Chapter 7
Statistical Mechanics of Inhomogeneous Fluids

While thermodynamics of interfaces provides a theoretical foundation for understanding various interfacial phenomena, its application depends on the availability of the fundamental equation. That is, the explicit form of the function (6.55) must be known. In the absence of experimental access to this information, this is a task best left to statistical mechanics. In this chapter, we introduce a powerful method from statistical mechanics that allows us to study interfaces and inhomogeneous systems in general based on underlying molecular-level models.

7.1 Functional

The concept of functionals and their derivatives play a central role in what follows. In this section, we introduce the functionals as a generalization of ordinary functions and explore the rules of computing with the functionals.

7.1.1 Definition

Given a function $f(x)$, we often represent it graphically using the horizontal axis for the independent variable x and the vertical axis for the dependent variable f. For a function $f(x,y)$ of two variables, the graph is a surface in a three-dimensional space. For a function of three or more variables, such a graphical representation is not possible.

We can devise a far less ambitious approach, in which we use two diagrams, one showing only the values assumed by the independent variables and the other showing the value of the function corresponding to the given values of the independent variables.

As an example, let us consider a function $f(u_1,u_2,u_3)$. A conventional graphical approach would require a four-dimensional space to plot it. Instead, we show the

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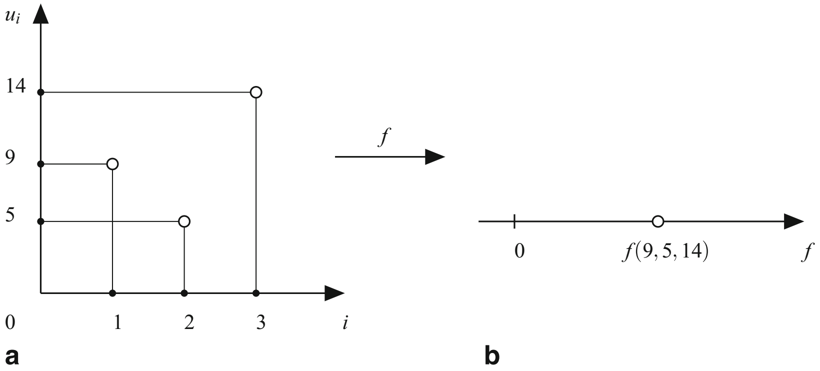

Fig. 7.1 The function $f(u_1, u_2, u_3)$ maps the triplet $(9, 5, 14)$ on **a** to a real number $f(9, 5, 14)$ on **b**.

values of u_1, u_2, and u_3 in one diagram as shown in Fig. 7.1a. The value of f corresponding to those specific u_1, u_2, and u_3 is then shown in another diagram, Fig. 7.1b. We can explore the behavior of the function by changing the values of u_1, u_2, and u_3, which amounts to vertical movements of the open circles in Fig. 7.1a, and then observing the corresponding horizontal movement of the open circle in Fig. 7.1b.

Admittedly, this new approach does not convey as much information as the conventional one. But, it has a virtue of being applicable regardless of the number of independent variables. Thus, a function $f(u_1, \ldots, u_n)$ of n variables can be expressed in the same manner even if $n = 1000$. In this case, we simply have 1000 open circles in Fig. 7.1a indicating the values of all these independent variables. Figure 7.1b will still contain just one open circle showing the value of f corresponding to those specific values of the independent variables.

Coming back to the case of just three independent variables, we note that nothing in our approach limits the index i on u_i to an integer. We could easily introduce new variables, such as $u_{1.2}$, $u_{\sqrt{2}}$, or $u_{7/3}$, and generate a new function

$$f(u_1, u_{1.2}, u_{\sqrt{2}}, u_2, u_{7/3}, u_3) \, . \tag{7.1}$$

All we have to do is draw more circles at appropriate positions in Fig. 7.1a. Continuing in this manner, we can include more and more circles between $i = 1$ and $i = 3$ until they form a continuous curve on the iu_i-plane in this interval. What we have then is a rule f of assigning a number to a function $u(i)$ defined for all *real numbers* i in the interval $1 \le i \le 3$. Such a rule of assignment is called a **functional**.

More generally, a functional is a rule of assigning a number $\mathscr{F}$ to a function $u(x)$ defined on some interval, such as $a \le x \le b$.[39] The functional dependence of $\mathscr{F}$ on the function $u(x)$ is indicated by a pair of square brackets. So, the functional is denoted by $\mathscr{F}[u]$. One particularly simple example of a functional is

$$\mathscr{F}_1[u] = \int_a^b u(x)\mathrm{d}x \, . \tag{7.2}$$

A slightly less trivial example is

$$\mathscr{F}_2[u] = \int_a^b x e^{u(x)} \mathrm{d}x \,. \tag{7.3}$$

The action integral $\mathscr{S}$ we encountered in Chap. 1 affords yet another example of a functional:

$$\mathscr{S}[q] = \int_{t_1}^{t_2} L(q, \dot{q}, t) \mathrm{d}t \,, \tag{7.4}$$

in which $\dot{q} = \mathrm{d}q/\mathrm{d}t$ is a known function of t once $q(t)$ is specified. Perhaps a little unexpectedly,

$$\mathscr{F}_3[u] = u(x_0) \,, \quad a \le x_0 \le b \,, \tag{7.5}$$

is also a functional. In fact, $\mathscr{F}_3$ assigns a number $u(x_0)$ to the function $u(x)$ defined on the interval $a \le x \le b$. The point becomes clearer if we rewrite (7.5) as

$$\mathscr{F}_3[u] = \int_a^b \delta(x - x_0) u(x) \mathrm{d}x \,, \quad a \le x_0 \le b \tag{7.6}$$

using the Dirac δ-function. (See Appendix D.) In what follows, we shall omit the explicit reference to the limits of integration unless demanded by the situation.

7.1.2 Functional Derivative

Let us consider a functional defined by

$$\mathscr{F}[u] := \int \ln[u(x) + 1] \mathrm{d}x \tag{7.7}$$

and compute the difference

$$\mathscr{F}[u + \delta u] - \mathscr{F}[u] = \int \{\ln[u(x) + \delta u(x) + 1] - \ln[u(x) + 1]\} \mathrm{d}x \,. \tag{7.8}$$

Using (B.6), we note that

$$\ln(x + a) = \ln x + \frac{a}{x} + \mathrm{h.o.} \tag{7.9}$$

Replacing x by $u(x) + 1$ and a by $\delta u(x)$ in this formula, we obtain

$$\ln[u(x) + \delta u(x) + 1] - \ln[u(x) + 1] = \frac{1}{u(x) + 1} \delta u(x) + \mathrm{h.o.} \tag{7.10}$$

So,

$$\mathscr{F}[u + \delta u] - \mathscr{F}[u] = \int \frac{1}{u(x) + 1} \delta u(x) \mathrm{d}x + \mathrm{h.o.} \tag{7.11}$$

The coefficient of $\delta u(x)$ in the integrand, $1/[u(x)+1]$, is called the first functional derivative of $\mathscr{F}[u]$.

More generally, we define the first **functional derivative** $\delta\mathscr{F}/\delta u(x)$ of $\mathscr{F}[u]$ by

$$\mathscr{F}[u+\delta u]-\mathscr{F}[u]=\int\frac{\delta\mathscr{F}}{\delta u(x)}\delta u(x)\mathrm{d}x+\text{h.o.} \tag{7.12}$$

We denote the first term on the right-hand side by $\delta\mathscr{F}$:

$$\delta\mathscr{F}:=\int\frac{\delta\mathscr{F}}{\delta u(x)}\delta u(x)\mathrm{d}x\,. \tag{7.13}$$

These equations generalizes the corresponding relations for ordinary functions,

$$f(u_1+\delta u_1,\ldots,u_n+\delta u_n)-f(u_1,\ldots,u_n)=\sum_{i=1}^{n}\frac{\partial f}{\partial u_i}\delta u_i+\text{h.o.} \tag{7.14}$$

and

$$\mathrm{d}f=\sum_{i=1}^{n}\frac{\partial f}{\partial u_i}\delta u_i\,, \tag{7.15}$$

respectively. When the index i on the variable u_i is replaced by x, which changes continuously, the summation with respect to i is replaced by the integration with respect to x.[40]

Example 7.1. Functional derivative:

a. For the functional $\mathscr{F}_1$ in (7.2),

$$\mathscr{F}_1[u+\delta u]-\mathscr{F}_1[u]=\int\delta u(x)\mathrm{d}x\,, \tag{7.16}$$

and hence

$$\frac{\delta\mathscr{F}_1}{\delta u(x)}=1\,. \tag{7.17}$$

b. For the functional $\mathscr{F}_2$ in (7.3),

$$\mathscr{F}_2[u+\delta u]-\mathscr{F}_2[u]=\int x[e^{u(x)+\delta u(x)}-e^{u(x)}]\mathrm{d}x=\int xe^{u(x)}\delta u(x)\mathrm{d}x+\text{h.o.} \tag{7.18}$$

