

Statistical Physics B

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Chapter 1

Introduction

Statistical Physics B can be seen as a continuation of an introductory course in statistical mechanics, such as Statistical Physics A or Termodynamika i fizyka statystyczna R. We assume that the student is familiar with the foundations of equilibrium statistical mechanics in terms of the various statistical ensembles. Furthermore, a typical introductory course covers some applications of ensemble theory to some simple systems, such as ideal (quantum) gases and the Ising model. The latter is often discussed only in the one-dimensional case or within the mean-field approximation. Here, we want to expand upon this knowledge to describe the equilibrium properties of interacting systems and/or systems in an external potential. Finally, we go beyond the concept of equilibrium systems by considering systems out of equilibrium that are characterized by non-vanishing fluxes.

1.1 Further reading

These lecture notes are based on various books, lecture notes, articles on this topic. A non-exhaustive list is shown below:

1. R. A. L. Jones, *Soft condensed matter*.
2. S. R. de Groot and P. Mazur, *Non-equilibrium thermodynamics*.
3. J.-P. Barrat and J.-P. Hansen, *Basic concepts for simple and complex fluids*.
4. R. Evans, *Lecture notes Kramer's course 2011, DFT: Classical and quantum*.
5. D. Chandler, *Introduction to modern statistical mechanics*.
6. R. P. Feynman, *Statistical mechanics: a set of lectures*.
7. R. van Roij, *Lecture notes for course "Soft Condensed Matter Theory"*.
8. P. van der Schoot, *Lecture notes for course "Self-organisation in Soft Condensed Matter"*.
9. J.-P. Hansen and I. R. McDonald, *Theory of simple liquids*.
10. J. Israelachvili, *Intermolecular and surface forces*.
11. P. G. de Gennes and J. Prost, *The physics of liquid crystals*.
12. J. K. G. Dhont, *An introduction to the dynamics of colloids*.
13. P. M. Chaikin and T. C. Lubensky, *Principles of condensed matter physics*.

Chapter 2

Many-body theory of classical interacting systems

2.1 A quick reminder on classical statistical mechanics

The central object that we will study in these lecture notes is the so-called classical *partition function*. For example, in the canonical ensemble where the number of (indistinguishable) particles N , the volume V , and temperature T are kept fixed, the canonical partition function is

$$Z(N, V, T) = \frac{1}{N!h^{3N}} \int d\Gamma e^{-\beta H(\Gamma)}, \quad (2.1)$$

with h the Planck constant, and $\beta = (k_B T)^{-1}$, with k_B the Boltzmann constant and T (absolute) temperature. Furthermore, $H(\Gamma)$ is the (classical) Hamiltonian of the system. The integral is over the classical phase space Γ which encodes all microscopic degrees of freedom of the particles in the system. For example, for a system of classical spherical particles they are the positional degrees of freedom, $\mathbf{r}^N := (\mathbf{r}_1, \dots, \mathbf{r}_N)$ and their conjugate linear momenta $\mathbf{p}^N := (\mathbf{p}_1, \dots, \mathbf{p}_N)$ of the particles. An *ensemble* is a subset of the phase space as imposed by macroscopic constraints (e.g. keeping the volume fixed). The general Hamiltonian for such a system is

$$H(\mathbf{p}^N, \mathbf{r}^N) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \Phi(\mathbf{r}^N), \quad (2.2)$$

with m the mass of a particle, and $\Phi(\mathbf{r}^N)$ the N -body interaction potential, which gives the force acting on particle i by all the other particles $\mathbf{F}_i = -\nabla_{\mathbf{r}_i} \Phi(\mathbf{r}^N)$. The potential Φ can be decomposed in terms of one-body, two-body contributions, etc

$$\Phi(\mathbf{r}^N) = \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j<i}^N v(|\mathbf{r}_i - \mathbf{r}_j|) + \dots$$

The one-body contribution $V_{\text{ext}}(\mathbf{r}_i)$ is called the external potential, which can be exerted by, for example, external objects such as walls, or the earth which provides us the gravitational field upon which particles respond to. For the pair potential $v(r)$, we assume the system to be isotropic and translationally invariant, as it only depends on the distance between particles (note that the external potential breaks this symmetry). Examples, are the van der Waals interaction, electrostatic interactions, etc. It is straightforward to extend Eq. (2.2) for systems with internal degrees of freedom, such as orientational degrees of freedom, which can be parametrised by, e.g., the Euler angles. For now, we do not include forces on particles that are non-conservative (i.e. forces that do not have a description in terms of a scalar potential).

The Hamiltonian provides the complete time evolution of a microstate as denoted by a trajectory in classical phase space $(\mathbf{p}^N(t), \mathbf{r}^N(t))$, via the Hamilton equations of motion,

$$\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i}, \quad i = 1, \dots, N,$$

together with $6N$ initial conditions. Note that classical phase space trajectories do not intersect. Obviously, it is very difficult to solve such a system of coupled differential equations, especially considering that $N \sim 10^{23}$. Here is where Eq. (2.1) comes into play: often we are not interested in the precise microstate of a system and its time evolution, but instead we are interested in the macroscopic state (that we observe in daily lives by performing a measurements). Statistical mechanics provides the link between the accessible microstates and the macrostates (as described by thermodynamics), by relating the partition function to the relevant *thermodynamic potential*. The thermodynamic potential quantifies for given constraints as set by the ensemble, how much work the system can perform. In the canonical ensemble, the partition function is related to the Helmholtz free energy

$$\beta F(N, V, T) = -\log Z(N, V, T), \quad (2.3)$$

which gives a complete thermodynamic description of the system. Furthermore, in ergodic systems –systems that are able to explore their whole phase space on the time scale of interest– measurable observables are given by *ensemble averages*. In the canonical ensemble, it is defined as

$$\langle \dots \rangle = \frac{1}{Z(N, V, T)} \int d\Gamma (\dots) e^{-\beta H(\Gamma)},$$

where the dots denote any observable. Note that ergodicity implies that ensemble averages are equal to the more “practical” time averages that one obtains in experiment. Furthermore, we recall some of the thermodynamic relations in the canonical ensemble,

$$S(N, V, T) = -\left(\frac{\partial F}{\partial T}\right)_{N, V}, \quad p(N, V, T) = -\left(\frac{\partial F}{\partial V}\right)_{N, T}, \quad \mu(N, V, T) = \left(\frac{\partial F}{\partial N}\right)_{V, T},$$

which follow from the fundamental relation $dF = -SdT - pdV + \mu dN$. Here, p is pressure, S is the entropy, and μ is the chemical potential.

Other ensembles can be obtained via the Legendre transformation which can be used to “exchange” in the macroscopic constraints intensive variables with their conjugate extensive variables, or vice versa. Recall that a product a conjugate pair of intensive and extensive variables denote a form of work, such as mechanical work $-pV$ or chemical work μN . For example, the thermodynamic potential of the grand-canonical ensemble as characterized by (μ, V, T) –the so-called grand potential Ω – can be obtained from the canonical ensemble, by the Legendre transformation

$$\Omega(\mu, V, T) = F(\langle N \rangle, V, T) - \mu \langle N \rangle, \quad \beta \Omega = -\log \Xi(\mu, V, T), \quad (2.4)$$

with grand-canonical partition function

$$\Xi = \sum_{N=0}^{\infty} \exp(\beta \mu N) Z(N, V, T). \quad (2.5)$$

We also list the useful relation (derive it!), $d\Omega = -SdT - pdV - Nd\mu$, from which various thermodynamic relations follow.

Other ensembles are the microcanonical ensemble (N, V, U) , where U is the internal energy and with entropy S the thermodynamic potential; the isobaric-isothermal ensemble (N, p, T) with the Gibbs free energy the thermodynamic potential; and the (N, p, S) ensemble described by the enthalpy H (apologies for the unlucky standard notation).

Having given a brief reminder on statistical mechanics that we need in this course, we investigate Eq. (2.1) a little bit more detail. For example, we note the factor $N!$ which stems from the indistinguishability of the particles (making the thermodynamic potential extensive), and the factor containing h which is there for dimensional reasons. It comes perhaps as a surprise to see a remnant of quantum mechanics in a classical mechanics. In the next section, we will show how Eq. (2.1) can be obtained from the quantum-mechanical partition function. People that are unfamiliar with quantum many-body theory can skip this section. For now, however, we stress that classical macroscopic observables do not depend on quantum mechanics, and h drops out from calculations.

2.2 The classical limit

As is derived in an introductory course of classical statistical mechanics, the quantum-mechanical canonical partition function is given by

$$Z(N, V, T) = \text{Tr}[e^{-\beta\hat{H}}] = \sum_{\nu} \langle \Psi_{\nu} | e^{-\beta\hat{H}} | \Psi_{\nu} \rangle = \sum_{\nu} e^{-\beta E_{\nu}}. \quad (2.6)$$

Here, $\text{Tr}[\dots]$ is a trace over a full set of states, which can be found by solving the equation $\hat{H}|\Psi_{\nu}\rangle = E_{\nu}|\Psi_{\nu}\rangle$, with \hat{H} the (quantum-mechanical) Hamiltonian. Note that $\{|\Psi_{\nu}\rangle\}$ forms a complete set spanning the N -particle Hilbert space \mathcal{H}_N (ν is here a multi-index enumerating the many-body wave functions). For illustration purposes, we consider spinless particles, for which we take for \hat{H}

$$\hat{H} = \sum_{i=1}^N \frac{\hat{\mathbf{p}}_i^2}{2m} + \sum_{i=1}^N V_{\text{ext}}(\hat{\mathbf{r}}_i) + \sum_{i=1}^N \sum_{j<i}^N v(|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|).$$

The momentum operators $\hat{\mathbf{p}}_i$ and position operators $\hat{\mathbf{r}}_i$ satisfy the canonical commutation relations $[\hat{\mathbf{r}}_i, \hat{\mathbf{p}}_i] = i\hbar\mathbf{I}$ for $i = 1, \dots, N$. Furthermore, we denote the position and momentum kets, which are eigenstates of the position and momentum operator, respectively. E.g., $\hat{\mathbf{r}}_i|\mathbf{r}_i\rangle = \mathbf{r}_i|\mathbf{r}_i\rangle$ and $\hat{\mathbf{p}}_i|\mathbf{p}_i\rangle = \mathbf{p}_i|\mathbf{p}_i\rangle$ for $i = 1, \dots, N$. Here $v(|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|)$ should be viewed as an "effective" interaction potential where electronic degrees of freedom are integrated out, so that we are only left with the degrees of freedom of the nuclei. See also Chapter 5.

From single-particle kets we can construct N -body kets using (tensor) product states. To rewrite Eq. (2.6) in terms of a trace over positions and momenta, we need the many-body position and momentum kets.

$$|\mathbf{r}_1, \dots, \mathbf{r}_N\rangle = \frac{1}{\sqrt{N!}} \sum_{P \in S_N} \zeta^P |\mathbf{r}_{P(1)}\rangle |\mathbf{r}_{P(2)}\rangle \dots |\mathbf{r}_{P(N)}\rangle,$$

with S_N the permutation group of N elements, and $\zeta^P = 1$ for identical bosons, and $\zeta^P = \text{sgn}(P)$ for identical fermions. The reader is invited to write the above expression for $N = 2$ for fermions and bosons to understand the notation. We recall that for one-body position kets, we have the properties,

$$\int d\mathbf{r} |\mathbf{r}\rangle \langle \mathbf{r}| = \mathbb{1}_1, \quad \langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}'),$$

with $\mathbb{1}_1$ the identity operator in the single-particle Hilbert space. The N -body generalisations are

$$\begin{aligned} \frac{1}{N!} \int d\mathbf{r}^N |\mathbf{r}_1, \dots, \mathbf{r}_N\rangle \langle \mathbf{r}_1, \dots, \mathbf{r}_N| &= \mathbb{1}_N, \\ \langle \mathbf{r}_1, \dots, \mathbf{r}_N | \mathbf{r}'_1, \dots, \mathbf{r}'_N \rangle &= \sum_{P \in S_N} \zeta^P \delta(\mathbf{r}_1 - \mathbf{r}'_{P(1)}) \dots \delta(\mathbf{r}_N - \mathbf{r}'_{P(N)}), \end{aligned} \quad (2.7)$$

with $\mathbb{1}_N$ the identity operator in the Hilbert space of properly symmetrised N -body wave functions. We obtain similarly many-body momentum kets $|\mathbf{p}_1, \dots, \mathbf{p}_N\rangle$ by replacing in above formulas \mathbf{r}_i by \mathbf{p}_i . Inserting the completeness relation (2.7) two times in Eq. (2.6) gives

$$\begin{aligned} Z(N, V, T) &= \sum_{\nu} \langle \Psi_{\nu} | \int d\mathbf{r}^N |\mathbf{r}_1, \dots, \mathbf{r}_N\rangle \langle \mathbf{r}_1, \dots, \mathbf{r}_N | e^{-\beta \hat{H}} \int d\mathbf{r}'^N |\mathbf{r}'_1, \dots, \mathbf{r}'_N\rangle \langle \mathbf{r}'_1, \dots, \mathbf{r}'_N | \Psi_{\nu} \rangle \\ &= \frac{1}{(N!)^2} \int d\mathbf{r}^N \int d\mathbf{r}'^N \langle \mathbf{r}_1, \dots, \mathbf{r}_N | e^{-\beta \hat{H}} | \mathbf{r}'_1, \dots, \mathbf{r}'_N \rangle \sum_{\nu} \langle \mathbf{r}'_1, \dots, \mathbf{r}'_N | \Psi_{\nu} \rangle \langle \Psi_{\nu} | \mathbf{r}_1, \dots, \mathbf{r}_N \rangle \\ &= \frac{1}{(N!)^2} \sum_{P \in S_N} \int d\mathbf{r}^N \int d\mathbf{r}'^N \langle \mathbf{r}_1, \dots, \mathbf{r}_N | e^{-\beta \hat{H}} | \mathbf{r}'_1, \dots, \mathbf{r}'_N \rangle \zeta^P \delta(\mathbf{r}_1 - \mathbf{r}'_{P(1)}) \dots \delta(\mathbf{r}_N - \mathbf{r}'_{P(N)}). \end{aligned}$$

Let us work out

$$\begin{aligned} & \int d\mathbf{r}'^N \sum_{P \in S_N} |\mathbf{r}'_1, \dots, \mathbf{r}'_N\rangle \zeta^P \delta(\mathbf{r}_1 - \mathbf{r}'_{P(1)}) \dots \delta(\mathbf{r}_N - \mathbf{r}'_{P(N)}) \quad (2.8) \\ &= \int d\mathbf{r}'^N \sum_{P \in S_N} \sum_{Q \in S_N} \zeta^P \zeta^Q |\mathbf{r}'_{Q(1)}\rangle |\mathbf{r}'_{Q(2)}\rangle \dots |\mathbf{r}'_{Q(N)}\rangle \delta(\mathbf{r}_1 - \mathbf{r}'_{P(1)}) \dots \delta(\mathbf{r}_N - \mathbf{r}'_{P(N)}) \\ &= \int d\mathbf{r}'^N \sum_{P \in S_N} \sum_{Q \in S_N} \zeta^P \zeta^Q |\mathbf{r}'_{QP^{-1}(1)}\rangle |\mathbf{r}'_{QP^{-1}(2)}\rangle \dots |\mathbf{r}'_{QP^{-1}(N)}\rangle \delta(\mathbf{r}_1 - \mathbf{r}'_1) \dots \delta(\mathbf{r}_N - \mathbf{r}'_N) \\ &= \int d\mathbf{r}'^N \sum_{P \in S_N} \sum_{Q \in S_N} \zeta^{QP^{-1}} |\mathbf{r}'_{QP^{-1}(1)}\rangle |\mathbf{r}'_{QP^{-1}(2)}\rangle \dots |\mathbf{r}'_{QP^{-1}(N)}\rangle \delta(\mathbf{r}_1 - \mathbf{r}'_1) \dots \delta(\mathbf{r}_N - \mathbf{r}'_N) \\ &= \int d\mathbf{r}'^N \sum_{P \in S_N} \sum_{R \in S_N} \zeta^R |\mathbf{r}'_{R(1)}\rangle |\mathbf{r}'_{R(2)}\rangle \dots |\mathbf{r}'_{R(N)}\rangle \delta(\mathbf{r}_1 - \mathbf{r}'_1) \dots \delta(\mathbf{r}_N - \mathbf{r}'_N) = N! |\mathbf{r}_1, \dots, \mathbf{r}_N\rangle. \end{aligned}$$

