of strong Coulomb interactions which may be responsible for other Coulomb-induced phase transitions (see Chaps. 6 and 8). Due to this difficulty the proof of a proper Bose–Einstein condensate in excitonic systems still seems to be lacking (see also Chap. 10).

Let us look now at helium at low temperatures. At very low temperatures, i.e., the region below 3 K for He-4, the He-4 gas shows a quite characteristic phase transition. This is evident, for example, by looking at measurements of the specific heat of He-4 gas in the region $1 < T < 5$ K (see Fig. 2.7). The data show a so-called lambda curve for the specific heat. The curve is reminiscent of the specific heat curve for an ideal Bose gas which we discussed above, but it differs too much in the details to allow us to conclude that the transition in He-4 is an Einstein transition.

The measurements show the specific heat of He-4 around the phase transition, which is located at

$$T_c = 2.172 \text{ K} , \quad n_c \sim 2.16 \times 10^{22} \text{ cm}^{-3} , \quad v_c = 46.2 \text{ \AA}^3/\text{atom} .$$

Around the phase transition, the He-4 fluid is a non-ideal Bose fluid in which interactions have an essential influence. As we have also seen, the simple Beth–Uhlenbeck theory is unable to describe the behavior near to the lambda phase transition. In the given region He-4 is a non-ideal Bose fluid. For this region, special methods have been developed, such as the Bogoliubov, Brueckner, Sawada, Feynman, and Landau methods (see Bogoliubov and Bogoliubov 1992; Bogoliubov 2005–2009; Pines and Nozieres 1967; Feynman 1954, 1972, Landau and Lifshits 1976, 1977, 1980; Bobrov and Trigger 2013).

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