Thus,

$$\frac{\delta\mathscr{F}_2}{\delta u(x)}=xe^{u(x)}\,. \tag{7.19}$$

c. Noting that (7.5) may be written as (7.6),

$$\mathscr{F}_3[u+\delta u]-\mathscr{F}_3[u]=\int\delta(x-x_0)\delta u(x)\mathrm{d}x\,. \tag{7.20}$$

So,
$$\frac{\delta \mathscr{F}_3}{\delta u(x)} = \frac{\delta u(x_0)}{\delta u(x)} = \delta(x - x_0)\ . \tag{7.21}$$

d. As a somewhat less trivial example, let
$$\mathscr{F}_4[u] = \int\int \phi(x_1,x_2)u(x_1)u(x_2)\mathrm{d}x_1\mathrm{d}x_2 \tag{7.22}$$

and suppose that the limits of integrations are the same for x_1 and x_2. Noting that
$$\begin{aligned}&[u(x_1)+\delta u(x_1)][u(x_2)+\delta u(x_2)] - u(x_1)u(x_2)\\ &\qquad = u(x_1)\delta u(x_2) + u(x_2)\delta u(x_1) + \text{h.o.}\ ,\end{aligned} \tag{7.23}$$

we find
$$\delta \mathscr{F}_4[u] = \int\int \phi(x_1,x_2)[u(x_1)\delta u(x_2) + u(x_2)\delta u(x_1)]\mathrm{d}x_1\mathrm{d}x_2\ . \tag{7.24}$$

Since x_1 and x_2 are just integration variables, they can be replaced by anything we like. For example, we can use x_2 for x_1 and x_1 for x_2, respectively. Thus,
$$\int\int \phi(x_1,x_2)u(x_1)\delta u(x_2)\mathrm{d}x_1\mathrm{d}x_2 = \int\int \phi(x_2,x_1)u(x_2)\delta u(x_1)\mathrm{d}x_1\mathrm{d}x_2\ . \tag{7.25}$$

Because the limits of integrations are the same for x_1 and x_2, we can now combine the two terms in (7.24) to find
$$\delta \mathscr{F}_4[u] = \int \left\{ \int [\phi(x_2,x_1) + \phi(x_1,x_2)]u(x_2)\mathrm{d}x_2 \right\} \delta u(x_1)\mathrm{d}x_1\ , \tag{7.26}$$

So,
$$\frac{\delta \mathscr{F}_4}{\delta u(x_1)} = \int [\phi(x_2,x_1) + \phi(x_1,x_2)]u(x_2)\mathrm{d}x_2\ . \tag{7.27}$$

If $\phi(x_1,x_2) = \phi(x_2,x_1)$, then,
$$\frac{\delta \mathscr{F}_4}{\delta u(x_1)} = 2\int \phi(x_1,x_2)u(x_2)\mathrm{d}x_2\ . \tag{7.28}$$

Exercise 7.1. Let
$$\mathscr{F}[u] = \int f(u(x),x)\mathrm{d}x\ . \tag{7.29}$$

Show that

$$\frac{\delta \mathscr{F}}{\delta u(x)} = \frac{\partial}{\partial u(x)} f(u(x),x) \,. \tag{7.30}$$

The functional derivatives of $\mathscr{F}_1$, $\mathscr{F}_2$, and $\mathscr{F}_3$ we considered in Example 7.1 can be found using this formula. ///

Exercise 7.2. Let

$$\mathscr{F}[u] = \int_V f(u(\boldsymbol{r}),\nabla u(\boldsymbol{r}))\mathrm{d}\boldsymbol{r} \,. \tag{7.31}$$

Assuming that $\delta u(\boldsymbol{r}) \equiv 0$ on the surface of V, show that

$$\frac{\delta \mathscr{F}}{\delta u(\boldsymbol{r})} = \frac{\partial f}{\partial u} - \nabla \cdot \frac{\partial f}{\partial \nabla u} \,. \tag{7.32}$$

Equations (7.31) and (7.32) should be compared with (1.59) and the integrand of (1.71), respectively. ///

From Example 7.1, we see that $\delta\mathscr{F}/\delta u(x)$ is either a function of $u(x)$ or a functional of $u(x)$. By (7.6), the former may also be regarded as a functional. Thus, the first functional derivative is not only a function of x but also a functional of $u(x)$. If needed, we can express this fact by writing

$$\mathscr{F}^{(1)}(x,u] := \frac{\delta \mathscr{F}}{\delta u(x)} \,. \tag{7.33}$$

We can now define the second functional derivative $\delta^2\mathscr{F}/\delta u(x_1)\delta u(x_2)$ of $\mathscr{F}$ by

$$\mathscr{F}^{(1)}(x_1,u+\delta u] - \mathscr{F}^{(1)}(x_1,u] = \int \frac{\delta^2 \mathscr{F}}{\delta u(x_1)\delta u(x_2)}\mathrm{d}x_2 + \text{h.o} \,. \tag{7.34}$$

Example 7.2. Second functional derivative: For $\mathscr{F}_1$ and $\mathscr{F}_3$ we saw in Example 7.1,

$$\frac{\delta^2 \mathscr{F}_1}{\delta u(x_1)\delta u(x_2)} = 0 \quad \text{and} \quad \frac{\delta^2 \mathscr{F}_3}{\delta u(x_1)\delta u(x_2)} = 0 \,. \tag{7.35}$$

Rewriting (7.19) as

$$\frac{\delta \mathscr{F}_2}{\delta u(x_1)} = \int x_2 e^{u(x_2)}\delta(x_2 - x_1)\mathrm{d}x_2 \,, \tag{7.36}$$

we find

$$\frac{\delta^2 \mathscr{F}_2}{\delta u(x_1)\delta u(x_2)} = x_2 e^{u(x_2)}\delta(x_2 - x_1) \,. \tag{7.37}$$

Finally, (7.27) gives

$$\frac{\delta^2 \mathscr{F}_4}{\delta u(x_1)\delta u(x_2)} = \phi(x_2,x_1) + \phi(x_1,x_2) \,, \tag{7.38}$$

which reduces to $2\phi(x_1,x_2)$ if $\phi(x_1,x_2) = \phi(x_2,x_1)$. We can reach the same conclusion if we start from (7.28). So, everything is consistent.

Recall the Taylor series expansion of a function f of multiple variables $u_1,\ldots,u_n$:

$$\begin{aligned} & f(u_1+\delta u_1,\ldots,u_n+\delta u_n) - f(u_1,\ldots,u_n) \\ &\qquad = \sum_{i=1}^{n} \frac{\partial f}{\partial u_i}\delta u_i + \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\partial^2 f}{\partial u_i \partial u_j}\delta u_i \delta u_j + \text{h.o.} \end{aligned} \tag{7.39}$$

Corresponding to this formula is the **functional Taylor series expansion** given by

$$\begin{aligned} \mathscr{F}[u+\delta u] - \mathscr{F}[u] = &\int \frac{\delta \mathscr{F}}{\delta u(x_1)}\delta u(x_1)\mathrm{d}x_1 \\ &+ \frac{1}{2}\int \frac{\delta^2 \mathscr{F}}{\delta u(x_1)\delta u(x_2)}\delta u(x_1)\delta u(x_2)\mathrm{d}x_1\mathrm{d}x_2 + \text{h.o.} \end{aligned} \tag{7.40}$$

Finally, if $u = u(x_1,x_2)$, the first functional derivative of $\mathscr{F}[u]$ is defined by

$$\mathscr{F}[u+\delta u] - \mathscr{F}[u] = \int\int \frac{\delta \mathscr{F}}{\delta u(x_1,x_2)}\delta u(x_1,x_2)\mathrm{d}x_1\mathrm{d}x_2 + \text{h.o.} \tag{7.41}$$

For example, if

$$\mathscr{F}[u] = \int\int\int \phi(x_1,x_2,x_3)u(x_1,x_2)u(x_2,x_3)u(x_3,x_1)\mathrm{d}x_1\mathrm{d}x_2\mathrm{d}x_3 \ , \tag{7.42}$$

and ϕ is invariant with respect to any permutation of the arguments, that is, $\phi(x_1,x_2,x_3) = \phi(x_2,x_1,x_3) = \cdots$, then,

$$\frac{\delta \mathscr{F}}{\delta u(x_1,x_2)} = 3\int\int \phi(x_1,x_2,x_3)u(x_2,x_3)u(x_3,x_1)\mathrm{d}x_3 \ . \tag{7.43}$$

Exercise 7.3. Derive (7.43). ///

7.2 Density Functional Theory

For simplicity, let us focus on a single component system and consider an open system of volume V. The system may contain an interfacial region or may otherwise be inhomogeneous. As we saw in Sect. 6.3.2, the temperature T and the chemical potential μ will be uniform throughout the system in equilibrium.[41] Their values are imposed by the surroundings serving as a reservoir of heat and molecules. In contrast, the number density n of molecules may vary across the system. How is

n determined as a function of position $\boldsymbol{r}$ in a system in equilibrium? How do we construct a fundamental equation of the system?