Therefore,

$$Z(N, V, T) = \frac{1}{N!} \int d\mathbf{r}^N \langle \mathbf{r}_1, \dots, \mathbf{r}_N | e^{-\beta \hat{H}} | \mathbf{r}_1, \dots, \mathbf{r}_N \rangle.$$

Using the identity $e^{\hat{A}\hat{B}} = e^{\hat{A} + \hat{B} + (1/2)[\hat{A}, \hat{B}] + \dots}$, we can write

$$e^{-\beta \hat{H}} = e^{-\beta \sum_i \hat{\mathbf{p}}_i^2 / (2m)} e^{-\beta [\sum_i V_{\text{ext}}(\hat{\mathbf{r}}_i) + \sum_i \sum_{j < i} \phi(|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|)]} + \mathcal{O}(\hbar),$$

we find

$$\begin{aligned} Z(N, V, T) &= \frac{1}{N!} \int d\mathbf{r}^N \langle \mathbf{r}_1, \dots, \mathbf{r}_N | e^{-\beta \sum_i \hat{\mathbf{p}}_i^2 / (2m)} e^{-\beta [\sum_i V_{\text{ext}}(\hat{\mathbf{r}}_i) + \sum_i \sum_{j < i} \phi(|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|)]} | \mathbf{r}_1, \dots, \mathbf{r}_N \rangle + \mathcal{O}(\hbar) \\ &= \frac{1}{N!} \int d\mathbf{r}^N e^{-\beta [\sum_i V_{\text{ext}}(\mathbf{r}_i) + \sum_i \sum_{j < i} \phi(|\mathbf{r}_i - \mathbf{r}_j|)]} \langle \mathbf{r}_1, \dots, \mathbf{r}_N | e^{-\beta \sum_i \hat{\mathbf{p}}_i^2 / (2m)} | \mathbf{r}_1, \dots, \mathbf{r}_N \rangle + \mathcal{O}(\hbar) \\ &= \frac{1}{(N!)^3} \int d\mathbf{r}^N \int d\mathbf{p}^N \int d\mathbf{p}'^N e^{-\beta [\sum_i V_{\text{ext}}(\mathbf{r}_i) + \sum_i \sum_{j < i} \phi(|\mathbf{r}_i - \mathbf{r}_j|)]} \langle \mathbf{r}_1, \dots, \mathbf{r}_N | \mathbf{p}_1, \dots, \mathbf{p}_N \rangle \\ & \quad \times \langle \mathbf{p}_1, \dots, \mathbf{p}_N | e^{-\beta \sum_i \hat{\mathbf{p}}_i^2 / (2m)} | \mathbf{p}'_1, \dots, \mathbf{p}'_N \rangle \langle \mathbf{p}'_1, \dots, \mathbf{p}'_N | \mathbf{r}_1, \dots, \mathbf{r}_N \rangle + \mathcal{O}(\hbar). \end{aligned}$$

We note that $\langle \mathbf{r} | \mathbf{p} \rangle = e^{i\mathbf{p} \cdot \mathbf{r} / \hbar} / (2\pi\hbar)^{3/2}$ (with Dirac constant $\hbar = h/(2\pi)$) and that

$$\langle \mathbf{r}_1, \dots, \mathbf{r}_N | \mathbf{p}_1, \dots, \mathbf{p}_N \rangle = \frac{1}{(2\pi\hbar)^{3N/2}} \sum_{P \in S_N} \zeta^P e^{i\mathbf{p}_1 \cdot \mathbf{r}_{P(1)}} \dots e^{i\mathbf{p}_N \cdot \mathbf{r}_{P(N)}},$$

we find using the same algebraic steps as in Eq. (2.8) that

$$\langle \mathbf{r}_1, \dots, \mathbf{r}_N | \mathbf{p}_1, \dots, \mathbf{p}_N \rangle \langle \mathbf{p}'_1, \dots, \mathbf{p}'_N | \mathbf{r}_1, \dots, \mathbf{r}_N \rangle = \frac{N!}{(2\pi\hbar)^{3N}} \sum_{P \in S_N} \zeta^P e^{i(\mathbf{p}_1 - \mathbf{p}'_1) \cdot \mathbf{r}_{P(1)}} \dots e^{i(\mathbf{p}_N - \mathbf{p}'_N) \cdot \mathbf{r}_{P(N)}}.$$

Doing the remaining algebraic steps in similar manner to perform the integral over \mathbf{p}^{iN} (giving an extra factor of $N!$), we find (omitting $\mathcal{O}(\hbar)$)

$$Z(N, V, T) = \frac{1}{N!h^{3N}} \int d\mathbf{p}^N \int d\mathbf{r}^N e^{-\beta H(\mathbf{p}^N, \mathbf{r}^N)}, \quad (2.9)$$

with H the classical Hamiltonian. One can generalise this calculation also to particles with internal degrees of freedom, from which we conclude that indeed Eq. (2.1) is the classical partition function with a prefactor that is consistent with the quantum-mechanical partition function (even in the presence of interactions and/or an external potential).

2.3 The virial expansion

Let us consider the classical Hamiltonian (2.2), for which we have found the classical partition function Eq. (2.9). The momentum part factorises and can be computed by the Gaussian integral $\int dx \exp(-\alpha x^2) = \sqrt{\pi/\alpha}$, for $\text{Re}(\alpha) > 0$, and we find

$$Z(N, V, T) = \frac{Q(N, V, T)}{N!\Lambda^{3N}}, \quad Q(N, V, T) = \int d\mathbf{r}^N e^{-\beta\Phi(\mathbf{R}^N)},$$

with $\Lambda = h(2\pi mk_{\text{B}}T)^{-1/2}$ the thermal de Broglie wavelength and $Q(N, V, T)$ is the so-called configurational integral. For example, for an ideal system in the absence of an external potential $\Phi = 0$ and $Q(N, V, T) = V^N$. We then obtain the Helmholtz free energy of an ideal gas using Eq. (2.3)

$$\beta f_{\text{id}}(\rho, T) = \frac{\beta F_{\text{id}}(N, V, T)}{V} = \rho[\log(\rho\Lambda^3) - 1], \quad (\text{ideal system}),$$

with $\rho = N/V$ the overall number density and f_{id} the Helmholtz free energy density of an ideal system. Furthermore, we used extensivity of F . We invite the reader to check that this free energy results in $\beta E = 3/2$, $\beta p = \rho$, and $\beta\mu = \log(\rho\Lambda^3)$ using thermodynamic relations.

For $\Phi \neq 0$, there are only few occasions where we can calculate $Q(N, V, T)$ analytically. We explore one such example in the problems. However, there are some approximative schemes that can be constructed when ρ is small for pair-wise interacting particles $\Phi(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j<i} \phi(r_{ij})$, with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Our scheme is most readily derived in the grand-canonical ensemble, with partition function (2.5)

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \frac{z^N}{N!} Q_N(V, T),$$

with $z = \exp(\beta\mu)/\Lambda^3$ the fugacity and we introduced the notation $Q_N(V, T) = Q(N, V, T)$. We will not express the grand potential Ω in terms of $Q_N(V, T)$ assuming implicitly that the Taylor expansion $\ln(1+x) = \sum_{n=0}^{\infty} (-1)^{n+1} x^n/n$ exists. Using Eq. (2.4), we define

$$\beta\Omega = -V \sum_{n=1}^{\infty} b_n z^n,$$

and we find for the first few coefficients,

$$b_1 = \frac{Q_1}{V}, \quad b_2 = \frac{Q_2 - Q_1^2}{2!V}, \quad b_3 = \frac{Q_3 - 3Q_2Q_1 + 2Q_1^3}{3!V}, \quad b_4 = \frac{Q_4 - 4Q_3Q_1 - 3Q_2^2 + 12Q_2Q_1^2 - 6Q_1^4}{4!V},$$

with $Q_1 = V$. In principle, it is possible to derive a general expression for the b_i coefficients, see e.g., the book of Pathria for a discussion. However, it will not lead to any additional physical

insights for our current purposes, so we will omit it here. Recall that $\Omega(\mu, V, T) = -p(\mu, T)V$ because of extensivity and the relation

$$\langle N \rangle = - \left(\frac{\partial \Omega(\mu, V, T)}{\partial \mu} \right)_{V, T} = -z \left(\frac{\partial \Omega(z, V, T)}{\partial z} \right)_{V, T},$$

that

$$\beta p(z, T) = \sum_{n=1}^{\infty} b_n z^n, \quad \rho(z, T) = \sum_{n=1}^{\infty} n b_n z^n.$$

Our goal now is to express p in terms of ρ . We expand $z = \sum_{n=1}^N a_n \rho^n$ and insert in the equation of $\rho(z, T)$. Equating both sides gives the relations for the first few coefficients

$$a_1 = 1, \quad a_2 = -2b_2, \quad a_3 = -3b_3 + 8b_2^2.$$

Inserting the expansion $\rho(z)$ in the equation for $p(z, T)$, we obtain the virial expansion of the pressure,

$$\beta p(\rho, T) = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots, \quad (2.10)$$

with first few coefficients $B_2(T) = -b_2$ and $B_3(T) = 4b_2^2 - 2b_3$. Explicitly writing out gives for the second virial coefficient

$$B_2(T) = -\frac{1}{2V} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \{ \exp[-\beta v(r_{12})] - 1 \} = -\frac{1}{2} \int d\mathbf{r} f_M(r),$$

where we used translational invariance in the second equality and we introduced the Mayer function $f_M(r) = \exp[-\beta v(r)] - 1$. That is why sometimes the virial expansion is also called the Mayer expansion. Furthermore, for r large $f_M(r) \sim -\beta v(r)$. Note that depending on the temperature dependence of $f_M(r)$, there is the possibility that $B_2(T)$ changes sign. We define the so-called Boyle temperature T_B as $B_2(T_B) = 0$. Furthermore, we find an expression for the third-virial coefficient,

$$B_3(T) = \frac{1}{3V} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 f_M(r_{12}) f_M(r_{13}) f_M(r_{23}).$$

Expressions for higher-order virial coefficients can be obtained with the recipe above.

We can also express the Helmholtz free energy in a virial expansion, which will turn out to be useful later. We write

$$f_{\text{ex}}(\rho, T) = \frac{F - F_{\text{id}}}{Vk_B T} = \sum_{n=2}^{\infty} C_n(T) \rho^n,$$

for the so called excess (i.e., over ideal) Helmholtz free energy density $f_{\text{ex}}(\rho, T)$. Using the thermodynamic relation

$$\beta p = - \left(\frac{\partial F}{\partial V} \right)_{N, T} = -\beta f + \rho \left(\frac{\partial \beta f}{\partial \rho} \right)_T,$$

and comparing with Eq. (2.10) gives $C_n = B_n/(n-1)$ for $n > 2$. Therefore, we have for the Helmholtz free energy density

$$f = \frac{\beta F}{V} = \rho [\log(\rho \Lambda^3) - 1] + B_2(T)\rho^2 + \frac{B_3(T)}{2}\rho^3 + \dots$$

It is interesting to note that $B_2(T)$ is only convergent for interaction potentials $\phi(r) \sim r^{-n}$ with $n > 3$. Therefore, Coulomb fluids and dipolar fluids consisting of point particles cannot

be treated in the virial expansion. An example of a “model” potential for which $B_2(T)$ is well defined, is the so-called Lennard-Jones¹ potential

$$v_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2.11)$$

Eq. (2.11) is a widely used model potential in classical fluids because it captures the Born repulsion and Pauli exclusion at short distances ($\sim r^{-12}$) and the van der Waals attraction ($\sim r^{-6}$) at larger distances. Here, ϵ is the “well depth”, and σ is a characteristic size. A simplification of the Lennard-Jones potential is the hard-core Yukawa potential

$$v_{\text{Y}}(r) = \begin{cases} \infty, & r < \sigma, \\ -\frac{\epsilon}{(r/\sigma)} \exp \left[-\lambda \left(\frac{r}{\sigma} - 1 \right) \right], & r > \sigma. \end{cases}$$

An even further simplification is the square-well potential

$$v_{\text{SW}}(r) = \begin{cases} \infty, & r < \sigma, \\ -\epsilon, & \sigma < r < \lambda\sigma, \\ 0, & r > \lambda\sigma. \end{cases}$$

Finally, one of the simplest model pair potentials is the hard-core or hard-sphere potential

$$v_{\text{HC}}(r) = \begin{cases} \infty, & r < \sigma, \\ 0, & r > \sigma. \end{cases}$$

Note that this potential ultimately stems from the Pauli exclusion principle. In the context of a hard-core potential, σ is called the hard-core diameter. For $v_{\text{HC}}(r)$ the virial coefficients $B_n(T)$ are analytically known up until $n = 4$,

$$B_2^{\text{HC}} = \frac{2}{3}\pi\sigma^3, \quad B_3^{\text{HC}} = \frac{5\pi^2}{18}\sigma^6, \quad B_4^{\text{HC}} = \left[-\frac{89}{280} + \frac{219\sqrt{2}}{2240\pi} + \frac{4131}{2240\pi} \arccos \left(\frac{1}{\sqrt{3}} \right) \right] (B_2^{\text{HC}})^3.$$

Furthermore, note that B_n^{HC} are independent of temperature. Higher-order virial coefficients can be computed numerically. To accurately describe the hard-sphere fluid up until the liquid-solid phase transition $\eta \approx 0.5$, with $\eta = (\pi/6)\sigma^3\rho$ the volume fraction, we need up until the eight virial coefficient. Numerically, we find

$$\frac{\beta p}{\rho} = 1 + 4\eta + 10\eta^2 + 18.365\eta^3 + 28.225\eta^4 + 39.74\eta^5 + 53.5\eta^6 + 70.8\eta^7 + \dots \approx 1 + \sum_{n=1}^{\infty} (n^2 + 3n)\eta^n.$$

In the last equality sign we made an approximation to the virial expansion for hard spheres. We can sum the resulting approximate geometric series, and find the so-called Carnahan-Starling (CS) equation of state,

$$\frac{\beta p_{\text{CS}}}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \quad (2.12)$$

with free energy

$$\frac{\beta F_{\text{CS}}}{N} = \log(\rho\Lambda^3) - 1 + \frac{4\eta - 3\eta^2}{(1 - \eta)^2}.$$

The CS free energy turns out to be a very good approximative equation of state. The deviations from computer simulations are at most 1% in the entire fluid range.

¹Although the name suggests that two people contributed in developing this model potential, it is actually named after one person. Namely, it has been devised by Sir John Edwards Lennard-Jones (1894-1954), who made important pioneering contributions to the development of modern computational chemistry.

2.4 Correlation functions in classical systems

We introduce the density operator

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i).$$

The corresponding one-point correlation function, is called the one-body density $\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle$. In the presence of $V_{\text{ext}}(\mathbf{r}) \neq 0$, $\rho(\mathbf{r})$ is spatially varying. However, for $V_{\text{ext}}(\mathbf{r}) = 0$ the system is translationally invariant and the one-body density is constant $\rho(\mathbf{r}) = \rho$. Furthermore, note the normalisation $\int d\mathbf{r} \rho(\mathbf{r}) = N$.