7.2.1 Equilibrium Density Profile

Following an analysis similar to what we saw in Sect. 2.13.2, we can deduce the condition of equilibrium of an open system:

Condition of Equilibrium 7 *For equilibrium of an open system held at a given temperature T, volume V, and chemical potential μ, it is necessary and sufficient that*

$$(\delta\Omega)_{T,V,\mu} \geq 0 \tag{7.44}$$

holds for any possible variation of the state of the system.

We recall that variations considered here are brought about through infinitesimal changes in the *unconstrained variables* $X_1, \ldots, X_m$. Thus,

$$(\delta\Omega)_{T,V,\mu} = \sum_{i=1}^{m} \left(\frac{\partial\Omega}{\partial X_i}\right)_{T,V,\mu,X_{j\neq i}} \delta X_i \,. \tag{7.45}$$

Equation (7.44) then determines the equilibrium values of $X_1, \ldots, X_m$.

Instead of $X_1, \ldots, X_m$, we now have a position-dependent function $n(\boldsymbol{r})$. Its value at each $\boldsymbol{r}$ is an unconstrained variable. Since $\boldsymbol{r}$ is capable of continuous variation, the sum over i in (7.45) must be replaced by the integration with respect to $\boldsymbol{r}$. Thus, the condition of equilibrium is that

$$\delta\Omega = \int_V \frac{\delta\Omega}{\delta n(\boldsymbol{r})} \delta n(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \geq 0 \tag{7.46}$$

holds for all possible values of $\delta n(\boldsymbol{r})$, where the integration is over the system volume V and we omitted the subscripts T, V, and μ.

Provided that $n(\boldsymbol{r})$ is positive everywhere, $\delta n(\boldsymbol{r})$ is capable of taking negative as well as positive values. Then, (7.46) leads to

$$\frac{\delta\Omega}{\delta n(\boldsymbol{r})} = 0 \,. \tag{7.47}$$

Given an explicit expression for the functional $\Omega[n]$, called a **density functional** or a **free energy functional**, (7.47) leads to an explicit equation for the equilibrium density profile $n^{\mathrm{eq}}(\boldsymbol{r})$. Once $n^{\mathrm{eq}}(\boldsymbol{r})$ is determined, we can compute the free energy $\Omega[n^{\mathrm{eq}}]$ of the system, which is then a fundamental equation of the inhomogeneous system. This method of computing $n^{\mathrm{eq}}(\boldsymbol{r})$ and the grand potential is known as the *statistical mechanical* or *classical* **density functional theory** (DFT), to be distinguished from the quantum mechanical DFT that aims to compute the electron density and the energy of quantum mechanical systems.

7.2.2 Microscopic Definition of Density

Before turning to the problem of finding the explicit form of $\Omega[n]$, we need to be a little more specific about what is meant by the density profile $n(\boldsymbol{r})$.

As we saw in Sect. 3.1, a measurable quantity of our interest is not a dynamical variable itself, but its ensemble average. So, what is the dynamical variable whose ensemble average gives $n(\boldsymbol{r})$?

It is very natural to demand that, for an arbitrary region of volume $\mathscr{R}$,

$$\int_{\mathscr{R}} n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{7.48}$$

should give the number of particles inside that region. The **density operator** defined by

$$\hat{n}(\boldsymbol{r},\boldsymbol{r}^N) := \sum_{i=1}^{N} \delta(\boldsymbol{r}-\boldsymbol{r}_i) \tag{7.49}$$

satisfies this demand. In fact,

$$\int_{\mathscr{R}} \delta(\boldsymbol{r}-\boldsymbol{r}_i)\mathrm{d}\boldsymbol{r} \tag{7.50}$$

is unity if the ith particle is inside $\mathscr{R}$ and zero otherwise. (See Appendix D.4 on the three-dimensional δ-function.) So, the integral of $\hat{n}$ over $\mathscr{R}$ gives the number of particles in $\mathscr{R}$. Taking the ensemble average, we identify

$$n(\boldsymbol{r}) = \langle \hat{n}(\boldsymbol{r},\boldsymbol{r}^N) \rangle = \left\langle \sum_{i=1}^{N} \delta(\boldsymbol{r}-\boldsymbol{r}_i) \right\rangle \tag{7.51}$$

as the **density profile**.

Given this definition of the density profile, let us see how it can be related to a partition function. For this purpose, consider a system subject to an external field $\psi(\boldsymbol{r})$. Its Hamiltonian is given by

$$H_N(\boldsymbol{r}^N,\boldsymbol{p}^N) = \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} + \phi(\boldsymbol{r}^N) + \sum_{i=1}^{N} \psi(\boldsymbol{r}_i)\ . \tag{7.52}$$

The grand canonical partition function of this system is given by

$$\Xi = \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N} N!} \int e^{-\beta\phi(\boldsymbol{r}^N)} e^{-\beta\sum_{i=1}^{N}\psi(\boldsymbol{r}_i)} \mathrm{d}\boldsymbol{r}^N\ , \tag{7.53}$$

in which we carried out the integration with respect to the momenta.

In order to introduce $\hat{n}$ into our formulation, we rewrite the external field term as follows:

$$\sum_{i=1}^{N} \psi(\boldsymbol{r}_i) = \sum_{i=1}^{N} \int_V \delta(\boldsymbol{r}-\boldsymbol{r}_i)\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \int_V \hat{n}(\boldsymbol{r},\boldsymbol{r}^N)\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \,. \tag{7.54}$$

Using this expression in (7.53), we see that Ξ is a functional of $\psi(\boldsymbol{r})$. By considering an infinitesimal variation of $\psi(\boldsymbol{r})$, we obtain

$$\frac{\delta \Xi}{\delta \psi(\boldsymbol{r})} = -\beta \sum_{N=0}^{\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N} N!} \int \hat{n}(\boldsymbol{r},\boldsymbol{r}^N) e^{-\beta\phi(\boldsymbol{r}^N)} e^{-\beta \sum_{i=1}^{N} \psi(\boldsymbol{r}_i)} \mathrm{d}\boldsymbol{r}^N \,. \tag{7.55}$$

Thus,

$$\frac{\delta \Omega}{\delta \psi(\boldsymbol{r})} = -k_B T \frac{\delta \ln \Xi}{\delta \psi(\boldsymbol{r})} = n(\boldsymbol{r}) \,. \tag{7.56}$$

Because the ensemble average is taken with respect to the equilibrium distribution, $n(\boldsymbol{r})$ computed by means of (7.56) actually is the equilibrium density profile $n^{\mathrm{eq}}(\boldsymbol{r})$ for given T, V, μ, and the external field $\psi(\boldsymbol{r})$.

Exercise 7.4. Derive (7.55). ///

Exercise 7.5. Consider an ideal gas in equilibrium in the presence of an external field $\psi(\boldsymbol{r})$. Using a grand canonical ensemble, derive the following results:

a.

$$n^{\mathrm{eq}}(\boldsymbol{r}) = \frac{e^{\beta[\mu-\psi(\boldsymbol{r})]}}{\Lambda^3} \,. \tag{7.57}$$

b.

$$\Omega[n^{\mathrm{eq}}] = -k_B T \int_V n^{\mathrm{eq}}(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \,. \tag{7.58}$$

For a homogeneous phase, $\Omega = -PV$ and (7.58) reduces to $PV = k_B T \langle N \rangle$, the ideal gas equation of state. ///

7.2.3 Ω for a Nonequilibrium Density Profile

Recall that the functional derivative $\delta\Omega/\delta n(\boldsymbol{r})$ is defined by the relation

$$\Omega[n+\delta n] - \Omega[n] = \int_V \frac{\delta \Omega}{\delta n(\boldsymbol{r})} \delta n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} + \text{h.o.} \,. \tag{7.59}$$

Thus, in order to apply (7.47), we need to know $\Omega[n]$ not only for the equilibrium density profile $n^{\mathrm{eq}}(\boldsymbol{r})$ but also for an arbitrary density profile $n(\boldsymbol{r})$. The following example illustrates the point.

Example 7.3. Ideal gas: Motivated by (7.58), let us suppose that

$$\Omega[n] = -k_BT \int_V n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} , \tag{7.60}$$

for an arbitrary $n(\boldsymbol{r})$. Then,

$$\frac{\delta\Omega}{\delta n(\boldsymbol{r})} = -k_BT . \tag{7.61}$$

According to (7.47), the left-hand side of this equation is zero at equilibrium. But, because the temperature of an ideal gas can be specified as we please, this is a contradiction. What went wrong?

We must remember that (7.58) applies only to the ideal gas in *equilibrium*. Thus, when we perturbed $n(\boldsymbol{r})$ in (7.60), we have also changed the external field so that the varied state is in equilibrium. In contrast, the functional derivative in (7.47) must be taken while holding the external field constant along with T, V, and μ. So, the contradiction is only apparent. But it does illustrate the need to develop an expression for $\Omega[n]$ for an arbitrary $n(\boldsymbol{r})$.