Similarly, we define the two-body density operator as

$$\hat{\rho}^{(2)}(\mathbf{r}, \mathbf{r}') = \sum_{i \neq j} \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j),$$

which naturally defines the two-body correlation function $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \langle \hat{\rho}^{(2)}(\mathbf{r}, \mathbf{r}') \rangle$, with normalisation $\int d\mathbf{r} \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') = N(N-1)$. For all suitable interaction potentials we have that $\rho^{(2)}(\mathbf{r}, \mathbf{r}') \rightarrow \rho(\mathbf{r})\rho(\mathbf{r}')$ for $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$. This motivates us to define the dimensionless correlation function

$$g(\mathbf{r}, \mathbf{r}') = \frac{\rho^{(2)}(\mathbf{r}, \mathbf{r}')}{\rho(\mathbf{r})\rho(\mathbf{r}')},$$

with $g(\mathbf{r}, \mathbf{r}') \rightarrow 1$ for $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$. In the absence of an external potential, translational and rotational invariance requires that $g(\mathbf{r}, \mathbf{r}') = g(|\mathbf{r} - \mathbf{r}'|)$. In this case $g(r)$ is called the radial distribution function or pair correlation function.

At this point it is good to recap some knowledge from elementary probability theory. For X and Y continuous stochastic variables with joint probability density $p(x, y)$ and marginal probability density functions $p_X(x) = \int_{-\infty}^{\infty} dy p(x, y)$ and $p_Y(y) = \int_{-\infty}^{\infty} dx p(x, y)$, the conditional probability density function of Y given that $X = x$ is $p(y|x) = p(x, y)/p_X(x)$. Because $\rho^{(2)}(\mathbf{r}, \mathbf{r}')/[N(N-1)]$ is the probability of finding of one particle at \mathbf{r} and another one at \mathbf{r}' , and $\rho(\mathbf{r})/N$ is the probability to find one particle at \mathbf{r} , it follows that $\rho(\mathbf{r})g(\mathbf{r}, \mathbf{r}')/(N-1)$ is the probability to find a particle at \mathbf{r} given that we know there is particle at \mathbf{r}' . In other words, for isotropic and translationally invariant systems, given a particle at the origin $4\pi r^2 \rho g(r) dr$ counts the number of particles between r and $r + dr$. In this way the first peak of $g(r)$ can be identified as a shell of nearest neighbours around a particle located in origin, the second peak to second nearest neighbours etc. The peaks have an exponentially decaying envelope because of particles becoming uncorrelated. Other properties of $g(r)$ are that $g(r) \approx 0$ for $r < \sigma$ due to the Pauli exclusion principle and that for an ideal gas of point particles $g(r) = 1$.

Using similar techniques as in Sec. 2.3, we find the low-density expansion of the radial distribution function,

$$g(r; \rho, T) = g^{(0)}(r; T) + \rho g^{(1)}(r; T) + \dots \quad (2.13)$$

where

$$g^{(0)}(r_{12}; T) = \exp[-\beta\phi(r_{12})], \quad g^{(1)}(r_{12}; T) = \exp[-\beta\phi(r_{12})] \int d\mathbf{r}_3 f_M(r_{13}) f_M(r_{32}). \quad (2.14)$$

At low densities, $g(r)$ is just the Boltzmann weight of the pair potential, which can be understood intuitively from the interpretation of $\rho g(r)$ as a conditional probability.

Another important correlation function is the density-density correlation function $G(\mathbf{r}, \mathbf{r}')$ defined as

$$G(\mathbf{r}, \mathbf{r}') = \langle \delta\hat{\rho}(\mathbf{r})\delta\hat{\rho}(\mathbf{r}') \rangle, \quad \delta\hat{\rho}(\mathbf{r}) = \hat{\rho}(\mathbf{r}) - \langle \hat{\rho}(\mathbf{r}) \rangle.$$

It is straightforward to show that $G(\mathbf{r}, \mathbf{r}') = \rho^{(2)}(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}') + \rho(\mathbf{r})\delta(\mathbf{r}' - \mathbf{r})$. For homogeneous systems we have $G(\mathbf{r}, \mathbf{r}') = G(\mathbf{r} - \mathbf{r}')$. In this case, we define the Fourier transform as

$$\tilde{G}(\mathbf{k}) = \int d\mathbf{r} G(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}, \quad G(\mathbf{r}) = \int \frac{d\mathbf{k}}{(2\pi)^3} \tilde{G}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}.$$

When the system is also isotropic $G(\mathbf{r}, \mathbf{r}') = G(|\mathbf{r} - \mathbf{r}'|)$, this defines the static structure factor $S(k)$ via $\tilde{G}(k) = \rho S(k)$. Note that $S(k)$ is dimensionless. It is possible to express $S(k)$ in terms of $g(r)$,

$$S(k) = 1 + \rho \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} [g(r) - 1] + (2\pi)^3 \delta(\mathbf{k}). \quad (2.15)$$

One can check that $S(k) \rightarrow 1$ as $k \rightarrow \infty$, and that for an ideal gas $S(k) = 1$. The first peak of $S(k)$ at $k^* \sim 2\pi/\sigma$ corresponds roughly to the first reciprocal lattice wave vector of the solid. Furthermore, we note that $S(k)$ can be experimentally measured using scattering experiments. In practice, this means we can neglect the last term in Eq. 2.15. For example, for an elastic scattering experiment with an incoming plane wave $\sim \exp(i\mathbf{q}_i \cdot \mathbf{r})$ and an outgoing wave $\sim \exp(i\mathbf{q}_o \cdot \mathbf{r})$, it turns out that the scattering amplitude is proportional to $S(k)$ with \mathbf{k} the momentum transferred to the sample. Here \mathbf{k} follows from momentum conservation $\hbar\mathbf{q}_o = \hbar(\mathbf{q}_i + \mathbf{k})$ and $|\mathbf{q}_i| = |\mathbf{q}_o|$.

2.5 From structure to thermodynamics

Besides providing a quantification for the local structure of a fluid, it turns out that the correlation functions from Sec. 2.4 determine the complete thermodynamics of the system. There are various ways to establish this connection. First, we focus on systems for which $\Phi(\mathbf{r}^N)$ only consists of pairwise-additive interaction potentials. Let us compute the internal energy of the system

$$\begin{aligned} U = \langle H \rangle &= \left\langle \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} \right\rangle + \left\langle \sum_{i=1}^N \sum_{j<i} v(|\mathbf{r}_i - \mathbf{r}_j|) \right\rangle \\ &= \frac{3}{2} N k_B T + \frac{1}{2} \left\langle \sum_{i \neq j} \sum_{j=1}^N \int d\mathbf{r} \int d\mathbf{r}' \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) v(|\mathbf{r} - \mathbf{r}'|) \right\rangle \\ &= \frac{3}{2} N k_B T + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') v(|\mathbf{r} - \mathbf{r}'|), \end{aligned}$$

where we used the equipartition theorem and the definition of $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$. The factor 1/2 occurs in the second line to avoid double counting. For homogeneous isotropic systems, we thus find the so-called *caloric route* to thermodynamics

$$\frac{U}{V} = \frac{3}{2} \rho k_B T + \frac{\rho^2}{2} \int d\mathbf{r} g(r) v(r).$$

Another relation can be obtained from the pressure. Using the fact that the system is ergodic, we can use the virial theorem from classical mechanics,

$$p = \rho k_B T - \frac{1}{3V} \left\langle \sum_{i=1}^N \sum_{j<i} \mathbf{r}_{ij} \cdot \frac{\partial \phi(r_{ij})}{\partial \mathbf{r}_{ij}} \right\rangle = \rho k_B T - \frac{1}{6V} \int d\mathbf{r} \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') (\mathbf{r} - \mathbf{r}') \cdot \frac{\partial v(|\mathbf{r} - \mathbf{r}'|)}{\partial (\mathbf{r} - \mathbf{r}')},$$

where we used the same steps as in deriving the caloric route. Again using that the system is homogeneous and isotropic, we find the *virial route* to thermodynamics,

$$p = \rho k_B T - \frac{\rho^2}{6} \int d\mathbf{r} r g(r) v'(r),$$

where we used that for radial symmetric functions F , that $\mathbf{r} \cdot \partial_{\mathbf{r}} F(r) = r F'(r)$, with prime denoting differentiation to the argument. We note that the caloric and virial routes can also be directly derived from the partition function of a pair-wise interacting classical system. We will explore this in the problems. Furthermore, note that the caloric and virial route are exact for pair-wise interacting systems.

The final route to thermodynamic is valid for arbitrary $\Phi(\mathbf{r}^N)$, which might also include three-body interactions. We switch to the grand-canonical ensemble, and denote the classical trace as

$$\text{Tr}_{\text{cl}}(\dots) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int d\mathbf{p}^N \int d\mathbf{r}^N (\dots). \quad (2.16)$$

In this notation, the grand-canonical partition function is $\Xi(\mu, V, T) = \text{Tr}_{\text{cl}}\{\exp[\beta(\mu N - H_N)]\}$, with H_N the N -particle classical Hamiltonian. The probability distribution function in the grand canonical ensemble is

$$f_N(\mathbf{p}^N, \mathbf{r}^N; N) = \frac{1}{\Xi} \exp[\beta(\mu N - H_N)].$$

Note that $\text{Tr}_{\text{cl}}(f_N) = 1$ as is required for probability distribution functions. Grand-canonical averages are given by

$$\langle \dots \rangle = \text{Tr}_{\text{cl}}[f_N(\dots)],$$

From the context it will be clear whether we mean canonical or grand-canonical ensemble averages. In the grand canonical ensemble the one-body and two-body density operators depends on the number of particles and, therefore, have normalisations

$$\int d\mathbf{r} \rho(\mathbf{r}) = \int d\mathbf{r} \langle \hat{\rho}(\mathbf{r}) \rangle = \langle N \rangle, \quad \int d\mathbf{r} \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r} \int d\mathbf{r}' \langle \hat{\rho}^{(2)}(\mathbf{r}, \mathbf{r}') \rangle = \langle N^2 \rangle - \langle N \rangle.$$

From these properties, we find that in the grand-canonical ensemble,

$$\int d\mathbf{r} \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') = \langle N^2 \rangle - \langle N \rangle^2. \quad (2.17)$$

Our goal is now to relate the number fluctuations to a thermodynamic quantity. We recall that for a uniform fluid, from the definition of the grand-canonical average we have for $\alpha = 0, 1, 2, \dots$

$$\begin{aligned} \langle N^\alpha \rangle &= \text{Tr}_{\text{cl}}(f_N N) = \frac{1}{\Xi} \text{Tr}_{\text{cl}}\{N^\alpha \exp[\beta(\mu N - H_N)]\} = \frac{1}{\Xi} \text{Tr}_{\text{cl}}\left\{\frac{\partial^\alpha}{\partial(\beta\mu)^\alpha} \exp[\beta(\mu N - H_N)]\right\} \\ &= \frac{1}{\Xi} \frac{\partial^\alpha}{\partial(\beta\mu)^\alpha} \text{Tr}_{\text{cl}}\{\exp[\beta(\mu N - H_N)]\} = \frac{1}{\Xi} \left(\frac{\partial^\alpha \Xi}{\partial(\beta\mu)^\alpha}\right)_{V,T}, \end{aligned}$$

where we used that the series in Eq. (2.16) is uniform convergent. We conclude that

$$\langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\Xi} \left(\frac{\partial^2 \Xi}{\partial(\beta\mu)^2}\right)_{V,T} - \frac{1}{\Xi^2} \left(\frac{\partial \Xi}{\partial(\beta\mu)}\right)_{V,T}^2 = \left(\frac{\partial^2 \ln \Xi}{\partial(\beta\mu)^2}\right)_{V,T} = \left(\frac{\partial \langle N \rangle}{\partial(\beta\mu)}\right)_{V,T}.$$

Furthermore, we have the Maxwell relation

$$\left(\frac{\partial p}{\partial \mu}\right)_{V,T} = - \left(\frac{\partial^2 \Omega}{\partial \mu \partial V}\right)_T = - \left(\frac{\partial^2 \Omega}{\partial V \partial \mu}\right)_T = \left(\frac{\partial \langle N \rangle}{\partial V}\right)_{\mu,T} = \rho.$$

Combining these two results, we have

$$\langle N^2 \rangle - \langle N \rangle^2 = V \left(\frac{\partial \rho}{\partial(\beta\mu)} \right)_T = V \left(\frac{\partial \rho}{\partial(\beta\mu)} \right)_T = V \left(\frac{\partial \rho}{\partial p} \right)_T \left(\frac{\partial p}{\partial(\beta\mu)} \right)_T = k_B T \langle N \rangle \left(\frac{\partial \rho}{\partial p} \right)_T.$$

We recall the definition of the isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{N,T} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T, \quad (2.18)$$

and we conclude that

$$\langle N^2 \rangle - \langle N \rangle^2 = \rho k_B T \langle N \rangle \kappa_T.$$

Combining with Eq. (2.17) and using that the system is homogeneous and isotropic, gives the *compressibility sum rule*

$$\int d\mathbf{r} G(r) = \rho^2 k_B T \kappa_T. \quad (2.19)$$

This general exact result is an example of a susceptibility sum rule. We can express Eq. (2.19) in terms of the radial distribution function,

$$1 + \rho \int d\mathbf{r} [g(r) - 1] = \rho k_B T \kappa_T. \quad (2.20)$$

Eq. (2.20) is also known as the *compressibility route* to thermodynamics, and is more general than the virial and caloric routes. Note that $\lim_{k \rightarrow 0} S(k) = \rho k_B T \kappa_T$ which follows from Eq. (2.15) when neglecting the delta function contribution.

2.6 The Ornstein-Zernike (OZ) integral equation

Now that we have discussed several properties of $g(r)$ and some applications, it is necessary that we have some tools to compute it. In Eqs. (2.13) and (2.14), we have discussed how to compute $g(r)$ in terms of a density expansion. Such virial expansions are, however, of limited use when we are interested in dense fluids. We introduce the *indirect correlation function* $h(r) = g(r) - 1$, which vanishes when particles become uncorrelated. It turns out that $h(r)$ satisfies the celebrated OZ integral equation

$$h(r) = c(r) + \rho \int d\mathbf{r}' c(|\mathbf{r} - \mathbf{r}'|) h(r'), \quad (2.21)$$

which we will derive in the next chapter using density functional theory. We have introduced the direct correlation function $c(r)$, which for now can be seen as an auxiliary correlation function, defined by the OZ equation. The name comes from the fact that in some sense $c(r)$ is more directly related to $v(r)$ as can be seen from the asymptotic behaviour, $c(r) \sim -\beta v(r)$ as $r \rightarrow \infty$ when the fluid is not close to the critical point. Unlike $h(r)$ it lacks the presence of oscillations. When $c(r)$ is known, we can compute $h(r)$.

Using the definitions of the Fourier transform, Eq. (2.21) becomes

$$\tilde{h}(k) = \frac{\tilde{c}(k)}{1 - \rho \tilde{c}(k)},$$

and from the definition of $S(k)$, which can be expressed as $S(k) = 1 + \rho \tilde{h}(k)$, we find

$$S(k) = \frac{1}{1 - \rho \tilde{c}(k)},$$

giving an additional interpretation of the direct correlation function.

For now, to compute $h(r)$ from $c(r)$, we need an additional relation, called the closure relation. Because there is no exact formulation of such a closure relation, we need to resort to approximations. The accuracy of the approximations can be assessed by comparing, e.g., to computer simulations. We list a few examples of approximative closure relations below.

- In the random phase approximation (RPA), we assume that for all r the direct correlation function takes its asymptotic form, i.e. $c_{\text{RPA}}(r) = -\beta v(r)$. This approximation turns out to be accurate for fluids consisting of particles with soft cores (e.g., liquid metals, polymers).
- The mean-spherical approximation (MSA) is an extension of the RPA approximation, but now includes the effect of a hard-core together with a long-ranged tail. For example, when $v(r) = \infty$ for $r < \sigma$ and $v(r) = \varphi(r)$ for $r > \sigma$. In this case, the MSA approximation is,

$$g_{\text{MSA}}(r) = 0, \quad (r < \sigma); \quad c(r) = -\beta v(r), \quad (r > \sigma).$$

The MSA approximation often allows for analytical results.

- In the hyper-netted chain (HNC) approximation, we use the approximation

$$c_{\text{HNC}}(r) = g_{\text{HNC}}(r) - 1 - \ln[g_{\text{HNC}}(r)] - \beta v(r).$$

This scheme turns out to be accurate for systems with long-ranged potentials, like the one-component plasma (OCP).

- In the Percus-Yevick (PY) approximation, we use

$$c_{\text{PY}}(r) = \{1 - \exp[\beta v(r)]\} g_{\text{PY}}(r),$$

which turns out to be an excellent approximation for hard spheres. Later, we will give a systematic derivation of the PY approximation. Note that for hard spheres the PY approximation is the same as the MSA.

In fact, it turns out that one can derive an analytical expression for $c(r)$ within the PY approximation. We find

$$c_{\text{PY}}(r) = \begin{cases} \frac{-(1+2\eta)^2 + 6\eta(1+\frac{1}{2}\eta)^2 \left(\frac{r}{\sigma}\right) - \frac{1}{2}\eta(1+2\eta)^2 \left(\frac{r}{\sigma}\right)^3}{(1-\eta)^4}, & r < \sigma, \\ 0, & r > \sigma. \end{cases}$$

It is straightforward to Fourier transform this expression, and therefore, determine $S(k)$. However, to obtain $g(r)$, we need to resort to numerical calculations. It turns out that the PY approximation is quantitative in the entire fluid regime up to $\eta \approx 0.494$. Above this volume fraction, the hard-sphere fluid freezes. Using $g_{\text{PY}}(r)$, we can obtain the equation of state using either the compressibility route (c) or the virial route (v), and we find

$$\frac{\beta p_c}{\rho} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3}, \quad \frac{\beta p_v}{\rho} = \frac{1 + 2\eta + 3\eta^2}{(1 - \eta)^2}.$$

It can be checked that both routes are consistent up until the third virial coefficient. Deviations occur from the fourth virial coefficient and higher. The inconsistency arises from the PY approximation, one would obtain a fully consistent result if an exact closure was used. Interestingly, we retrieve the CS equation of state Eq. (2.12) by a suitable linear combination of the above result, $p_{\text{CS}} = (2p_c + p_v)/3$. It turns out that for dense fluids, the attractions give rise to a $g(r)$ that is almost indistinguishable from the hard-sphere radial distribution function. Unlike dilute systems, the correlations in a dense fluid are thus mainly determined by the short-range repulsions.

2.7 Multi-component systems

The concepts of this chapter up until now focused on one-component systems. It is, however, straightforward to generalise to multi-component systems. Suppose we have N_α particles of species $\alpha = 1, \dots, s$. The canonical partition function becomes

$$Z(N_1, \dots, N_s, V, T) = \prod_{\alpha=1}^s \left(\int \frac{d\mathbf{r}_{(\alpha)}^{N_\alpha}}{N_\alpha! \Lambda_\alpha^{3N_\alpha}} \right) \exp \left[-\beta \Phi \left(\mathbf{r}_{(1)}^{N_1}, \dots, \mathbf{r}_{(s)}^{N_s} \right) \right],$$

with $\mathbf{r}_{(\alpha)}^{N_\alpha} = (\mathbf{r}_1^{(\alpha)}, \dots, \mathbf{r}_{N_\alpha}^{(\alpha)})$, Λ_α the thermal de Broglie wavelength of a particle of species α . Like usual, the Helmholtz free energy is $\beta F(N_1, \dots, N_s, V, T) = -\log Z(N_1, \dots, N_s, V, T)$. If we concentrate only on pair interactions, with pair interaction potential between particles of species α and β with separation vector \mathbf{r} , given by $\phi_{\alpha\beta}(\mathbf{r})$, we find the generalisation of the virial expansion

$$\frac{\beta F}{V} = \sum_{\alpha=1}^s \rho_\alpha [\log(\rho_\alpha \Lambda_\alpha^3) - 1] + \sum_{\alpha, \beta} B_2^{(\alpha\beta)} \rho_\alpha \rho_\beta + \frac{1}{2} \sum_{\alpha, \beta, \gamma} B_3^{(\alpha\beta\gamma)} \rho_\alpha \rho_\beta \rho_\gamma + \dots,$$

with $\rho_\alpha = N_\alpha/V$. For example, the second virial coefficient for a multi-component system is given by

$$B_2^{(\alpha\beta)}(T) = -\frac{1}{2} \int d\mathbf{r} \{ \exp[-\beta v_{\alpha\beta}(\mathbf{r})] - 1 \}.$$

The multicomponent generalisations of the density operator and two-body density operator are

$$\hat{\rho}_\alpha(\mathbf{r}) = \sum_{i=1}^{N_\alpha} \delta(\mathbf{r} - \mathbf{r}_i^{(\alpha)}),$$

and we define the density-density correlation function as

$$G_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \langle \delta \hat{\rho}_\alpha(\mathbf{r}) \delta \hat{\rho}_\beta(\mathbf{r}') \rangle,$$

which defines the partial structure factor $S_{\alpha\beta}(\mathbf{k})$ for homogeneous and isotropic fluids via $\tilde{G}_{\alpha\beta}(\mathbf{k}) = \rho S_{\alpha\beta}(\mathbf{k})$ with $\rho = N/V$ the overall average density where $N = \sum_{\alpha=1}^s N_\alpha$. We define the two-body density operator as

$$\hat{\rho}_{\alpha\beta}^{(2)}(\mathbf{r}, \mathbf{r}') = \delta_{\alpha\beta} \sum_{j \neq i} \sum_{i=1}^{N_\alpha} \delta(\mathbf{r} - \mathbf{r}_i^{(\alpha)}) \delta(\mathbf{r}' - \mathbf{r}_j^{(\alpha)}) + (1 - \delta_{\alpha\beta}) \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \delta(\mathbf{r} - \mathbf{r}_i^{(\alpha)}) \delta(\mathbf{r}' - \mathbf{r}_j^{(\beta)}).$$

Denoting $\rho_\alpha(\mathbf{r}) = \langle \hat{\rho}_\alpha(\mathbf{r}) \rangle$ and $\rho_{\alpha\beta}^{(2)}(\mathbf{r}, \mathbf{r}') = \langle \hat{\rho}_{\alpha\beta}^{(2)}(\mathbf{r}, \mathbf{r}') \rangle$, we define

$$g_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \frac{\rho_{\alpha\beta}^{(2)}(\mathbf{r}, \mathbf{r}')}{\rho_\alpha(\mathbf{r}) \rho_\beta(\mathbf{r}')},$$

which for homogeneous and isotropic mixtures defines the radial distribution function $g_{\alpha\beta}(r) = g_{\beta\alpha}(r)$ of a multi-component system. Note that $4\pi r^2 \rho_\alpha g_{\alpha\beta}(r) dr$ counts the number of particles of type α in a range r to $r + dr$ given a reference particle of type β in the origin. The indirect correlation function defined by $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$ satisfies the multi-component OZ equation,

$$h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \sum_{\lambda=1}^s \rho_\lambda \int d\mathbf{r}' c_{\alpha\lambda}(|\mathbf{r} - \mathbf{r}'|) h_{\lambda\beta}(r').$$

Chapter 3

Classical density functional theory

3.1 Construction of the density functional

In the previous chapter, we have mainly looked at situations where the one-particle density is constant ($V_{\text{ext}}(\mathbf{r}) = 0$). Here, we will consider the situation when $V_{\text{ext}}(\mathbf{r}) \neq 0$. In this case we have an inhomogeneous fluid where the density is spatially varying. Such systems are well described using density functional theory (DFT), and in this Chapter we will set up the formalism of this method. We will use DFT to describe inhomogeneous hard-sphere fluids from very dilute to dense systems up until the crystallisation transition. In later chapters, we will focus on further applications of DFT.

We will work in the grand-canonical ensemble, and we use the same notation as in Sec. 2.5. Consider the combination $u(\mathbf{r}) = \mu - V_{\text{ext}}(\mathbf{r})$, which is known as the *intrinsic chemical potential*. The grand potential can be viewed as a *functional* of $u(\mathbf{r})$, i.e. $\Omega = \Omega[u]$, given by

$$\exp(-\beta\Omega[u]) = \sum_{n=0}^{\infty} \frac{1}{N! \Lambda^{3N}} \int d\mathbf{r}^N \exp \left\{ -\beta \left[\Phi(\mathbf{r}^N) - \int d\mathbf{r} u(\mathbf{r}) \hat{\rho}(\mathbf{r}) \right] \right\}. \quad (3.1)$$

Explicitly, we find by functional differentiation that

$$\rho(\mathbf{r}) = -\frac{\delta\Omega[u]}{\delta u(\mathbf{r})}. \quad (3.2)$$

Because $\rho(\mathbf{r})$ can be obtained from a functional differentiation of $\Omega[u]$, clearly it means that it can be viewed also as a functional of $V_{\text{ext}}(\mathbf{r})$. Generalizing the Legendre transformation to functionals, we define the intrinsic Helmholtz free-energy functional

$$\mathcal{F}[\rho] = \Omega[u] - \int d\mathbf{r} u(\mathbf{r}) \frac{\delta\Omega[u]}{\delta u(\mathbf{r})} = \Omega[u] + \int d\mathbf{r} \rho(\mathbf{r}) [\mu - V_{\text{ext}}(\mathbf{r})]$$

Note that we retrieve the bulk result in the limit $V_{\text{ext}}(\mathbf{r}) \rightarrow 0$, with $\rho(\mathbf{r}) \rightarrow \langle N \rangle / V$. Alternatively, we can write this functional as an ensemble average

$$\mathcal{F}[\rho] = \langle K_N + \Phi_N + k_B T \ln f_N \rangle = \text{Tr}_{\text{cl}}(K_N + \Phi_N + k_B T \ln f_N), \quad (3.3)$$

with K_N the N -particle kinetic energy, Φ_N the N -particle interaction potential (*excluding* the external potential), and f_N the N -particle distribution function.

In the density-functional approach, we focus purely on functionals of $\rho(\mathbf{r})$ instead of $u(\mathbf{r})$. One can prove the not so obvious result that for a given Φ_N and fixed μ and T that there is a unique $V_{\text{ext}}(\mathbf{r})$ that gives rise to a specific density profile $\rho(\mathbf{r})$. Because f_N is a functional of $V_{\text{ext}}(\mathbf{r})$, and therefore any quantity which for given Φ_N , T , and μ , is fully determined by f_N is necessarily a functional of $\rho(\mathbf{r})$ and the specific functional dependence is independent of $V_{\text{ext}}(\mathbf{r})$. From Eq. (3.3) it follows that $\mathcal{F}[\rho]$ is a unique functional of $\rho(\mathbf{r})$ and has the same form for *every* external potential. Let us formalise the above.

Lemma 1. Let f be a phase space probability density function with $\text{Tr}_{\text{cl}} f = 1$. We define the functional

$$\Omega[f] = \text{Tr}_{\text{cl}} f (H_N - \mu N + k_B T \ln f),$$

then $\Omega[f] \geq \Omega[f_N]$.

Proof. We recall the definition of $f_N = \exp[\beta(\mu N - H_N)]/\Xi$. We find that $\Omega[f_N] = -k_B T \ln \Xi =: \Omega$, with Ω the equilibrium grand potential. We conclude that $H_N - \mu N = -k_B T \ln(f_N \Xi)$. Using this relation and that $\text{Tr}_{\text{cl}} f = 1$, we conclude that

$$\Omega[f] = k_B T \text{Tr}_{\text{cl}} (f \ln f - f \ln f_N) + \Omega[f_N].$$

Rearranging this expression, we find

$$\Omega[f] - \Omega[f_N] = k_B T \text{Tr}_{\text{cl}} f_N \left(\frac{f}{f_N} \ln \frac{f}{f_N} \right) = k_B T \text{Tr}_{\text{cl}} f_N \left(\frac{f}{f_N} \ln \frac{f}{f_N} - \frac{f}{f_N} + 1 \right),$$

where in the last equality we used that $\text{Tr}_{\text{cl}} f = \text{Tr}_{\text{cl}} f_N = 1$. Note that f and f_N are positive phase space functions (as they are probability densities), and using the inequality $x \ln x \geq x - 1$ for $x > 0$, we conclude that $\Omega[f] - \Omega[f_N] \geq 0$, which completes the proof. \square

Using this lemma, we can prove the theorem

Theorem 1. For given Φ_N , T , and μ , the quantity $\mathcal{F}[\rho]$ is a unique functional of the equilibrium density $\rho(\mathbf{r})$.

Proof. Assume there is an external potential $V'_{\text{ext}}(\mathbf{r}) \neq V_{\text{ext}}(\mathbf{r})$ that gives rise to the same $\rho(\mathbf{r})$. We define $V_N = \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i)$ and $V'_N = \sum_{i=1}^N V'_{\text{ext}}(\mathbf{r}_i)$. We define the Hamiltonians

$$H_N = K_N + \Phi_N + V_N, \quad H'_N = K_N + \Phi_N + V'_N,$$

with corresponding equilibrium density distribution functions $f_N \neq f'_N$

$$f_N = \exp[\beta(\mu N - H_N)]/\Xi, \quad f'_N = \exp[\beta(\mu N - H'_N)]/\Xi'.$$

The corresponding grand potential to f'_N is defined as Ω' , and using the definition,

$$\Omega' := \Omega[f'_N] = \text{Tr}_{\text{cl}} f'_N (H'_N - \mu N + k_B T \ln f'_N) < \text{Tr}_{\text{cl}} f_N (H'_N - \mu N + k_B T \ln f_N), \quad (3.4)$$

where in the last step we used Lemma 1 for Hamiltonian H'_N . Using that $H'_N = H_N + V'_N - V_N$, we find that

$$\text{Tr}_{\text{cl}} f_N (H'_N - \mu N + k_B T \ln f_N) = \Omega + \text{Tr}_{\text{cl}} f_N (V'_N - V_N).$$

Insertion in Eq. (3.4) gives

$$\Omega' < \Omega + \int d\mathbf{r} \rho(\mathbf{r}) [V'_{\text{ext}}(\mathbf{r}) - V_{\text{ext}}(\mathbf{r})]. \quad (3.5)$$

Here we used that

$$\text{Tr}_{\text{cl}} f_N V_N = \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) \text{Tr}_{\text{cl}} [\hat{\rho}(\mathbf{r}) f_N] = \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}). \quad (3.6)$$

Using similar arguments, we find that

$$\Omega < \Omega' + \int d\mathbf{r} \rho(\mathbf{r}) [V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})]. \quad (3.7)$$

Addition of Eqs. (3.5) and (3.7) results in $\Omega + \Omega' < \Omega' + \Omega$. This is a contradiction, from which we conclude that $V_{\text{ext}}(\mathbf{r}) = V'_{\text{ext}}(\mathbf{r})$. In other words there is a unique $V_{\text{ext}}(\mathbf{r})$ that determines $\rho(\mathbf{r})$ which then fixes f_N . Because $\mathcal{F}[\rho]$ can be expressed as Eq. (3.3), we have completed the proof. \square

Let us now consider the functional

$$\Omega_V[\tilde{\rho}] = \mathcal{F}[\tilde{\rho}] - \int d\mathbf{r} u(\mathbf{r})\tilde{\rho}(\mathbf{r}), \quad (3.8)$$

with $\tilde{\rho}(\mathbf{r})$ some density profile (not necessarily the equilibrium one). This functional gives rise to an important variational principle.