For given T, V, μ, and the external field, Ω of the system in equilibrium is, at least conceptually, a well-defined quantity. Thus, let us suppose in this section that $\Omega[n^{\mathrm{eq}}]$ is known and establish its relation to $\Omega[n]$ for an arbitrary $n(\boldsymbol{r})$.

For clarity, we denote by $n_a(\boldsymbol{r})$ the equilibrium density profile of a system under the influence of an external field $\psi_a(\boldsymbol{r})$. In general, the value of n_a at some point in the system depends on the form of the function $\psi_a(\boldsymbol{r})$ throughout the system. That is, n_a is not only a function of $\boldsymbol{r}$ but also a function*al* of ψ_a. To emphasize this fact, we write

$$n_a(\boldsymbol{r}) = n^{\mathrm{eq}}(\boldsymbol{r}, \psi_a] . \tag{7.62}$$

Our goal is to express $\Omega[n_a, \psi_b]$, the grand potential of the system with the density profile $n_a(\boldsymbol{r})$ and the external field $\psi_b(\boldsymbol{r})$, in terms of the known quantity $\Omega[n_a, \psi_a]$. To figure out their difference $\Omega[n_a, \psi_b] - \Omega[n_a, \psi_a]$, we consider the system in equilibrium under ψ_a and imagine suddenly changing the field to ψ_b. At this very moment, that is, before the system starts to respond to the new field, the system is characterized by the density profile n_a and the external field ψ_b. What would the value of Ω be? We recall the definition of the grand potential (2.202) and Gibbs's entropy formula

$$S = -k_B\langle \ln(h^{3N}N!\rho)\rangle \tag{7.63}$$

from Exercise 4.9. Then,

$$\Omega = U - TS - \mu\langle N\rangle = \langle H_N\rangle + k_BT\langle \ln(h^{3N}N!\rho)\rangle - \mu\int_V n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} , \tag{7.64}$$

in which ρ is the statistical weight. If we suppose that ρ has yet to adjust itself to the new field, the only difference between $\Omega[n_a, \psi_a]$ and $\Omega[n_a, \psi_b]$ is in $\langle H_N\rangle$, implying that

$$\Omega[n_a,\psi_b]-\Omega[n_a,\psi_a]=\left\langle\sum_{i=1}^{N}[\psi_b(\boldsymbol{r}_i)-\psi_a(\boldsymbol{r}_i)]\right\rangle=\int_V n_a(\boldsymbol{r})[\psi_b(\boldsymbol{r})-\psi_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\,, \tag{7.65}$$

where the last step follows from (7.54). So,

$$\Omega[n_a,\psi_b]=\Omega[n_a,\psi_a]+\int_V n_a(\boldsymbol{r})[\psi_b(\boldsymbol{r})-\psi_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\,. \tag{7.66}$$

To compute $\Omega[n_a,\psi_b]$, we need to find the field ψ_a that produces n_a as the equilibrium density profile. Theorem 7.3 in Sect. 7.3 guarantees the existence of such ψ_a.

Gibbs's entropy formula was established *only* for systems in equilibrium. By applying (7.63) to the nonequilibrium state, we have actually adopted a particular *definition* of $\Omega[n_a,\psi_b]$ among others that may be equally plausible. What matters here, though, is that (7.66) is compatible with the principle of thermodynamics. That is, $n_a=n_b$ is a solution of (7.47) when Ω is given by (7.66). Exercise 7.6 verifies this statement for the case of an ideal gas. For a more general demonstration, see Exercise 7.8. The issue discussed here has a statistical mechanical counterpart. See paragraph containing (7.94).

Exercise 7.6. Let us build on the Exercise 7.5 and examine the density functional for an ideal gas:

a. Show that

$$\Omega[n_a,\psi_b]=k_BT\int_V n_a(\boldsymbol{r})\left[\ln\frac{n_a(\boldsymbol{r})}{n_b(\boldsymbol{r})}-1\right]\mathrm{d}\boldsymbol{r}\,. \tag{7.67}$$

b. Show that

$$\Omega[n_a,\psi_b]=k_BT\int_V n_a(\boldsymbol{r})[\ln\Lambda^3 n_a(\boldsymbol{r})-1]\mathrm{d}\boldsymbol{r}-\int_V n_a(\boldsymbol{r})[\mu-\psi_b(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\,. \tag{7.68}$$

c. Use (7.67) in (7.47) to show that $n_a=n_b$ at equilibrium.
d. Use (7.68) in (7.47) to obtain (7.57). ///

7.2.4 †A Few Remarks on $\Omega[n_a,\psi_b]$

Taking the functional derivative of (7.66) with respect to ψ_b while holding n_a fixed, we find

$$\frac{\delta\Omega[n_a,\psi_b]}{\delta\psi_b(\boldsymbol{r})}=n_a(\boldsymbol{r})\,,\quad \text{fixed } n_a\,. \tag{7.69}$$

Similarly, the functional derivative of (7.66) with respect to ψ_a with n_a fixed yields

$$\frac{\delta\Omega[n_a,\psi_a]}{\delta\psi_a(\boldsymbol{r})} = n_a(\boldsymbol{r}) \,, \quad \text{fixed } n_a \,. \tag{7.70}$$

These results appear identical to (7.56). However, (7.56) was obtained without imposing any constraint on the density profile. In fact, our derivation of (7.56) amounts to comparing the values of Ω of the system *in equilibrium* under slightly different external fields.

Therefore, it is of some interest to derive (7.56) directly from (7.66). Given a system in equilibrium under the external field ψ_a, we perturb the field while allowing the system to adjust n_a so as to maintain the equilibrium. We denote the modified field by $\psi_a + \delta\psi$ and the corresponding equilibrium density profile by $n_a + \delta n$. Then,

$$\begin{aligned}&\Omega[n_a+\delta n,\psi_a+\delta\psi]-\Omega[n_a,\psi_a]\\&\quad=\Omega[n_a+\delta n,\psi_a+\delta\psi]-\Omega[n_a+\delta n,\psi_a]+\Omega[n_a+\delta n,\psi_a]-\Omega[n_a,\psi_a]\,.\end{aligned} \tag{7.71}$$

Using (7.66),

$$\begin{aligned}&\Omega[n_a+\delta n,\psi_a+\delta\psi]-\Omega[n_a+\delta n,\psi_a]\\&\qquad=\int_V[n_a(\boldsymbol{r})+\delta n(\boldsymbol{r})]\delta\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r}=\int_V n_a(\boldsymbol{r})\delta\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r}+\text{h.o.}\,,\end{aligned} \tag{7.72}$$

while

$$\Omega[n_a+\delta n,\psi_a]-\Omega[n_a,\psi_a]=\text{h.o.} \tag{7.73}$$

because n_a is the equilibrium density profile for the field ψ_a. It follows that

$$\delta\Omega=\int_V n_a(\boldsymbol{r})\delta\psi(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{7.74}$$

for the perturbation under consideration. Thus,

$$\frac{\delta\Omega}{\delta\psi_a(\boldsymbol{r})}=n_a(\boldsymbol{r})\,, \tag{7.75}$$

which is (7.56).

Equation (7.66) may be rewritten in a physically more illuminating manner. For this purpose, let us first define what may be referred to as the **intrinsic grand potential** by

$$\Omega_{\text{int}}[n_a,\psi_a]:=\Omega[n_a,\psi_a]-\int_V n_a(\boldsymbol{r})\psi_a(\boldsymbol{r})\mathrm{d}\boldsymbol{r}\,, \tag{7.76}$$

which is the part of the grand potential of the system in equilibrium that excludes the contribution to $\langle H_N\rangle$ from the external field.

We also recall from (7.62) that $n_a(\boldsymbol{r})$ is uniquely determined by $\psi_a(\boldsymbol{r})$. Thus, the explicit reference to n_a in $\Omega_{\text{int}}[n_a, \psi_a]$ is redundant and can be dropped. Moreover, as we shall show in Sect. 7.3, it is also true that $n_a(\boldsymbol{r})$ uniquely determines $\psi_a(\boldsymbol{r})$. That is, $\psi_a(\boldsymbol{r})$ is a functional of $n_a(\boldsymbol{r})$:

$$\psi_a(\boldsymbol{r}) = \psi(\boldsymbol{r}, n_a] \tag{7.77}$$

and the functional dependence on ψ_a may be replaced by that on n_a. In summary, therefore,

$$\Omega_{\text{int}}[n_a, \psi_a] = \Omega_{\text{int}}[\psi_a] = \Omega_{\text{int}}[n_a] \,. \tag{7.78}$$

Using (7.76) and (7.78), we can rewrite (7.66) as

$$\Omega[n_a, \psi_b] = \Omega_{\text{int}}[n_a] + \int_V n_a(\boldsymbol{r})\psi_b(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \,, \tag{7.79}$$

which is the desired expression indicating that $\Omega[n_a, \psi_b]$ is the sum of two contributions. One is the intrinsic part of the grand potential of the system in equilibrium with the density profile n_a. The other is the potential energy due to the external field ψ_b.

Dropping references to ψ_a and n_a, respectively, from Ω_{int} and Ω in (7.76), we obtain

$$\Omega_{\text{int}}[n_a] = \Omega[\psi_a] - \int_V n_a(\boldsymbol{r})\psi_a(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \,. \tag{7.80}$$

In view of (7.75), Ω_{int} is a Legendre transform of Ω.[42] Accordingly, we anticipate that

$$\frac{\delta\Omega_{\text{int}}}{\delta n_a(\boldsymbol{r})} = -\psi_a(\boldsymbol{r}) \,. \tag{7.81}$$

Exercise 7.7. Derive (7.81). ///

Exercise 7.8. Using (7.66), show that $n_b(\boldsymbol{r})$ satisfies (7.47). ///

7.3 Formal Development

In Sect. 7.2.1, we introduced the notion of density functional purely on the basis of thermodynamics. The subsequent development made only a very modest use of the concepts from statistical mechanics. While this may help us develop physical intuitions about DFT, the ultimate goal of the theory is to generate the fundamental equation of an inhomogeneous system starting from the Hamiltonian. That is, DFT is one example among many applications of statistical mechanics, and warrants a purely statistical mechanical formulation.

7.3.1 Definitions

Consider a grand canonical ensemble and let $\rho(\boldsymbol{r}^N, \boldsymbol{p}^N, N)$ denote a probability distribution over all possible microstates. The equilibrium probability distribution

$$\rho^{\text{eq}}(\boldsymbol{r}^N, \boldsymbol{p}^N, N) = \frac{1}{\Xi^{\text{eq}}} \frac{e^{\beta[\mu N - H_N(\boldsymbol{r}^N, \boldsymbol{p}^N)]}}{h^{3N} N!} , \tag{7.82}$$

in which Ξ^{eq} is the grand canonical partition function, is an example of ρ. In DFT, however, we consider more general probability distributions. So, the form of the function ρ is arbitrary except that it must satisfy the normalization condition:

$$\mathrm{Tr}^{\text{cl}}\{\rho(\boldsymbol{r}^N, \boldsymbol{p}^N, N)\} = 1 , \tag{7.83}$$

where Tr^{cl} is the so-called **classical trace**, and is defined by

$$\mathrm{Tr}^{\text{cl}}\{A(\boldsymbol{r}^N, \boldsymbol{p}^N, N)\} = \sum_{N=0}^{\infty} \int A(\boldsymbol{r}^N, \boldsymbol{p}^N, N) \mathrm{d}\boldsymbol{r}^N \mathrm{d}\boldsymbol{p}^N . \tag{7.84}$$

For example,

$$\Xi^{\text{eq}} = \mathrm{Tr}^{\text{cl}} \left\{ \frac{e^{\beta(\mu N - H_N)}}{h^{3N} N!} \right\} . \tag{7.85}$$

We now define a functional of ρ by

$$\Omega[\rho] := \mathrm{Tr}^{\text{cl}} \left\{ \rho \left[H_N - \mu N + k_B T \ln(h^{3N} N! \rho) \right] \right\} . \tag{7.86}$$

7.3.2 Key Properties of the Density Functional

Let us record the following three key properties of the functional $\Omega[\rho]$ as theorems and collect their proofs in Sect. 7.3.3.

Theorem 7.1.

$$\Omega[\rho^{\text{eq}}] = -k_B T \ln \Xi^{\text{eq}} , \tag{7.87}$$

which we recognize as the grand potential.

Theorem 7.2.

$$\Omega[\rho] \geq \Omega[\rho^{\text{eq}}] , \tag{7.88}$$

where the equality holds if and only if $\rho \equiv \rho^{\text{eq}}$.

Theorem 7.3. *Suppose that* ρ *may be written as*

$$\rho(\boldsymbol{r}^N, \boldsymbol{p}^N, N) = \frac{1}{\Xi} \frac{e^{\beta[\mu N - H_N^0 - \sum_{i=1}^N u(\boldsymbol{r}_i)]}}{h^{3N} N!} \tag{7.89}$$

with the constant Ξ *determined by (7.83). Here,*

$$H_N^0 := \sum_{i=1}^{N} \frac{\|\boldsymbol{p}_i\|^2}{2m} + \phi(\boldsymbol{r}^N) \tag{7.90}$$

is the Hamiltonian of the system excluding the external field ψ*. If we limit our consideration to* ρ *that can be expressed as (7.89), there is a one-to-one correspondence between* ρ *and the density profile*

$$n(\boldsymbol{r}) = \mathrm{Tr}^{\mathrm{cl}}\{\rho \hat{n}\}\,, \tag{7.91}$$

where $\hat{n}$ *is the density operator defined by (7.49).*

The actual system of our interest is subject to the external field $\psi(\boldsymbol{r})$. Thus, ρ defined by (7.89) is not the equilibrium distribution unless $u(\boldsymbol{r}) \equiv \psi(\boldsymbol{r})$. Equation (7.91) gives the equilibrium density profile of the system if it is subject to the external field $u(\boldsymbol{r})$ in place of $\psi(\boldsymbol{r})$.

By virtue of Theorem 7.3, Ω may be expressed as a functional of n:

$$\Omega[\rho] = \Omega[n]\,. \tag{7.92}$$

(It must be clearly understood that the explicit form of the functional $\Omega[\rho]$ differs from that of $\Omega[n]$.) Theorem 7.2 then reads

$$\Omega[n] \geq \Omega[n^{\mathrm{eq}}] \tag{7.93}$$

with the equality holding if and only if $n \equiv n^{\mathrm{eq}}$. This is a statistical mechanical version of (7.44).

Finally, (7.89) does *not* exhaust all possible forms of ρ. For example,

$$\rho(\boldsymbol{r}^N, \boldsymbol{p}^N, N) \propto \exp\left\{\beta\left[\mu N - H_N^0(\boldsymbol{r}^N, \boldsymbol{p}^N) + f(\boldsymbol{p}^N)\right]\right\} \tag{7.94}$$

cannot be written in the form of (7.89). The same applies if we have $f(\|\boldsymbol{r}_2 - \boldsymbol{r}_1\|)$ in place of $f(\boldsymbol{p}^N)$, for example. The point, however, is that ρ in the form of (7.89) is sufficient to guarantee the existence of the density functional $\Omega[n]$ that is compatible with the principle of thermodynamics embodied in (7.44).

Example 7.4. Statistical mechanical derivation of (7.66): Consider a system with the density profile $n_a(\boldsymbol{r})$ in the presence of the external field $u_b(\boldsymbol{r})$. Given $n_a(\boldsymbol{r})$, Theorem 7.3 guarantees the existence of the corresponding ρ_a (and hence of u_a):

$$\rho_a = \frac{1}{\Xi_a} \frac{e^{\beta[\mu N - H_N^0 - \sum_{i=1}^{N} u_a(\boldsymbol{r}_i)]}}{h^{3N} N!}\,. \tag{7.95}$$

Using this expression in (7.86), we obtain

$$\Omega[n_a,u_b] = \mathrm{Tr}^{\mathrm{cl}}\left\{\rho_a\left[H_N^0 + \sum_{i=1}^N u_b(\boldsymbol{r}_i) - \mu N + k_B T \ln(h^{3N} N! \rho_a)\right]\right\} \tag{7.96}$$

Replacing u_b by u_a,

$$\Omega[n_a,u_a] = \mathrm{Tr}^{\mathrm{cl}}\left\{\rho_a\left[H_N^0 + \sum_{i=1}^N u_a(\boldsymbol{r}_i) - \mu N + k_B T \ln(h^{3N} N! \rho_a)\right]\right\} \tag{7.97}$$

Subtracting (7.97) from (7.96), we obtain

$$\Omega[n_a,u_b] - \Omega[n_a,u_a] = \mathrm{Tr}^{\mathrm{cl}}\left\{\rho_a \sum_{i=1}^N [u_b(\boldsymbol{r}_i) - u_a(\boldsymbol{r}_i)]\right\} . \tag{7.98}$$

Using the density operator,

$$\begin{aligned} \mathrm{Tr}^{\mathrm{cl}}\left\{\rho_a \sum_{i=1}^N [u_b(\boldsymbol{r}_i) - u_a(\boldsymbol{r}_i)]\right\} &= \mathrm{Tr}^{\mathrm{cl}}\left\{\rho_a \int_V \hat{n}(\boldsymbol{r},\boldsymbol{r}^N)[u_b(\boldsymbol{r}) - u_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\right\} \\ &= \int_V \mathrm{Tr}^{\mathrm{cl}}\{\rho_a \hat{n}\}[u_b(\boldsymbol{r}) - u_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} = \int_V n_a(\boldsymbol{r})[u_b(\boldsymbol{r}) - u_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} , \end{aligned} \tag{7.99}$$

where we used (7.91). Thus,

$$\Omega[n_a,u_b] - \Omega[n_a,u_a] = \int_V n_a(\boldsymbol{r})[u_b(\boldsymbol{r}) - u_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} , \tag{7.100}$$

which is (7.66).