Theorem 2. *Let $\Omega_V[\tilde{\rho}]$ be the functional defined in Eq. (3.8). Then*

$$\left. \frac{\delta\Omega_V[\tilde{\rho}]}{\delta\tilde{\rho}(\mathbf{r})} \right|_{\tilde{\rho}=\rho} = 0, \quad \Omega_V[\rho] = \Omega.$$

In other words, when $\tilde{\rho}(\mathbf{r})$ equals the equilibrium density profile $\rho(\mathbf{r})$, then Ω_V reduces to the equilibrium grand potential. Furthermore, Ω is the minimum value of $\Omega_V[\tilde{\rho}]$.

Proof. The assertion that $\Omega_V[\rho] = \Omega$ follows from Eq. (3.3) and manipulations like in Eq. (3.6). Explicitly,

$$\Omega_V[\rho] = \mathcal{F}[\rho] - \int d\mathbf{r} u(\mathbf{r})\rho(\mathbf{r}) = \text{Tr}_{\text{cl}} f_N (H_N - V_N + k_B T \ln f_N - \mu N + V_N) = \Omega[f_N] = \Omega. \quad (3.9)$$

For the other assumption, we assume the existence of a different density profile $\rho'(\mathbf{r})$ for a given $V_{\text{ext}}(\mathbf{r})$ and Hamiltonian H_N . We denote the associated probability density with $f'[\rho'(\mathbf{r})]$ where $\text{Tr}_{\text{cl}} f' = 1$. Then

$$\Omega[f'] = \text{Tr}_{\text{cl}} f' (H_N - \mu N + k_B T \ln f') = \mathcal{F}[\rho'] - \int d\mathbf{r} u(\mathbf{r})\rho'(\mathbf{r}) =: \Omega_V[\rho']. \quad (3.10)$$

Here, we assumed the existence of another external potential $V'_{\text{ext}}(\mathbf{r})$ that would give rise to an equilibrium density $\rho'(\mathbf{r})$ in order that f' exists. This ensures the existence of $\mathcal{F}[\rho']$. Using Lemma 1, it follows that $\Omega[f'] > \Omega[f_N]$ and thus from Eqs. (3.9) and (3.10) that $\Omega_V[\rho] < \Omega_V[\rho']$. \square

The name intrinsic Helmholtz free energy functional is now clear. Namely, we have for the total Helmholtz free energy the relation

$$F(N, V, T) = \Omega(\mu, V, T) + \mu \int d\mathbf{r} \rho(\mathbf{r}) = \mathcal{F}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}),$$

i.e. it is the part contributing to the Helmholtz free energy that does not depend explicitly on the external potential. Therefore, the variational principle in Theorem 2, leads to constancy of the chemical potential μ throughout the inhomogeneous fluid,

$$\mu = V_{\text{ext}}(\mathbf{r}) + \frac{\delta\mathcal{F}[\rho]}{\delta\rho(\mathbf{r})}. \quad (3.11)$$

Sometimes, $\delta\mathcal{F}/\delta\rho(\mathbf{r})$ is called the intrinsic chemical potential, and generally it is not a local function of $\rho(\mathbf{r})$.

In the case of an ideal gas $\Phi_N = 0$, we can explicitly calculate the intrinsic Helmholtz functional,

$$\beta\mathcal{F}_{\text{id}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \{\ln[\rho(\mathbf{r})\Lambda^3] - 1\}.$$

Note that this functional of the local form $\int d\mathbf{r} f_{\text{id}}(\rho(\mathbf{r}))$, with $f_{\text{id}}(\rho)$ the free energy density of a bulk ideal gas.

3.2 Hierarchies of correlation functions

Recall the definition of $\Omega[u]$, see Eq. (3.1) and that $\rho(\mathbf{r}) = -\delta\beta\Omega/\delta\beta u(\mathbf{r})$. Further functional differentiation of $\Omega[u]$ produces the density-density correlation function (see Chapter 2),

$$G(\mathbf{r}, \mathbf{r}') = -\frac{\delta^2\beta\Omega[u]}{\delta\beta u(\mathbf{r})\delta\beta u(\mathbf{r}')}. \quad (3.12)$$

Higher-order correlation functions can be obtained in a similar matter,

$$G^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \langle \delta\hat{\rho}(\mathbf{r}_1)\dots\delta\hat{\rho}(\mathbf{r}_n) \rangle = -\frac{\delta^n\beta\Omega[u]}{\delta\beta u(\mathbf{r}_1)\dots\delta\beta u(\mathbf{r}_n)}, \quad n \geq 2,$$

with $G^{(2)}(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}, \mathbf{r}')$. Clearly, $\Omega[u]$ is a generating functional for density-density correlation functions.

A second hierarchy of correlation functions can be obtained from $\mathcal{F}[\rho]$. We define the excess (over ideal) Helmholtz free-energy functional as $\mathcal{F}_{\text{ex}}[\rho] = \mathcal{F}[\rho] - \mathcal{F}_{\text{id}}[\rho]$. This functional generates the direct correlation functions defined by

$$c^{(1)}(\mathbf{r}) = -\frac{\delta\beta\mathcal{F}_{\text{ex}}[\rho]}{\delta\rho(\mathbf{r})}, \quad c^{(2)}(\mathbf{r}, \mathbf{r}') = -\frac{\delta^2\beta\mathcal{F}_{\text{ex}}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}. \quad (3.13)$$

Note that from the definition we have that $c^{(2)}(\mathbf{r}, \mathbf{r}') = c^{(2)}(\mathbf{r}', \mathbf{r})$. Higher order direct correlation functions can be obtained via

$$c^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = -\frac{\delta^n\beta\mathcal{F}_{\text{ex}}[\rho]}{\delta\rho(\mathbf{r}_1)\dots\delta\rho(\mathbf{r}_n)}.$$

We can explicitly write down, using Eq. (3.11)

$$c^{(1)}(\mathbf{r}) = \ln[\rho(\mathbf{r})\Lambda^3] - \beta u(\mathbf{r}). \quad (3.14)$$

We can reexpress this result into $\rho(\mathbf{r})\Lambda^3 = \exp[\beta u(\mathbf{r}) + c^{(1)}(\mathbf{r})]$, which shows that $-k_{\text{B}}Tc^{(1)}(\mathbf{r})$ acts as an effective one-body potential that determines the equilibrium density profile. A further functional differentiation of Eq. (3.14) gives

$$c^{(2)}(\mathbf{r}, \mathbf{r}') = \frac{\delta(\mathbf{r} - \mathbf{r}')}{\rho(\mathbf{r})} - \beta \frac{\delta u(\mathbf{r})}{\delta\rho(\mathbf{r}')} = \frac{\delta(\mathbf{r} - \mathbf{r}')}{\rho(\mathbf{r})} - G^{-1}(\mathbf{r}, \mathbf{r}')$$

The latter equality follows from Eqs. (3.2) and (3.12). Here the functional inverse is defined as

$$\int d\mathbf{r}'' G(\mathbf{r}, \mathbf{r}'')G^{-1}(\mathbf{r}'', \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (3.15)$$

Compare this definition with the inverse of a matrix \mathbf{A} , $A_{ik}A_{kj}^{-1} = \delta_{ij}$. We see that the two-body direct correlation function is roughly the functional inverse of the density-density correlation function. Using that $G(\mathbf{r}, \mathbf{r}') = \rho^{(2)}(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}') + \rho(\mathbf{r})\delta(\mathbf{r}' - \mathbf{r})$ and the definition of the inhomogeneous indirect correlation function $h(\mathbf{r}, \mathbf{r}')$,

$$\rho(\mathbf{r})\rho(\mathbf{r}')h(\mathbf{r}, \mathbf{r}') = \rho^{(2)}(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}'),$$

we find the inhomogeneous Ornstein-Zernike relation,

$$h(\mathbf{r}, \mathbf{r}') = c^{(2)}(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}'' h(\mathbf{r}, \mathbf{r}'')\rho(\mathbf{r}'')c^{(2)}(\mathbf{r}'', \mathbf{r}'),$$

which reduces to (bulk) OZ equation for $V_{\text{ext}}(\mathbf{r}) \rightarrow 0$ that was posed without derivation in Sec. 2.6. The OZ equation is thus a natural consequence of having two generating functionals $\Omega_V[u]$ and $\mathcal{F}[\rho]$ that are linked via a Legendre transform. That is, Eq. (3.15) is equivalent to

$$\int d\mathbf{r}'' \frac{\delta^2\mathcal{F}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}'')} \frac{\delta^2\Omega_V[u]}{\delta u(\mathbf{r}'')\delta u(\mathbf{r}')} = -\delta(\mathbf{r} - \mathbf{r}').$$

In field-theoretical treatments of statistical mechanics the hierarchy of direct correlation function are equivalent to the vertex functions. The OZ relation is therefore very general.

3.3 Excess functional via integration

In some cases we can obtain $\mathcal{F}_{\text{ex}}[\rho]$ via integration over some parameter. We provide two examples.

Integration with respect to the particle density

We define the quantity $\rho(\mathbf{r}; \alpha)$ for some parameter $\alpha \in [0, 1]$, with $\rho(\mathbf{r}; \alpha = 0) = \rho_{\text{ref}}(\mathbf{r})$ for some reference density profile and $\rho(\mathbf{r}; \alpha = 1) = \rho(\mathbf{r})$. We find by integration over α and using the chain rule for functional differentiation,

$$\mathcal{F}_{\text{ex}}[\rho] = \mathcal{F}_{\text{ex}}[\rho_{\text{ref}}] + \int_0^1 d\alpha \frac{\partial \mathcal{F}_{\text{ex}}[\rho_\alpha]}{\partial \alpha} = \mathcal{F}_{\text{ex}}[\rho_{\text{ref}}] + \int_0^1 d\alpha \int d\mathbf{r} \frac{\partial \mathcal{F}_{\text{ex}}[\rho_\alpha]}{\delta \rho(\mathbf{r}; \alpha)} \frac{\partial \rho(\mathbf{r}; \alpha)}{\partial \alpha}.$$

Let us choose a linear path in the space of density profiles $\rho(\mathbf{r}; \alpha) = \rho_{\text{ref}}(\mathbf{r}) + \alpha[\rho(\mathbf{r}) - \rho_{\text{ref}}(\mathbf{r})]$ and using Eq. (3.13), we find

$$\beta \mathcal{F}_{\text{ex}}[\rho] = \beta \mathcal{F}_{\text{ex}}[\rho_{\text{ref}}] - \int_0^1 d\alpha \int d\mathbf{r} c^{(1)}([\rho_\alpha]; \mathbf{r}) [\rho(\mathbf{r}) - \rho_{\text{ref}}(\mathbf{r})]. \quad (3.16)$$

By a similar procedure we obtain

$$c^{(1)}([\rho_\alpha]; \mathbf{r}) = c^{(1)}([\rho_{\text{ref}}]; \mathbf{r}) + \int_0^\alpha d\alpha' \int d\mathbf{r}' c^{(2)}([\rho_{\alpha'}]; \mathbf{r}, \mathbf{r}') [\rho(\mathbf{r}') - \rho_{\text{ref}}(\mathbf{r}')]. \quad (3.17)$$

We thus obtain by combining Eqs. (3.16) and (3.17)

$$\begin{aligned} \beta \mathcal{F}_{\text{ex}}[\rho] = & \beta \mathcal{F}_{\text{ex}}[\rho_{\text{ref}}] - \int d\mathbf{r} [\rho(\mathbf{r}) - \rho_{\text{ref}}(\mathbf{r})] c^{(1)}([\rho_{\text{ref}}]; \mathbf{r}) \\ & - \int_0^1 d\alpha \int d\mathbf{r} [\rho(\mathbf{r}) - \rho_{\text{ref}}(\mathbf{r})] \int_0^\alpha d\alpha' \int d\mathbf{r}' [\rho(\mathbf{r}') - \rho_{\text{ref}}(\mathbf{r}')] c^{(2)}([\rho_{\alpha'}]; \mathbf{r}, \mathbf{r}'). \end{aligned} \quad (3.18)$$

This result is independent of the choice of integration path since $\mathcal{F}_{\text{ex}}[\rho]$ is a unique functional of the density. Note that for this scheme we need a prescription for the direct correlation functions and we need to determine the equilibrium density profile.

At this point it is worthwhile to consider the bulk limit, where $V_{\text{ext}} = 0$ and ρ is constant. In this limit, while taking $\rho_{\text{ref}}(\mathbf{r}) = 0$, we see that Eq. (3.16) reduces to

$$c^{(1)}(\rho) = \int_0^\rho d\rho' \int d\mathbf{r}' c^{(2)}(\rho'; \mathbf{r}, \mathbf{r}') \quad (3.19)$$

Taking the bulk limit in Eq. (3.14), we find that $\beta\mu(\rho) = \beta\mu_{\text{id}} - c^{(1)}(\rho)$, and we conclude that Eq. (3.19) is equivalent to

$$\beta\rho \left(\frac{\partial \mu}{\partial \rho} \right)_T = 1 - \rho \int d\mathbf{r} c^{(2)}(\rho; r),$$

which is just a form of the compressibility sum rule that we derived in Chapter 2. Furthermore, we find in this limit that

$$\beta f(\rho) = \beta f_{\text{id}}(\rho) + \rho^2 \int_0^1 d\alpha (\alpha - 1) \int d\mathbf{r} c^{(2)}(\alpha\rho; r), \quad (3.20)$$

where we used that for any function g , that $\int_0^1 d\alpha \int_0^\alpha d\alpha' g(\alpha') = \int_0^1 d\alpha (1 - \alpha)g(\alpha)$. Use of Eq. (3.20) is only possible when integration paths are performed in a single phase region.

Integration with respect to the interaction potential

Assume that the interaction potential is purely pairwise additive, i.e. $\Phi(\mathbf{r}^N) = \sum_{i < j} v(\mathbf{r}_i, \mathbf{r}_j)$. When viewed as a functional of ϕ , we find that

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = 2 \frac{\delta \Omega}{\delta v(\mathbf{r}, \mathbf{r}')}$$

We define the one-parameter family of pair potentials

$$v_\lambda(\mathbf{r}, \mathbf{r}') = v_0(\mathbf{r}, \mathbf{r}') + \lambda v_1(\mathbf{r}, \mathbf{r}')$$

By using again functional integration, we find

$$\mathcal{F}_{\text{ex}}[\rho] = \mathcal{F}_{\text{ex}}^{\text{ref}}[\rho] + \frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r} \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}'; \lambda) v_1(\mathbf{r}, \mathbf{r}').$$

Note that in this scheme there is no need to determine correlations functions at various densities after the equilibrium density has been determined. We can write,

$$\mathcal{F}_{\text{ex}}[\rho] = \mathcal{F}_{\text{ex}}^{\text{ref}}[\rho] + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') v_1(\mathbf{r}, \mathbf{r}') + \mathcal{F}_{\text{corr}}[\rho]. \quad (3.21)$$

The function that incorporates the correlations due to presence of $v(\mathbf{r}, \mathbf{r}')$ is given by

$$\mathcal{F}_{\text{corr}}[\rho] = \frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') h(\mathbf{r}, \mathbf{r}'; \lambda) v_1(\mathbf{r}, \mathbf{r}').$$

3.4 Approximations for the excess functional

Generally, we do not know the precise form of $\mathcal{F}[\rho]$, and it is therefore often necessary to resort to approximations. We list a few examples.

Local density approximation (LDA)

The simplest approximation is the LDA. Here we make the approximation

$$\mathcal{F}[\rho] = \int d\mathbf{r} f(\rho(\mathbf{r})),$$

with $f(\rho)$ the Helmholtz free energy density of the homogeneous bulk system. The LDA is a good approximation in case the density is slowly varying compared to the dimensions of the particle. One could, for example, take for $f(\rho)$ the Carnahan-Starling or the van der Waals form. Note that the LDA is exact for an ideal gas.

Weighted density approximation

An upgrade from the LDA is constructed by the weighted density approximation,

$$\mathcal{F}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \psi(\bar{\rho}(\mathbf{r})), \quad \psi(\rho) = f(\rho)/\rho.$$

Note that $\psi(\rho)$ is the free energy *per particle* for a bulk system, i.e. $\psi(\rho) = F(N, V, T)/N$. The weighted density $\bar{\rho}(\mathbf{r})$ is given by

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}' w(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}'),$$

with weight functions $w(r)$ to be determined. This approximation turns out to be an excellent way of providing a nearly exact treatment of hard-sphere systems, as we shall see later.

Virial expansion

We can generalise the virial expansion to inhomogeneous systems. For example, within the second virial approximation

$$\beta\mathcal{F}[\rho] = \beta\mathcal{F}_{\text{id}}[\rho] - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' f_{\text{M}}(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') \rho(\mathbf{r}). \quad (3.22)$$

Here $f_{\text{M}}(\mathbf{r}, \mathbf{r}') = \exp[-\beta\phi(|\mathbf{r} - \mathbf{r}'|)] - 1$ is the Mayer function. This approximation is expected to be exact in the low-density limit.

Gradient expansion

In the square-gradient approximation, where we allow for density profiles that are not slowly varying, we set

$$\mathcal{F}[\rho] = \int d\mathbf{r} [f_0(\rho(\mathbf{r})) + f_2(\rho(\mathbf{r}))|\nabla\rho(\mathbf{r})|^2 + \dots],$$

with $f_0(\rho)$ the Helmholtz free energy density of a uniform system, and $f_2(\rho)$ a to be determined coefficient. The form of this approximation is constrained by symmetry arguments such as translational and rotational invariance. One can derive expressions for $f_2(\rho)$ by imposing consistency with the linear response result. We will come back to this when we discuss the gas-liquid interface. Note that when we truncate above approximation after the first term, we obtain the LDA. Truncation after the second term is called the square-gradient approximation.

The mean-field approximation and random-phase approximation

Consider the exact result Eq. (3.21). When we neglect correlations and set the reference system to be an ideal gas, we obtain the so called mean-field approximations

$$\mathcal{F}_{\text{ex}}[\rho] = \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') v(\mathbf{r}, \mathbf{r}').$$

Sometimes this approximation is also known as the random-phase approximation. This approximation is useful for describing soft-core systems, such as polymer blobs. Furthermore, we will apply this approximation to the study of fluids with ions.

Density expansions

Now we consider the exact result Eq. (3.18). As a reference system we choose the uniform bulk fluid with constant density ρ_{b} . The grand potential functional in this case becomes

$$\begin{aligned} \beta\Omega_V[\rho] &= \beta\Omega[\rho_{\text{b}}] + \int d\mathbf{r} \beta V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) + \int d\mathbf{r} \left[\rho(\mathbf{r}) \ln \frac{\rho(\mathbf{r})}{\rho_{\text{b}}} - \rho(\mathbf{r}) + \rho_{\text{b}} \right] \\ &+ \int_0^1 d\alpha (\alpha - 1) \int d\mathbf{r} \int d\mathbf{r}' c^{(2)}([\rho_{\alpha}]; \mathbf{r}, \mathbf{r}') [\rho(\mathbf{r}) - \rho_{\text{b}}] [\rho(\mathbf{r}') - \rho_{\text{b}}]. \end{aligned}$$

We not approximate $c^{(2)}([\rho_{\alpha}]; \mathbf{r}, \mathbf{r}') \approx c^{(2)}(\rho_{\text{b}}; |\mathbf{r} - \mathbf{r}'|)$ and we obtain the density expansion,

$$\begin{aligned} \beta\Omega_V[\rho] &= \beta\Omega[\rho_{\text{b}}] + \int d\mathbf{r} \beta V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) + \int d\mathbf{r} \left[\rho(\mathbf{r}) \ln \frac{\rho(\mathbf{r})}{\rho_{\text{b}}} - \rho(\mathbf{r}) + \rho_{\text{b}} \right] \\ &- \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' c^{(2)}(\rho_{\text{b}}; |\mathbf{r} - \mathbf{r}'|) [\rho(\mathbf{r}) - \rho_{\text{b}}] [\rho(\mathbf{r}') - \rho_{\text{b}}]. \end{aligned} \quad (3.23)$$

One can show that Eq. (3.23) is equivalent to a functional Taylor expansion of the excess functional around the uniform bulk density. This type of approximation works quite well in the case of hard spheres next to a hard wall. However, problems occur when attractions are added, because then one has the possibility to have surface phase transitions, as we shall discuss later.

3.5 The Percus' test particle formulation

Recall the interpretation of the radial distribution function $g(r)$ in terms of a conditional probability to find a particle between r and $r + dr$ given that there is a particle at the origin. We can view the particle in the origin as a test particle that exerts an external potential on the surrounding fluid, given by the interaction potential $v(r)$. We can thus view the density profile resulting from the test particle as

$$\rho(\mathbf{r}) = \rho(r) = \rho_b g(r), \quad (3.24)$$

with ρ_b the bulk density. Using Eq. (3.14), we find that the density profile satisfies

$$\rho(r) = \rho_b \exp[-\beta v(r) + c^{(1)}([\rho]; r) - c^{(1)}(\rho_b)]. \quad (3.25)$$

Combining Eqs. (3.24) and (3.25) gives the self-consistency equation

$$g(r) = \exp[-\beta v(r) + c^{(1)}([\rho_b g]; r) - c^{(1)}(\rho_b)]$$

Using Eq. (3.17) with $\rho_{\text{ref}}(\mathbf{r}) = \rho_b$, we find

$$\ln g(r) = -\beta v(r) + \int_0^1 d\alpha \int d\mathbf{r}' \rho_b [g(r') - 1] c^{(2)}([\rho_\alpha]; \mathbf{r}, \mathbf{r}'). \quad (3.26)$$

Although this is an exact equation, we still need to perform approximations in order to be able to calculate $g(r)$. One approximation is $c^{(2)}([\rho_\alpha]; \mathbf{r}, \mathbf{r}') \approx c^{(2)}(\rho_b; |\mathbf{r} - \mathbf{r}'|)$. Recalling that $h(r) = g(r) - 1$ and using the OZ equation, Eq. (3.26) can be re-expressed as

$$g(r) \approx \exp[-\beta v(r) + g(r) - 1 - c^{(2)}(\rho_b; r)].$$

which is just the hypernetted chain approximation as introduced in Sec. 2.6.

Alternatively, we can approximate,

$$\exp[c^{(1)}([\rho_b g]; r) - c^{(1)}(\rho_b)] \approx 1 + \int d\mathbf{r}' \rho_b [g(r') - 1] c^{(2)}(\rho_b; \mathbf{r}, \mathbf{r}').$$

This results in

$$g(r) \approx \exp[-\beta v(r)] [g(r) - c^{(2)}(\rho_b; r)],$$

which is just the Percus-Yevick closure.

3.6 An exactly solvable model: hard rods in one dimension

Other than the ideal gas, there is no other model in three dimensional dimension for which we have an exact expression for $\mathcal{F}[\rho]$. However, in one dimension it is possible to obtain an analytical solution for a system of hard rods with length σ in an arbitrary external potential $V_{\text{ext}}(z)$. We find

$$\Omega_V[\rho] = \mathcal{F}_{\text{id}}[\rho] + \mathcal{F}_{\text{ex}}[\rho] + \int dz [V_{\text{ext}}(z) - \mu] \rho(z),$$

where the ideal gas functional is

$$\beta \mathcal{F}_{\text{id}}[\rho] = \int dz \rho(z) \{ \ln[\rho(z)\Lambda] - 1 \}$$

and the excess functional

$$\beta \mathcal{F}_{\text{ex}}[\rho] = - \int dz \rho(z) \ln[1 - t(z)], \quad t(z) = \int_{z-\sigma}^z dz' \rho(z').$$

The density profiles satisfy $\delta\Omega_V[\rho]/\delta\rho(z) = 0$,

$$\beta[\mu - V_{\text{ext}}(z)] = \ln \frac{\rho(z)\Lambda}{1-t(z)} + \int_z^{z+\sigma} dz' \frac{\rho(z')}{1-t(z')}.$$

Up until now we have only considered the case of a one-component system of hard rods. It turns out that the excess functional of a s -component mixture of hard rods can be expressed as

$$\mathcal{F}_{\text{ex}}[\{\rho_i\}] = \int dz \Phi(\{n_\alpha(z)\}) \quad (3.27)$$

with $\rho_i(z)$ the density profile and $2R_i$ the length of a rod of species i . The weighted densities are defined by

$$n_\alpha(z) = \sum_{i=1}^s \int dz' \rho_i(z') w_i^{(\alpha)}(z-z'), \quad \alpha = 0, 1.$$

The weight functions capture the geometry of the particles, and are given in one dimension by

$$w_i^{(0)}(z) = \frac{1}{2}[\delta(z-R_i) + \delta(z+R_i)], \quad w_i^{(1)}(z) = \Theta(R_i - |z|),$$

with Θ the Heaviside step function. The first weight function is associated with the "surface" area of the rod and the second weight function with the "volume" of a rod. The excess free energy density is then given by

$$\Phi(\{n_\alpha\}) = -n_0(z) \ln[1 - n_1(z)].$$

One can check that this expression reduces to the result for uniform hard-rod fluids. Also we note that the Mayer function of the hard-rod mixture in 1D can be written as

$$-f_{ij}(z) = (w_i^{(1)} * w_j^{(0)})(z) + (w_i^{(0)} * w_j^{(1)})(z),$$

with $*$ denoting the one dimensional convolution product.

3.7 Fundamental measure theory

Let us consider s -component hard-sphere mixtures, defined by the interaction potential

$$v_{ij}(r) = \begin{cases} \infty, & r > \sigma_{ij}, \\ 0, & r < \sigma_{ij}. \end{cases}$$

Here $\sigma_i = 2R_i$, with R_i the particle radius, and for additive mixtures that we consider here, we define $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$. Using the exact result for the excess functional of a hard-rod mixture in one spatial dimension, Rosenfeld considered whether this exact result can be generalised to the case of three spatial dimensions. His fundamental measure theory had two main ingredients. First, he used the exact result in 1D Eq. (3.27). Second, he insisted consistency with the exact low-density result,

$$\beta\mathcal{F}_{\text{ex}}[\{\rho_i\}] = -\frac{1}{2} \sum_{i,j} \int d\mathbf{r} \int d\mathbf{r}' \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') f_{ij}(|\mathbf{r} - \mathbf{r}'|), \quad (3.28)$$

which is a generalisation of Eq. (3.22) to the multicomponent case. Here $f_{ij}(r) = \exp[-\beta v_{ij}(r)] - 1$ is the multicomponent Mayer function. For additive hard spheres, we find $f_{ij}(r) = \Theta(R_i + R_j - r)$. It turns out we can write

$$\begin{aligned} -f_{ij}(r) &= (w_i^{(3)} * w_j^{(0)})(\mathbf{r}) + (w_i^{(0)} * w_j^{(3)})(\mathbf{r}) + (w_i^{(2)} * w_j^{(1)})(\mathbf{r}) + (w_i^{(1)} * w_j^{(2)})(\mathbf{r}) \\ &\quad + (w_{i,\alpha}^{(2)} * w_{j,\alpha}^{(1)})(\mathbf{r}) + (w_{i,\alpha}^{(1)} * w_{j,\alpha}^{(2)})(\mathbf{r}), \end{aligned}$$

with Einstein summation convention implied over repeated Greek indices. Furthermore we defined the convolution product between two function p and q as

$$(p * q)(\mathbf{r}) = \int d\mathbf{r}' p(\mathbf{r} - \mathbf{r}')q(\mathbf{r}').$$

The weight functions are

$$\begin{aligned} w_i^{(3)}(\mathbf{r}) &= \Theta(R_i - r), & w_i^{(2)}(\mathbf{r}) &= \delta(R_i - r), & \mathbf{w}_i^{(2)}(\mathbf{r}) &= \hat{\mathbf{r}}\delta(R_i - r), \\ w_i^{(1)}(\mathbf{r}) &= \frac{w_i^{(2)}(r)}{4\pi R_i}, & \mathbf{w}_i^{(1)}(\mathbf{r}) &= \frac{\mathbf{w}_i^{(2)}(\mathbf{r})}{4\pi R_i}, & w_i^{(0)}(\mathbf{r}) &= \frac{w_i^{(2)}(r)}{4\pi R_i^2}. \end{aligned}$$

Analogously to the one-dimensional case we define weighted densities. We have four scalar densities and two vector densities,

$$n_\alpha(\mathbf{r}) = \sum_{i=1}^s \int d\mathbf{r}' w_i^{(\alpha)}(\mathbf{r} - \mathbf{r}')\rho_i(\mathbf{r}'), \quad \alpha = 0, \dots, 3, \quad \mathbf{n}_\alpha(\mathbf{r}) = \sum_{i=1}^s \int d\mathbf{r}' \mathbf{w}_i^{(\alpha)}(\mathbf{r} - \mathbf{r}')\rho_i(\mathbf{r}'), \quad \alpha = 1, 2.$$

By using the same form as in the one-dimensional case,

$$\mathcal{F}_{\text{ex}}[\{\rho_i\}] = \int d\mathbf{r} \Phi(\{n_\alpha(\mathbf{r})\}), \quad (3.29)$$

invoking that the low-density result should be obtained Eq. (3.31), and the exact scaled-particle result

$$p = \lim_{R_i \rightarrow \infty} \left(\frac{\mu_{\text{ex}}^i}{V_i} \right). \quad (3.30)$$

The functional that satisfies these condition can be found by making the ansatz (motivated by dimensional analysis),

$$\Phi(\{n_\alpha\}) = f_1(n_3) + f_2(n_3)n_1n_2 + f_3(n_3)\mathbf{n}_1 \cdot \mathbf{n}_2 + f_4(n_3)n_2^3 + f_5(n_3)n_2\mathbf{n}_2 \cdot \mathbf{n}_2,$$

with to be determined coefficients $f_\alpha(n_3)$. Consistency with the low-density limit constraints these coefficients to have the form

$$\begin{aligned} f_1(n_3) &= n_3 + \mathcal{O}(n_3), & f_2(n_3) &= 1 + \mathcal{O}(n_3), & f_3 &= -1 + \mathcal{O}(n_3), \\ f_4(n_3) &= \frac{1}{24\pi} + \mathcal{O}(n_3), & f_5 &= -\frac{1}{8}\pi + \mathcal{O}(n_3). \end{aligned} \quad (3.31)$$

Eq. (3.30) translates to the scaled particle differential equation,

$$\frac{\partial \Phi(\{n_\alpha\})}{\partial n_3} = -\Phi(\{n_\alpha\}) + \sum_{\alpha=0}^3 \frac{\partial \Phi(\{n_\alpha\})}{\partial n_\alpha} n_\alpha + \sum_{\alpha=1,2} \frac{\partial \Phi(\{n_\alpha\})}{\partial \mathbf{n}_\alpha} \cdot \mathbf{n}_\alpha.$$

Solving this differential equation with the conditions Eqs. (3.31)

$$\Phi_{\text{FMT}}(\{n_\alpha\}) = -n_0 \ln(1 - n_3) + \frac{n_1n_2 - \mathbf{n}_1 \cdot \mathbf{n}_2}{1 - n_3} + \frac{n_2^3 - 3n_2\mathbf{n}_2 \cdot \mathbf{n}_2}{24\pi(1 - n_3)^2}.$$

Remarkably, the fundamental measure theory as presented here reproduces the free energy density and the pair correlation function of the uniform hard-sphere mixture within the Percus-Yevick approximation. The pressure using this scheme is equivalent to PY result within the compressibility route, and one finds that in the bulk limit that the pressure differs at most 7% from simulations from densities up until freezing. The shortcomings of the theory are, however, that it does not account correctly for hard-sphere freezing or when the dimensionality

of the problem is reduced. The latter notion is called dimensional crossover which means that the three-dimensional DFT should still be approximately valid for situations at lower effective dimensionality. In other words the theory should be applicable to fluids confined to narrow slits (2D), narrow cylinders (1D), or cavities (0D). For example, the 2D limit can be taken by setting $\rho(\mathbf{r}) = \rho_{2D}(x, y)\delta(z)$.