7.3.3 †Proofs of Theorems

Let us prove the theorems just introduced.

Proof of Theorem 7.1

We have only to replace ρ in (7.86) by ρ^{eq} and substitute (7.82) for the second ρ^{eq}. □

Proof of Theorem 7.2

$$\begin{aligned}\Omega[\rho] &= \mathrm{Tr}^{\mathrm{cl}}\left\{\rho\left[H_N-\mu N+k_BT\ln(h^{3N}N!\rho)\right]\right\}\\ &= \mathrm{Tr}^{\mathrm{cl}}\left\{\rho\left[H_N-\mu N+k_BT\ln(h^{3N}N!\rho^{\mathrm{eq}})\right]\right\}+k_BT\,\mathrm{Tr}^{\mathrm{cl}}\left\{\rho\left(\ln\rho-\ln\rho^{\mathrm{eq}}\right)\right\}\\ &\geq \mathrm{Tr}^{\mathrm{cl}}\left\{\rho\left[H_N-\mu N+k_BT\ln(h^{3N}N!\rho^{\mathrm{eq}})\right]\right\}\ ,\end{aligned} \tag{7.101}$$

where we used the Gibbs–Bogoliubov inequality discussed in Appendix B.5. The equality in (7.101) holds if and only if $\rho\equiv\rho^{\mathrm{eq}}$.

From (7.82),

$$k_BT\ln(h^{3N}N!\rho^{\mathrm{eq}})=\mu N-H_N-k_BT\ln\Xi^{\mathrm{eq}}=\mu N-H_N+\Omega[\rho^{\mathrm{eq}}]\ , \tag{7.102}$$

which is now substituted into (7.101) to give

$$\Omega[\rho]\geq\mathrm{Tr}^{\mathrm{cl}}\{\rho\Omega[\rho^{\mathrm{eq}}]\}=\Omega[\rho^{\mathrm{eq}}]\mathrm{Tr}^{\mathrm{cl}}\{\rho\}=\Omega[\rho^{\mathrm{eq}}]\ . \tag{7.103}$$

The second step is justified because $\Omega[\rho^{\mathrm{eq}}]$, being a quantity obtained after the classical trace, does not dependent on $\boldsymbol{r}^N$, $\boldsymbol{p}^N$, or N. The last step follows from the normalization condition (7.83). □

Proof of Theorem 7.3

For a given $u(\boldsymbol{r})$, ρ is completely determined by (7.89). The corresponding $n(\boldsymbol{r})$ follows from (7.91). Pictorially, we have

$$u\longrightarrow\rho\longrightarrow n\ . \tag{7.104}$$

The content of Theorem 7.3 is that, if we limit ourselves to ρ written in the form of (7.89), there is always one and only one ρ that corresponds to *any* density $n(\boldsymbol{r})$ we prescribe to the system. In view of (7.104), it is sufficient to prove the existence and the uniqueness of $u(\boldsymbol{r})$ that produces the given $n(\boldsymbol{r})$:

$$n\longrightarrow u\ . \tag{7.105}$$

By (7.91), $n(\boldsymbol{r})$ is the *equilibrium* density profile of the system subject to the field $u(\boldsymbol{r})$ instead of $\psi(\boldsymbol{r})$. Using the notation introduced in (7.62), therefore, we have

$$n(\boldsymbol{r})=n^{\mathrm{eq}}(\boldsymbol{r},u]\ . \tag{7.106}$$

The claim we wish to prove is that (7.106), regarded as an equation for $u(\boldsymbol{r})$, has a unique solution for any $n(\boldsymbol{r})$. We prove the uniqueness of $u(\boldsymbol{r})$ first and then argue for its existence.

Uniqueness

The proof is by contradiction. Suppose that

$$n(\boldsymbol{r}) = n^{\mathrm{eq}}(\boldsymbol{r}, u_a] = n^{\mathrm{eq}}(\boldsymbol{r}, u_b] \,, \tag{7.107}$$

where u_a and u_b are two *distinct* external fields, for which (7.89) reads

$$\rho_a = \frac{1}{\Xi_a} \frac{e^{\beta[\mu N - H_N^0 - \sum_{i=1}^N u_a(\boldsymbol{r}_i)]}}{h^{3N} N!} \quad \text{and} \quad \rho_b = \frac{1}{\Xi_b} \frac{e^{\beta[\mu N - H_N^0 - \sum_{i=1}^N u_b(\boldsymbol{r}_i)]}}{h^{3N} N!} \,, \tag{7.108}$$

respectively. By (7.86) and Theorem 7.2, we have

$$\begin{aligned}
\Omega[\rho_a] &= \mathrm{Tr}^{\mathrm{cl}} \left\{ \rho_a \left[H_N^0 - \mu N + k_B T \ln(h^{3N} N! \rho_a) + \sum_{i=1}^N u_a(\boldsymbol{r}_i) \right] \right\} \\
&< \mathrm{Tr}^{\mathrm{cl}} \left\{ \rho_b \left[H_N^0 - \mu N + k_B T \ln(h^{3N} N! \rho_b) + \sum_{i=1}^N u_a(\boldsymbol{r}_i) \right] \right\} \\
&= \Omega[\rho_b] + \mathrm{Tr}^{\mathrm{cl}} \left\{ \rho_b \sum_{i=1}^N [u_a(\boldsymbol{r}_i) - u_b(\boldsymbol{r}_i)] \right\} .
\end{aligned} \tag{7.109}$$

Using (7.99), we find

$$\Omega[\rho_a] < \Omega[\rho_b] + \int_V n(\boldsymbol{r})[u_a(\boldsymbol{r}) - u_b(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} \,. \tag{7.110}$$

Similarly,

$$\Omega[\rho_b] < \Omega[\rho_a] + \int_V n(\boldsymbol{r})[u_b(\boldsymbol{r}) - u_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} \,. \tag{7.111}$$

Adding these two inequalities, we arrive at the contradiction:

$$\Omega[\rho_a] + \Omega[\rho_b] < \Omega[\rho_a] + \Omega[\rho_b] \,. \tag{7.112}$$

Thus, $u_a \equiv u_b$. ☐

Existence

Suppose that a system is under the external field $u(\boldsymbol{r})$. Left undisturbed, the system will eventually reach a state of equilibrium, in which

$$n(\boldsymbol{r}) = n^{\mathrm{eq}}(\boldsymbol{r}, u] \,. \tag{7.113}$$

So, at least for this $n(\boldsymbol{r})$, the corresponding external field does exist.

Now we show that the external field exists also for any density profile that is infinitesimally different from $n(\boldsymbol{r})$. For this purpose, we consider an infinitesimal perturbation $\delta u(\boldsymbol{r})$ to the field. According to the definition of the functional derivative, the response is given by

$$\delta n(\boldsymbol{r}) = \int_V \frac{\delta n(\boldsymbol{r})}{\delta u(\boldsymbol{r}')} \delta u(\boldsymbol{r}') \mathrm{d}\boldsymbol{r}' \tag{7.114}$$

to the first order of the variation.

As we have seen, $u(\boldsymbol{r})$ for a given $n(\boldsymbol{r})$ is unique. So, any distinct perturbations $\delta u_1(\boldsymbol{r}')$ and $\delta u_2(\boldsymbol{r}')$ produce distinct responses $\delta n_1(\boldsymbol{r})$ and $\delta n_2(\boldsymbol{r})$, respectively.[43] Conversely, it is clear from (7.89) and (7.91) that distinct responses can result only from distinct perturbations of the field. It follows that (7.114) is invertible and we can write

$$\delta u(\boldsymbol{r}') = \int_V \frac{\delta u(\boldsymbol{r}')}{\delta n(\boldsymbol{r})} \delta n(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \,. \tag{7.115}$$

By means of this equation, we can compute $\delta u(\boldsymbol{r}')$ that produces any response $\delta n(\boldsymbol{r})$ we desire.[44]

What about an arbitrary density profile $n_b(\boldsymbol{r})$ that may differ from the initial equilibrium profile $n_a(\boldsymbol{r}) = n^{\mathrm{eq}}(\boldsymbol{r}, u_a]$ by more than an infinitesimal amount? In this case, we can apply (7.115) repeatedly to a series of infinitesimal variations $\delta n(\boldsymbol{r})$ until we eventually arrive at the desired profile. The corresponding field $u_b(\boldsymbol{r}')$ is the initial field $u_a(\boldsymbol{r}')$ plus the sum of all the infinitesimal variations $\delta u(\boldsymbol{r}')$ evaluated by (7.115) along the way. As an example, consider a particular path specified by

$$n_\lambda(\boldsymbol{r}) = n_a(\boldsymbol{r}) + \lambda[n_b(\boldsymbol{r}) - n_a(\boldsymbol{r})] \,, \quad 0 \le \lambda \le 1 \,. \tag{7.116}$$

The thermodynamic integration method described in the next section leads to

$$u_b(\boldsymbol{r}') = u_a(\boldsymbol{r}') + \int_0^1 \int_V \frac{\delta u_\lambda(\boldsymbol{r}')}{\delta n_\lambda(\boldsymbol{r})} [n_b(\boldsymbol{r}) - n_a(\boldsymbol{r})] \mathrm{d}\boldsymbol{r} \mathrm{d}\lambda \,, \tag{7.117}$$

where $n_\lambda(\boldsymbol{r}) = n^{\mathrm{eq}}(\boldsymbol{r}, u_\lambda]$. ☐

Substituting (7.115) with $\boldsymbol{r}$ replaced by $\boldsymbol{r}''$ into (7.114), we see that

$$\begin{aligned}
\delta n(\boldsymbol{r}) &= \int_V \frac{\delta n(\boldsymbol{r})}{\delta u(\boldsymbol{r}')} \left[\int_V \frac{\delta u(\boldsymbol{r}')}{\delta n(\boldsymbol{r}'')} \delta n(\boldsymbol{r}'') \mathrm{d}\boldsymbol{r}'' \right] \mathrm{d}\boldsymbol{r}' \\
&= \int_V \left[\int_V \frac{\delta n(\boldsymbol{r})}{\delta u(\boldsymbol{r}')} \frac{\delta u(\boldsymbol{r}')}{\delta n(\boldsymbol{r}'')} \mathrm{d}\boldsymbol{r}' \right] \delta n(\boldsymbol{r}'') \mathrm{d}\boldsymbol{r}'' \,.
\end{aligned} \tag{7.118}$$

It follows that

$$\int_V \frac{\delta n(\boldsymbol{r})}{\delta u(\boldsymbol{r}')} \frac{\delta u(\boldsymbol{r}')}{\delta n(\boldsymbol{r}'')} \mathrm{d}\boldsymbol{r}' = \delta(\boldsymbol{r} - \boldsymbol{r}'') \,. \tag{7.119}$$

The two functional derivatives in the integrand are said to be the **functional inverse** of each other.

7.4 Construction of a Density Functional

Before DFT can be utilized for any practical purposes, we must identify the explicit form of the density functional. The basic tool we use for this purpose is the **thermodynamic integration method**. That is, we first compute $\delta\Omega$ in response to a particular variation either of the external field and/or the intermolecular potential. The resulting expression is then integrated from a reference state for which Ω is known to the actual state of our interest.

Because the functional derivative, to which $\delta\Omega$ is related, and the subsequent integration are the opposite operations, it seems strange to suggest that anything useful should come out of this. Nevertheless, the functional derivative gives rise to quantities which afford direct physical interpretations. This opens up the possibility of developing physically meaningful approximations for them even if they may be difficult to evaluate exactly.

7.4.1 Variation of the External Field

Consider a system in equilibrium subject to the external field ψ_a. The quantity of interest is the difference

$$\Omega[n_b, \psi_b] - \Omega[n_a, \psi_a] \,. \tag{7.120}$$

Since the expression involves only the equilibrium density profiles, this is the reversible work required to change the external field from ψ_a to ψ_b. To compute this quantity, we use a reversible work source to generate an external field

$$\lambda[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})] \tag{7.121}$$

so that the total external field experienced by the system is

$$\psi_\lambda(\boldsymbol{r}) := \psi_a(\boldsymbol{r}) + \lambda[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})] \,. \tag{7.122}$$

Clearly, $\psi_{\lambda=0} = \psi_a$ and $\psi_{\lambda=1} = \psi_b$. If we change λ very slowly from 0 to 1, the system will have a sufficient time to establish the equilibrium density profile

$$n_\lambda(\boldsymbol{r}) := n^{\text{eq}}(\boldsymbol{r}, \psi_\lambda] \tag{7.123}$$

at each value of λ. Such a process is reversible.

Now, recalling the definition of the functional derivative and using (7.56), in which $n(\boldsymbol{r})$ is the equilibrium density profile for a given external field, we have

$$\delta\Omega[\psi_\lambda] = \int_V \frac{\delta\Omega}{\delta\psi_\lambda(\boldsymbol{r})}\delta\psi_\lambda(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \int_V n_\lambda(\boldsymbol{r})\delta\psi_\lambda(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \,. \tag{7.124}$$

According to (7.122),

$$\delta\psi_\lambda(\boldsymbol{r}) = [\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})]\delta\lambda \tag{7.125}$$

for an infinitesimal change in λ and (7.124) becomes

$$\delta\Omega[\psi_\lambda] = \int_V n_\lambda(\boldsymbol{r})[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})]\delta\lambda \mathrm{d}\boldsymbol{r} . \tag{7.126}$$

Dividing both sides by $\delta\lambda$ and taking the limit of $\delta\lambda \to 0$, we obtain

$$\frac{\partial\Omega}{\partial\lambda} = \int_V n_\lambda(\boldsymbol{r})[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} . \tag{7.127}$$

We now integrate this expression from $\lambda = 0$ to $\lambda = 1$ and obtain

$$\Omega[n_b, \psi_b] = \Omega[n_a, \psi_a] + \int_0^1 \int_V n_\lambda(\boldsymbol{r})[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\mathrm{d}\lambda . \tag{7.128}$$

7.4.2 Variation of the Intermolecular Potential: Case 1

Consider a system in equilibrium under the external field ψ. This time, the thermodynamic integration involves a continuous change in the intermolecular potential $\phi(\boldsymbol{r}^N)$. But, the external field will be held fixed.

We assume the **pairwise additivity** of the intermolecular potential and write

$$\phi(\boldsymbol{r}^N) = \frac{1}{2}\sum_{i=1}^{N}{\sum_{j=1}^{N}}' v(\boldsymbol{r}_i, \boldsymbol{r}_j) , \tag{7.129}$$

where v is referred to as the **pair potential** and $'$ indicates that the $j = i$ term is excluded from the second sum.

The quantity of our interest is the difference

$$\Omega[n_b, v_b] - \Omega[n_a, v_a] , \tag{7.130}$$

where

$$n_a(\boldsymbol{r}) := n^{\mathrm{eq}}(\boldsymbol{r}, v_a] . \tag{7.131}$$

is the equilibrium density profile when the pair potential is $v_a(\boldsymbol{r})$. Similarly for n_b.

In order to consider the functional derivative of Ω with respect to v, we define

$$\hat{I}(\boldsymbol{r}, \boldsymbol{r}') := \sum_{i=1}^{N}{\sum_{j=1}^{N}}' \delta(\boldsymbol{r} - \boldsymbol{r}_i)\delta(\boldsymbol{r}' - \boldsymbol{r}_j) \tag{7.132}$$

and rewrite (7.129) as

$$\phi(\boldsymbol{r}^N) = \frac{1}{2}\int_V \int_V \hat{I}(\boldsymbol{r}, \boldsymbol{r}')v(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' . \tag{7.133}$$

Using (7.133) in (7.53) and recalling (7.41), we observe that

$$\frac{\delta \Omega}{\delta v(\boldsymbol{r},\boldsymbol{r}')} = \frac{1}{2}\langle \hat{I}(\boldsymbol{r},\boldsymbol{r}',\boldsymbol{r}^N)\rangle =: \frac{1}{2}n^{(2)}(\boldsymbol{r},\boldsymbol{r}') =: \frac{1}{2}n(\boldsymbol{r})n(\boldsymbol{r}')g(\boldsymbol{r},\boldsymbol{r}') \,, \tag{7.134}$$

in which $n^{(2)}(\boldsymbol{r},\boldsymbol{r}')$ and $g(\boldsymbol{r},\boldsymbol{r}')$ are called, respectively, the **pair distribution function** and the **radial distribution function**. Their physical content will be discussed in Sect. 7.4.4. Using g, we can write

$$\delta \Omega = \frac{1}{2}\int_V \int_V n(\boldsymbol{r})n(\boldsymbol{r}')g(\boldsymbol{r},\boldsymbol{r}')\delta v(\boldsymbol{r},\boldsymbol{r}')\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \,, \tag{7.135}$$

in which n and g are to be computed for the system in equilibrium before we made an infinitesimal change in the pair potential.