A more pragmatic improvement of Rosenfeld's fundamental measure theory can be obtained by replacing Eq. (3.30) by $p = p_{\text{MCSL}}$, where the right-hand side is given by Mansoori-Carnahan-Starling-Leland (MCSL) equation of state for binary hard-sphere mixtures. This method is therefore more consistent with the bulk result that Rosenfeld's original formulation, which violates that the exact scaled-particle result for the pressure is equal to the thermodynamic pressure, by the assumption that \mathcal{F}_{ex} can be written down in terms of weighted densities. Following the same procedure as before, one finds the modified excess free energy density,

$$\Phi_{\text{WB}}(\{n_\alpha\}) = -n_0 \ln(1-n_3) + \frac{n_1 n_2 - \mathbf{n}_1 \cdot \mathbf{n}_2}{1-n_3} + (n_2^3 - 3n_2 \mathbf{n}_2 \cdot \mathbf{n}_2) \frac{n_3 + (1-n_3)^2 \ln(1-n_3)}{36\pi n_3^2 (1-n_3)^2}. \quad (3.32)$$

Notice that only the last term is affected. Using Eq. (3.32) in Eq. (3.29) gives the so-called White-Bear functional. Improvements to the functional were also constructed by using more accurate expressions for the MCSL equation of state. This, for example, gives rise to the White Bear Mark II functional, which is the current state of the art DFT for hard-sphere mixtures. It is given by,

$$\Phi_{\text{WBII}}(\{n_\alpha\}) = -n_0 \ln(1-n_3) + \left[1 + \frac{1}{9} n_3^2 \phi_2(n_3)\right] \frac{n_1 n_2 - \mathbf{n}_1 \cdot \mathbf{n}_2}{1-n_3} + \left[1 - \frac{4}{9} n_3 \phi_3(n_3)\right] \frac{n_2^3 - 3n_2 \mathbf{n}_2 \cdot \mathbf{n}_2}{24\pi(1-n_3)^2},$$

with

$$\begin{aligned} \phi_2(n_3) &= [6n_3 - 3n_3^2 + 6(1-n_3)\ln(1-n_3)]/n_3^3, \\ \phi_3(n_3) &= [6n_3 - 9n_3^2 + 6n_3^3 + 6(1-n_3)^2 \ln(1-n_3)]/(4n_3^3). \end{aligned}$$

In the White-Bear mark II approach the equilibrium density profiles in simple geometries do not differ much from the first version of the White Bear approach. However, the increased self-consistency of the WBII version gives better results for e.g., surface tensions and bending rigidities.

Irrespective of the version of the fundamental measure theory, there is a big advantage that correlation function to arbitrary order have the following expression

$$c_{i_1, \dots, i_m}^{(m)}(\mathbf{r}_1, \dots, \mathbf{r}_m) = - \int d\mathbf{r} \sum_{\alpha_1, \dots, \alpha_m} \frac{\partial^m \Phi}{\partial n_{\alpha_1}(\mathbf{r}) \dots \partial n_{\alpha_m}(\mathbf{r})} w_{i_1}^{(\alpha_1)}(\mathbf{r}_1 - \mathbf{r}) \dots w_{i_m}^{(\alpha_m)}(\mathbf{r}_m - \mathbf{r}).$$

Note that DFT turned out to be very successful in describing the many-body equilibrium physics of particles interacting via steric interactions, such as the hard-sphere potential. However, currently there is no satisfying DFT that describes the many-body physics when long-ranged potentials and their resulting correlations are included. This should be contrasted with homogeneous fluids, where there are well-defined schemes to incorporate such potentials (e.g., via thermodynamic perturbation theory).

3.8 Relation with quantum density functional theory

In this chapter we have considered up until now how to apply density functional theory for classical fluids. However, the original formulation of DFT, which was pioneered by Hohenberg, Kohn, and Sham, found the applications in quantum systems. Here, one could for example be interested in the ground state energy of an atom, molecule, or the band structure of a

crystal lattice. Within the Born-Oppenheimer approximation where the M nuclei are assumed to be much heavier than the electrons, one needs to solve the time-independent non-relativistic Schrodinger equation $\hat{H}\Psi = E\Psi$, for the N -body (electronic) wave function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$, where

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{l=1}^M \frac{Z_l e^2}{|\mathbf{r}_i - \mathbf{R}_l|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} =: \hat{T} + \hat{V} + \hat{\Phi}. \quad (3.33)$$

For simplicity, we ignore spin degrees of freedom. Here, m is the rest mass of an electron, Z_l is the atomic number of nucleus l , e is the elementary charge unit. The electrons have coordinates $\mathbf{r}_1, \dots, \mathbf{r}_N$, while the nuclei have coordinates $\mathbf{R}_1, \dots, \mathbf{R}_M$. Note that in Eq. (3.33), the first term defines the kinetic energy operator \hat{T} and the third term is the electron-electron interaction operator $\hat{\Phi}$. The second term within the Born-Oppenheimer approximation acts as an external potential because the nuclei are assumed to be stationary, and therefore the quantum dynamics decouples from that of the electrons. The external potential operator is denoted by \hat{V} .

Solving the N -body Schrodinger equation is a daunting task, since the wavefunction depends on $3N$ degrees of freedom. Similar to the treatment of classical density functional theory, we look for a simplification of this problem, by instead focusing on the electron density,

$$n(\mathbf{r}) = \langle \Psi | \hat{n} | \Psi \rangle = \int d\mathbf{r}_1 \dots d\mathbf{r}_N \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \hat{n}(\mathbf{r}) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N),$$

with electronic density operator $\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$. Similar to the classical DFT, we have a variational principle for the ground state electronic energy, given by the functional

$$E = \min_{\tilde{n}} E_V[\tilde{n}], \quad E_V[\tilde{n}] = \int d\mathbf{r} \tilde{n}(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) + F[\tilde{n}].$$

The external potential is in this case

$$V_{\text{ext}}(\mathbf{r}) = - \sum_{l=1}^M \frac{Z_l e^2}{|\mathbf{r} - \mathbf{R}_l|}.$$

The proof is roughly the same as the in the classical case (with some extra details, such as V -representability¹ and possible degeneracy), and this is called the Hohenberg-Kohn variational principle. In the case of a non-degenerate ground state E_V is minimised by any of the ground states electron densities. Here, $F[\tilde{n}]$ is a unique functional of the electron density that does not depend on the external potential, defined by the Levy constrained method

$$\mathcal{F}[\tilde{n}] = \min_{\alpha} \langle \tilde{\Psi}_{\tilde{n}}^{\alpha} | \hat{T} + \hat{\Phi} | \tilde{\Psi}_{\tilde{n}}^{\alpha} \rangle.$$

In other words, we have to search over all many-body wavefunctions $\tilde{\Psi}_{\tilde{n}}^{\alpha}$ that integrate to the electron density $\tilde{n}(\mathbf{r})$. Just like in the classical case, $F[n]$ is not known explicitly. It is standard practice to separate the Coulomb piece from $F[n]$,

$$F[\tilde{n}] = G[\tilde{n}] + \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\tilde{n}(\mathbf{r}) \tilde{n}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

In contrast to classical DFT, in the quantum case the kinetic energy is not exactly known. In this case, $G[\tilde{n}]$ thus contains kinetic contributions and so-called exchange-correlation contributions defined by subtracting the kinetic contribution from $G[\tilde{n}]$.

¹V-representability categorizes whether a positive function $\tilde{n}(\mathbf{r})$, with $\int d\mathbf{r} \tilde{n}(\mathbf{r}) = N$ is a possible ground state electron density for *some* $V_{\text{ext}}(\mathbf{r})$.

Finally, we mention that the above formulation of quantum DFT focuses only on the ground state of the system at $T = 0$ K. The generalisation to finite temperature has been performed by Mermin. He showed that there is a unique functional $\mathcal{F}[n]$ independent of $V_{\text{ext}}(\mathbf{r})$, such that

$$\Omega_V[n] = \int d\mathbf{r} [V_{\text{ext}}(\mathbf{r}) - \mu]n(\mathbf{r}) + \mathcal{F}[n]$$

is minimum and equal to the equilibrium grand potential Ω when $n(\mathbf{r})$ is the equilibrium electron density in the presence of $V_{\text{ext}}(\mathbf{r})$. It is clear that the form is the same as the classical case, but now

$$\mathcal{F}[n] = \text{Tr}[\hat{\rho}_Q(\hat{T} + \hat{\Phi} + k_B T \ln \hat{\rho}_Q)].$$

Here, we defined the grand-canonical density matrix

$$\hat{\rho}_Q = \frac{\exp[-\beta(\hat{H} - \mu\hat{N})]}{\text{Tr}\{\exp[-\beta(\hat{H} - \mu\hat{N})]\}},$$

with $\text{Tr}(\dots)$ the quantum-mechanical trace and $\hat{N} = \int d\mathbf{r} \hat{n}(\mathbf{r})$ the total number operator. The electron density in the finite-temperature case is

$$n(\mathbf{r}) = \text{Tr}(\hat{\rho}_Q \hat{n}).$$

We see that the finite temperature quantum DFT has the same form as the classical DFT. Furthermore, we remark that although we have worked here in first quantization, one could equally well formulate the above within the language of second quantization.

Chapter 4

Phase behaviour

4.1 The liquid-gas phase transition

Up until now we have focused mainly on hard-sphere systems in bulk and in the presence of an external potential. In this chapter, we will consider what happens when we add attractive contribution to the interaction potential in the microscopic Hamiltonian. We shall see that the presence of attractions can lead to *condensation*, i.e., there can be a phase coexistence between a dilute gas and a dense liquid. Such a gas-liquid phase transition is absent when the particles are purely repulsive (and it does not matter whether this repulsion is short or long-ranged).

As an example, let us consider the Lennard-Jones fluid with interaction potential given by Eq. (2.11). The idea now is to approximate this potential by a reference part described by hard spheres plus a perturbation. Recall that we have accurate expressions for the hard-sphere reference part at our disposal. A rough approximation is

$$v_{\text{LJ}}(r) \approx \begin{cases} v_{\text{HS}}(r), & r < \sigma, \\ -4\epsilon \left(\frac{\sigma}{r}\right)^6, & r > \sigma. \end{cases} \quad (4.1)$$

A splitting like this in a known reference part and a long-ranged perturbation is not unique. We will come back at this point at the end of this section. However, for now we will focus on the simplest prescription possible to understand the qualitative behaviour of having attractions. Using, for example, Eq. (3.21) in the homogeneous limit and by neglecting correlations $\mathcal{F}_{\text{corr}}[\rho] = 0$, we find for the Helmholtz free energy density,

$$f(\rho, T) = f_{\text{HS}}(\rho) - \frac{\rho^2}{2} \int d\mathbf{r} 4\epsilon \left(\frac{\sigma}{r}\right)^6 = f_{\text{HS}}(\rho) - 16\epsilon v_0 \rho^2 =: f_{\text{HS}}(\rho) - a\rho^2,$$

with $v_0 = (\pi/6)\sigma^3$. Although we have a very accurate expression for $f_{\text{HS}}(\rho)$ in the form of the Carnahan-Starling formula, we opt here for a simpler route. First, we note that if we have a given sphere with volume v_0 in the system, then the volume available for a second sphere $V - 8v_0$. Neglecting, multi-particle overlaps, we can therefore approximate the configurational integral as

$$\begin{aligned} Q(N, V, T) &= \int d\mathbf{r}^N \exp \left[-\beta \sum_{i=1}^N \sum_{j < i} v_{\text{HS}}(r_{ij}) \right] \approx V(V - 8v_0)(V - 2 \cdot 8v_0) \dots [V - (N - 1)8v_0] \\ &= V^N \left(1 - \frac{N^2}{2} \frac{8v_0}{V} + \dots \right) \approx \left(V - \frac{N}{2} 8v_0 \right)^N =: (V - Nb)^N. \end{aligned}$$

In the last approximation we used than $8v_0 \ll V$. Calculating from $Q(N, V, T)$ the contribution to the Helmholtz free energy, we find the so-called van der Waals free energy density,

$$\beta f(\rho) = \rho \left(\log \frac{\rho \Lambda^3}{1 - b\rho} - 1 \right) - \beta a \rho^2. \quad (4.2)$$

We can interpret b as one half of the excluded volume between two spheres, and a is a measure for the attractions. Both constants are independent of ρ and T . However, this depends on the scheme of how we establish the reference system (i.e., the hard-core diameter). In general, a and b depend on temperature and density.

Let us compute the pressure:

$$p = - \left(\frac{\partial F}{\partial V} \right)_{N,T} = -f + \rho \left(\frac{\partial f}{\partial \rho} \right)_T = \frac{\rho k_B T}{1 - \rho b} - a \rho^2 \quad (4.3)$$

This celebrated equation of state was derived by van der Waals in 1873 when the existence of atoms and molecules was not yet accepted!

A careful investigation of the equation of state $p(\rho, T)$ for a fixed T (i.e. isotherms), reveals that there for $T < T_c$ there is a regime for which $(\partial p / \partial \rho)_T < 0$: the isothermal compressibility would be negative (recall Eq. (2.18)). However, this is not possible because the compressibility is a measure for the number fluctuations in the system as we have seen in Chapter 2 and is therefore always a positive quantity. We conclude that there is a thermodynamic instability. The critical temperature T_c denotes the lowest temperature for which the isotherm does not exhibit such a thermodynamic instability and separates two regimes for which thermodynamic instabilities occur or not. At $T = T_c$, there is an inflection point in the pressure isotherm at the critical density. At the critical point (ρ_c, T_c) we thus have

$$\left(\frac{\partial p}{\partial \rho} \right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial \rho^2} \right)_T = 0.$$

In the van der Waals model the critical point can be analytically determined, and we find

$$\rho_c b = \frac{1}{3}, \quad k_B T_c = \frac{8a}{27b}.$$

From Eq. (4.3) we conclude that the thermodynamic stability criterion $(\partial p / \partial \rho)_T > 0$ is equivalent to $(\partial^2 f / \partial \rho^2)_T > 0$ where isotherms of the free energy density are convex. The locus of all points $\rho(T)$ for which $(\partial^2 f / \partial \rho^2)_T = 0$ is called the *spinodal*. Within the spinodal, where the system is absolutely unstable, and we find that isotherms of the free energy are concave.

We shall see that the presence of a spinodal for $T < T_c$ implies that the system can lower its total free energy by phase separation of the homogeneous system with density ρ and volume V into a dilute gas with density ρ_g with volume V_g and a dense liquid of density ρ_l with volume V_l . Let us demonstrate this explicitly and consider the Helmholtz free energy of the phase-separated (ps) system $F_{ps} = V f_{ps} = V_l f(\rho_l) + V_g f(\rho_g)$, omitting surface terms. In the canonical ensemble, N and V are fixed, so we have a constraint on the volume, $V = V_l + V_g$ and a constraint on the number of particles $\rho V = \rho_g V_g + \rho_l V_l$. Using these constraints, we find

$$f_{ps}(\rho, T) = f(\rho_g, T) + \frac{\rho - \rho_g}{\rho_l - \rho_g} [f(\rho_l, T) - f(\rho_g, T)], \quad \rho_g \leq \rho \leq \rho_l.$$

Note that $f_{ps}(\rho, T)$ linearly interpolates between densities $f(\rho_g, T)$ and $f(\rho_l, T)$. We conclude that if $f(\rho, T)$ contains a part that is concave, there is a density regime where the system can lower its total free energy with $f_{ps}(\rho, T) < f(\rho, T)$ for a given ρ with suitably chosen densities ρ_g and ρ_l . The coexisting densities of gas and liquid are set by the condition that the total free energy F_{ps} of the system is minimised. Graphically, it can be seen that this occurs when

$$\left. \frac{\partial f}{\partial \rho} \right|_{\rho=\rho_g} = \left. \frac{\partial f}{\partial \rho} \right|_{\rho=\rho_l} = \frac{f(\rho_l) - f(\rho_g)}{\rho_l - \rho_g}.$$

The first equality is none other than a statement that the chemical potentials are equal $\mu(\rho_g, T) = \mu(\rho_l, T) =: \mu_{\text{co}}(T)$. The second equality follows from the condition of equal pressure $p(\rho_g, T) = p(\rho_l, T)$, which can be rewritten using Eq. (4.3) to

$$p(\rho_g, T) - p(\rho_l, T) = 0 \Rightarrow (\rho_g - \rho_l) \left[\mu_{\text{co}}(T) - \frac{f(\rho_l, T) - f(\rho_g, T)}{\rho_l - \rho_g} \right] = 0.$$

We conclude that for $T < T_c$ the total free energy density is given by $f_{\text{ps}}(\rho, T)$ for $\rho_g \leq \rho \leq \rho_l$ and $f(\rho)$ otherwise. The lines $\rho_g(T)$ and $\rho_l(T)$ form the gas branch and liquid branch, respectively, of the so-called *binodal* or *coexistence curve*. When $\rho < \rho_g$ the system is in the gas phase and for $\rho > \rho_l$ in the liquid phase. For $\rho_g \leq \rho \leq \rho_l$ we have gas-liquid coexistence.

For $T > T_c$, it follows that $f(\rho, T)$ is always convex, the system would always increase its total free energy upon phase separation $f_{\text{ps}}(\rho, T) > f(\rho, T)$ for any choice of ρ_l and ρ_g . The homogeneous system has the lowest free energy and there is no phase separation for $T > T_c$. The recipe we described above is often denoted as the common-tangent construction. In a plot of p versus V it can be shown that this construction is equivalent to the Maxwell construction when we consider p as a function of V .

Finally, we remark on the somewhat arbitrary splitting into a reference hard-sphere part and attractive part (Eq. (4.1)), which gave us constant parameter b in the van der Waals equation of state. In other words, this splitting does not properly take into account the "softness" in the repulsive part of $v_{\text{LJ}}(r)$. A different choice was derived by Barker and Henderson (BH). This scheme was developed for general potential $v(r)$ with a steep repulsive part and an attractive tail. Furthermore, they defined σ as $v(r = \sigma) = 0$, as in e.g., the Lennard-Jones potential. Recall the first-order result of thermodynamic perturbation theory (Problem 2.8),

$$F(N, V, T) = F_0(N, V, T) + \frac{V\rho^2}{2} \int d\mathbf{r} g_0(r)v_1(r). \quad (4.4)$$

Within the BH scheme, we have

$$v_0(r) = \begin{cases} v(r), & r < \sigma, \\ 0, & r > \sigma, \end{cases} \quad v_1(r) = \begin{cases} 0, & r < \sigma, \\ v(r), & r > \sigma, \end{cases}$$

The reference system is then approximated as a hard-sphere fluid with hard-core diameter d given by

$$d = \int_0^\infty dr \{1 - \exp[-\beta v_0(r)]\}.$$

Note that now the hard-sphere reference part is temperature dependent within this scheme (but not density dependent). Furthermore, it can be shown that the convergence of this scheme is rather slow, such that quantitative results can only be obtained within second-order thermodynamic perturbation theory.

An improvement of this scheme is the Weeks-Chandler-Andersen (WCA) prescription that focuses on potentials for which r^* is defined as the minimum of $v(r)$ with $v(r^*) = -\epsilon$. In the Lennard-Jones case we have $r^* = 2^{1/6}\sigma$. In the WCA scheme,

$$v_0(r) = \begin{cases} v(r) + \epsilon, & r < r^*, \\ 0, & r > r^*, \end{cases} \quad v_1(r) = \begin{cases} -\epsilon, & r < r^*, \\ v(r), & r > r^*. \end{cases}$$

Similar to the BH scheme, the reference part is not exactly known. We make the exact factorization (see Problem 2.7), $g_0(r) = \exp[-\beta v(r)]y(r)$, with the cavity function $y(r)$. In the WCA scheme, we approximate $y \approx y_d(r)$, with $y_d(r)$ the cavity function of a hard-sphere system with hard-sphere diameter d and hard-sphere potential $v_d(r)$. Here, d is determined by the condition

$$\int d\mathbf{r} y_d(r) \{ \exp[-\beta v_0(r)] - \exp[-\beta v_d(r)] \} = 0.$$

In contrast to the BH scheme d becomes dependent on T and ρ . Consequently, the van der Waals parameter b becomes T and ρ dependent, but also a , see the second term in Eq. (4.4).

4.2 The lattice gas and the Braggs-William approximation

The van der Waals model discussed in Sec. 4.1 with constant a and b is an example of a mean-field model, where fluctuations around the average density are neglected. We have discussed how some of the correlations can be introduced via the scheme of thermodynamic perturbation theory, with suitable soft-core reference systems. However, going to higher orders in thermodynamic perturbation theory becomes progressively more difficult, where often three-body correlation functions are needed. An alternative framework to include the effect of fluctuations is via field-theoretical methods. From a didactic point of view, it is good to first introduce these methods in the language of so-called lattice models which approximate a real fluid with continuous degrees of freedom.

In the lattice gas description, we assume a lattice with N lattice sites. Each lattice site $i = 1, \dots, N_s$ can be occupied with a particle, characterised by the occupation number $n_i \in \{0, 1\}$. The total number of particles is $N = \sum_{i=1}^{N_s} n_i$. The fact that each lattice site can host at most one particle reflects the repulsion due to the Pauli-exclusion principle. Attractive interactions and an external potential are incorporated via the Hamiltonian

$$H(\{n_i\}) = -\frac{1}{2} \sum_{i \neq j} \epsilon_{ij} n_i n_j + \sum_{i=1}^{N_s} K_i n_i.$$

Here $\epsilon_{ij} = \epsilon_{ji} > 0$ is the attractive interaction strength between sites i and j and K_i acts as an external potential. Note that this Hamiltonian is equivalent to the Ising model. The canonical partition function is

$$Z(N, V, T) = \sum_{n_1, \dots, n_{N_s}=0,1} \exp[-\beta H(\{n_i\})] \delta_{N, \sum_{i=1}^{N_s} n_i},$$

with $\delta_{i,j}$ the Kronecker delta. The constraint can be removed by going to the grand canonical ensemble

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \exp(\beta \mu N) Z(N, V, T) = \sum_{n_1, \dots, n_{N_s}=0,1} \exp \left\{ -\beta \left[H(\{n_i\}) - \mu \sum_{i=1}^{N_s} n_i \right] \right\},$$

To get some insights in the lattice-gas model we take only nearest-neighbour interactions and set $\epsilon_{ij} = \epsilon$ for sites i and j nearest neighbours and 0 otherwise. Furthermore, we set $K_i = 0$ for all i . In this case we have a (discrete) translational invariance of the underlying Hamiltonian. We make the fluctuation expansion, $n_i = \langle n \rangle + n'_i$. The Hamiltonian becomes

$$\begin{aligned} H(\{n_i\}) - \mu \sum_{i=1}^{N_s} n_i &= -\frac{1}{2} \epsilon \sum_{i=1}^{N_s} \sum_{j(i)=1}^z n_i n_j - \mu \sum_{i=1}^{N_s} n_i \\ &= -\frac{1}{2} \epsilon z N_s \langle n \rangle^2 - \epsilon z \langle n \rangle \sum_{i=1}^{N_s} n'_i - \mu N_s \langle n \rangle - \mu \sum_{i=1}^{N_s} n'_i + \mathcal{O}(\{n_i'^2\}) \approx \frac{1}{2} \epsilon z N_s \langle n \rangle^2 - (\mu + \epsilon z \langle n \rangle) \sum_{i=1}^{N_s} n_i \end{aligned}$$

The mean-field (MF) partition function becomes

$$\begin{aligned} \Xi_{\text{MF}}(N, V, T) &= \exp \left(-\frac{1}{2} \beta \epsilon z N_s \langle n \rangle^2 \right) \sum_{n_1=0,1} \dots \sum_{n_{N_s}=0,1} \exp \left[\beta (\mu + \epsilon z \langle n \rangle) \sum_{i=1}^{N_s} n_i \right] \\ &= \exp \left(-\frac{1}{2} \beta \epsilon z N_s \langle n \rangle^2 \right) \prod_{i=1}^{N_s} \sum_{n_i=0,1} \exp [\beta (\mu + \epsilon z \langle n \rangle) n_i] \\ &= \exp \left(-\frac{1}{2} \beta \epsilon z N_s \langle n \rangle^2 + N_s \log \{1 + \exp [\beta (\mu + \epsilon z \langle n \rangle)]\} \right) =: \exp[-\beta \Omega_{\text{MF}}(\mu, V, T)] \end{aligned}$$

We find the mean-field grand potential

$$\Omega_{\text{MF}}(\mu, V, T) = \frac{1}{2}\varepsilon z N_s \langle n \rangle^2 - N_s k_B T \ln \left[1 + e^{\beta(\mu + \varepsilon z \langle n \rangle)} \right],$$

with the average number of particles given by the self consistency equation

$$\langle n \rangle = - \left(\frac{\partial \Omega / N_s}{\partial \mu} \right)_{V, T} = \frac{1}{1 + e^{-\beta(\mu + \varepsilon z \langle n \rangle)}}. \quad (4.5)$$

We obtain the mean-field Helmholtz free energy via a Legendre transform $F_{\text{MF}}(N, V, T) = \Omega_{\text{MF}}(\mu, V, T) + \mu \langle N \rangle$. We find

$$F_{\text{MF}}(N, V, T) = N_s k_B T [n \ln n + (1 - n) \ln(1 - n)] - \frac{1}{2} \varepsilon z N_s n^2 =: N_s \tilde{f}, \quad (4.6)$$

with $n = N/N_s$. From the second law of thermodynamics, we know that $\partial \mu / \partial N \geq 0$, so the spinodal is given by $\partial^2 \tilde{f} / \partial n^2 = 0$. For the critical point, we have in addition that $\partial^3 \tilde{f} / \partial n^3 = 0$ and we find $n_c = 1/2$ and $k_B T_c = \varepsilon z / 4$. The binodal can be computed by the condition that the chemical potential and pressure should be equal. Note that the treatment of the lattice gas model is a bit different than the Ising model. The reason is that the number of particles and therefore also the volume fraction within the canonical ensemble is a conserved quantity. In contrast, in the grand-canonical ensemble Eq. (4.5) is equivalent to $\partial \Omega_{\text{MF}} / \partial \langle n \rangle = 0$. This should not come as a surprise, as we can compare this result to density functional theory. Furthermore, note the resemblance of Eq. (4.6) with Eq. (4.2).

4.3 Gaussian integrals

Consider the multi-dimensional Gaussian integral,

$$\begin{aligned} \mathcal{Z}(\mathbf{J}) &= \int_{-\infty}^{\infty} dx_1 \dots \int_{-\infty}^{\infty} dx_M \exp \left[-\frac{1}{2} \sum_{i,j=1}^M (x_i - x_i^*) A_{ij} (x_j - x_j^*) + \sum_{i=1}^M J_i x_i \right] \\ &= \exp \left(\sum_{i=1}^M J_i x_i^* \right) \int_{-\infty}^{\infty} dx_1 \dots \int_{-\infty}^{\infty} dx_M \exp \left(-\frac{1}{2} \sum_{i,j=1}^M x_i A_{ij} x_j + \sum_{i=1}^M J_i x_i \right), \end{aligned}$$

with \mathbf{x}^* a constant vector. The second line is obtained by making the coordinate transformation $\mathbf{x} \rightarrow \mathbf{x} + \mathbf{x}^*$. Moreover, the matrix \mathbf{A} is a positive definite matrix (i.e., has positive eigenvalues). Without loss of generality we take \mathbf{A} to be symmetric, since any antisymmetric part will not contribute to the integral. Furthermore, one notes that the argument of the exponent within the integral is a quadratic form with minimum determined by

$$\frac{\partial}{\partial x_k} \left(\frac{1}{2} \sum_{i,j=1}^M x_i A_{ij} x_j - \sum_{i=1}^M J_i x_i \right) = 0 \quad \Rightarrow \quad \sum_{j=1}^M A_{kj} x_j - J_k = 0.$$

This motivates us to perform a coordinate transformation (completing the square),

$$\mathbf{x} = \mathbf{A}^{-1} \cdot \mathbf{J} + \mathbf{y},$$

with unit Jacobian. The integral is transformed into

$$\mathcal{Z}(\mathbf{J}) = \exp \left(\frac{1}{2} \sum_{i,j=1}^M J_i (A^{-1})_{ij} J_j + \sum_{i=1}^M J_i x_i^* \right) \int_{-\infty}^{\infty} dy_1 \dots \int_{-\infty}^{\infty} dy_M \exp \left(-\frac{1}{2} \sum_{i,j=1}^M y_i A_{ij} y_j \right) \quad (4.7)$$

Note that any antisymmetric part of \mathbf{A} will not contribute to the integral. Every real, symmetric matrix can be diagonalised with an orthogonal matrix $\mathbf{O}^T \mathbf{O} = \mathbf{I}$, i.e., $\mathbf{A} = \mathbf{O} \mathbf{\Lambda} \mathbf{O}^T$, where $\mathbf{\Lambda} = \text{diag}(\lambda_1, \dots, \lambda_M)$. We define yet another coordinate transformation, $y_i = \sum_{j=1}^m O_{ij} z_j$, which has also unit Jacobian, giving,

$$\sum_{i,j=1}^M y_i A_{ij} y_j = \sum_{i,j,k,m=1}^M z_k O_{ik} A_{ij} O_{jm} z_m = \sum_{k,m=1}^M z_k (\mathbf{O}^T \mathbf{A} \mathbf{O})_{km} z_m = \sum_{k=1}^M \lambda_k z_k^2$$

Hence, the remaining integral in Eq. (4.7) can be factorized

$$\begin{aligned} \int_{-\infty}^{\infty} dy_1 \dots \int_{-\infty}^{\infty} dy_M \exp \left(-\frac{1}{2} \sum_{i,j=1}^M y_i A_{ij} y_j \right) &= \prod_{i=1}^M \int_{-\infty}^{\infty} dz_i \exp \left(-\frac{1}{2} \lambda_i z_i^2 \right) = \frac{(2\pi)^{M/2}}{(\prod_{i=1}^M \lambda_i)^{1/2}} \\ &= (2\pi)^{M/2} (\det \mathbf{A})^{-1/2} \end{aligned}$$

We conclude that

$$\mathcal{Z}(\mathbf{J}) = (2\pi)^{M/2} (\det \mathbf{A})^{-1/2} \exp \left(\frac{1}{2} \sum_{i,j=1}^M J_i (A^{-1})_{ij} J_j + \sum_{i=1}^M J_i x_i^* \right)$$

Next, let us define the average

$$\langle \dots \rangle = \frac{1}{\mathcal{Z}(\mathbf{0})} \int_{-\infty}^{\infty} dx_1 \dots \int_{-\infty}^{\infty} dx_M (\dots) \exp \left[-\frac{1}{2} \sum_{i,j=1}^M (x_i - x_i^*) A_{ij} (x_j - x_j^*) \right]$$

Note that

$$\langle x_i \rangle = \frac{1}{\mathcal{Z}(\mathbf{J})} \frac{\partial \mathcal{Z}(\mathbf{J})}{\partial J_i} \Bigg|_{\mathbf{J}=\mathbf{0}} = x_i^*.$$