As in the previous subsection, let

$$v_\lambda(\boldsymbol{r},\boldsymbol{r}') := v_a(\boldsymbol{r},\boldsymbol{r}') + \lambda[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')] \,, \tag{7.136}$$

which is v_a if $\lambda = 0$ and v_b if $\lambda = 1$. For this particular choice of v_λ,

$$\delta v_\lambda(\boldsymbol{r},\boldsymbol{r}') = [v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\delta\lambda \,. \tag{7.137}$$

Substituting this expression into (7.135), dividing the resulting equation by $\delta\lambda$, and then taking the $\delta\lambda \to 0$ limit, we obtain

$$\frac{\partial \Omega}{\partial \lambda} = \frac{1}{2}\int_V \int_V n_\lambda(\boldsymbol{r})n_\lambda(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \,, \tag{7.138}$$

where g_λ and n_λ are, respectively, the radial distribution function and the equilibrium density profile in the system in which the pair potential is v_λ. Integrating (7.138) with respect to λ, we find

$$\begin{aligned}\Omega[n_b, v_b] = {} & \Omega[n_a, v_a] \\ & + \frac{1}{2}\int_0^1 \int_V \int_V n_\lambda(\boldsymbol{r})n_\lambda(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathrm{d}\lambda \,.\end{aligned} \tag{7.139}$$

7.4.3 Variation of the Intermolecular Potential: Case 2

In Sect. 7.4.1, we considered the variation of the external field $\psi(\boldsymbol{r})$ without changing the functional form of the pair potential $v(\boldsymbol{r},\boldsymbol{r}')$. In Sect. 7.4.2, the functional form of $\psi(\boldsymbol{r})$ was fixed while $v(\boldsymbol{r},\boldsymbol{r}')$ was varied. In both cases, this meant that the density profile had to change along the integration path.

However, Theorem 7.3 guarantees the existence of $\psi(\boldsymbol{r})$ for *any* equilibrium density profile we prescribe to the system. This means that, as we vary $v(\boldsymbol{r},\boldsymbol{r}')$, we can always adjust $\psi(\boldsymbol{r})$ to maintain the same equilibrium density profile. For the particular variation given by (7.137), we have

$$\delta\Omega = \int_V n(\boldsymbol{r})\delta\psi_\lambda(\boldsymbol{r})\mathrm{d}\boldsymbol{r} + \frac{1}{2}\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\delta\lambda\,\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' , \tag{7.140}$$

where $\delta\psi_\lambda(\boldsymbol{r})$ is the adjustment that must be made to the external field in order to keep the density profile unchanged when v_λ is varied by an infinitesimal amount. Dividing (7.140) by $\delta\lambda$ and taking the $\delta\lambda \to 0$ limit, we obtain

$$\frac{\partial\Omega}{\partial\lambda} = \int_V n(\boldsymbol{r})\frac{\partial\psi_\lambda(\boldsymbol{r})}{\partial\lambda}\mathrm{d}\boldsymbol{r} + \frac{1}{2}\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' . \tag{7.141}$$

We integrate this equation with respect to λ and obtain

$$\begin{aligned}\Omega[n,v_b] = \Omega[n,v_a] &+ \int_V n(\boldsymbol{r})[\psi_b(\boldsymbol{r}) - \psi_a(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} \\ &+ \frac{1}{2}\int_0^1\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathrm{d}\lambda ,\end{aligned} \tag{7.142}$$

where $\psi_a(\boldsymbol{r})$ is the external field that yield $n(\boldsymbol{r})$ as the equilibrium density profile when the pair potential is $v_a(\boldsymbol{r},\boldsymbol{r}')$. Similarly for $\psi_b(\boldsymbol{r})$. Using (7.76), we rewrite (7.142) as

$$\begin{aligned}\Omega[n,v_b] = \Omega_{\mathrm{int}}[n,v_a] &+ \int_V n(\boldsymbol{r})\psi_b(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \\ &+ \frac{1}{2}\int_0^1\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathrm{d}\lambda .\end{aligned} \tag{7.143}$$

We now recall the relation $F = \Omega + \mu N$ and define the **intrinsic Helmholtz free energy** by

$$F_{\mathrm{int}}[n,v_a] := \Omega_{\mathrm{int}}[n,v_a] + \mu\int_V n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} . \tag{7.144}$$

Then, we can rewrite (7.143) as

$$\begin{aligned}\Omega[n,v_b] = F_{\mathrm{int}}[n,v_a] &- \int_V n(\boldsymbol{r})[\mu - \psi_b(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} \\ &+ \frac{1}{2}\int_0^1\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r},\boldsymbol{r}')[v_b(\boldsymbol{r},\boldsymbol{r}') - v_a(\boldsymbol{r},\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathrm{d}\lambda ,\end{aligned} \tag{7.145}$$

which relates the grand potential of the system of our interest (with v_b) to the intrinsic Helmholtz free energy of the reference system (with v_a).

Combining (7.68), (7.79), and (7.144), we find

$$F_{\mathrm{int}}^{\mathrm{id}}[n] = k_BT\int_V n(\boldsymbol{r})[\ln\Lambda^3 n(\boldsymbol{r}) - 1]\mathrm{d}\boldsymbol{r} \tag{7.146}$$

for an ideal gas. As with (7.68), this result is exact. We now define the intrinsic **excess Helmholtz free energy** by

$$F_{\text{int}}^{\text{exc}}[n, v_a] := F_{\text{int}}[n, v_a] - F_{\text{int}}^{\text{id}}[n] \tag{7.147}$$

and rewrite (7.145) as

$$\begin{aligned}\Omega[n, v_b] = k_B T \int_V n(\boldsymbol{r})[\ln \Lambda^3 n(\boldsymbol{r}) - 1]\mathrm{d}\boldsymbol{r} + F_{\text{int}}^{\text{exc}}[n, v_a] - \int_V n(\boldsymbol{r})[\mu - \psi_b(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} \\ + \frac{1}{2}\int_0^1 \int_V \int_V n(\boldsymbol{r})n(\boldsymbol{r}')g_\lambda(\boldsymbol{r}, \boldsymbol{r}')[v_b(\boldsymbol{r}, \boldsymbol{r}') - v_a(\boldsymbol{r}, \boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'\mathrm{d}\lambda\ .\end{aligned} \tag{7.148}$$

This is the desired expression. Of course, we still have to choose the reference pair potential v_a, determine the explicit form of the functional $F_{\text{int}}^{\text{exe}}[n, v_a]$, and then evaluate $g_\lambda(\boldsymbol{r}, \boldsymbol{r}')$ for $0 \le \lambda \le 1$.

7.4.4 Pair Distribution Function

In this section, we make a few key observations about g of homogeneous systems. This will guide our choice for the reference potential v_a.

We start by seeking for the physical content of $n^{(2)}$. For this purpose, it is actually easier to work with a canonical ensemble. Thus, we define the **density profile** and the **pair distribution function** by

$$n_N(\boldsymbol{r}) := \langle \hat{n}(\boldsymbol{r}, \boldsymbol{r}^N)\rangle_N \tag{7.149}$$

and

$$n_N^{(2)}(\boldsymbol{r}, \boldsymbol{r}') := \langle \hat{I}(\boldsymbol{r}, \boldsymbol{r}', \boldsymbol{r}^N)\rangle_N\ , \tag{7.150}$$

respectively, where the subscript N reminds us of the canonical ensemble in which N is fixed. For the Hamiltonian given by (7.52), we have

$$\begin{aligned}&\langle \delta(\boldsymbol{r} - \boldsymbol{r}_1)\rangle_N \\ &\qquad = \frac{1}{Z}\frac{1}{\Lambda^{3N}N!}\int \delta(\boldsymbol{r} - \boldsymbol{r}_1)e^{-\beta\phi(\boldsymbol{r}^N)}e^{-\beta\sum_{i=1}^N \psi(\boldsymbol{r}_i)}\mathrm{d}\boldsymbol{r}^N \\ &\qquad = \frac{1}{Z}\frac{1}{\Lambda^{3N}N!}\int e^{-\beta\phi(\boldsymbol{r}, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)}e^{-\beta\psi(\boldsymbol{r})}e^{-\beta\sum_{i=2}^N \psi(\boldsymbol{r}_i)}\mathrm{d}\boldsymbol{r}_2\cdots\mathrm{d}\boldsymbol{r}_N\ .\end{aligned} \tag{7.151}$$

This is a function of $\boldsymbol{r}$ and represents the probability density of finding particle 1 at $\boldsymbol{r}$. Because particle 1 is no different from any other in the system, we have

$$\langle \delta(\boldsymbol{r} - \boldsymbol{r}_1)\rangle_N = \langle \delta(\boldsymbol{r} - \boldsymbol{r}_i)\rangle_N\ , \quad \text{for } i = 2, \ldots, N\ , \tag{7.152}$$

and (7.149) becomes

$$n_N(\boldsymbol{r}) = N\langle \delta(\boldsymbol{r} - \boldsymbol{r}_1)\rangle_N\ . \tag{7.153}$$

Similarly, we have

$$\begin{aligned}
&\langle\delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N \\
&\quad=\frac{1}{Z}\frac{1}{\Lambda^{3N}N!}\int\delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)e^{-\beta\phi(\boldsymbol{r}^N)}e^{-\beta\sum_{i=1}^N\psi(\boldsymbol{r}_i)}\mathrm{d}\boldsymbol{r}^N \\
&\quad=\frac{1}{Z}\frac{1}{\Lambda^{3N}N!}\int e^{-\beta\phi(\boldsymbol{r},\boldsymbol{r}',\boldsymbol{r}_3,\ldots,\boldsymbol{r}_N)}e^{-\beta[\psi(\boldsymbol{r})+\psi(\boldsymbol{r}')]}e^{-\beta\sum_{i=3}^N\psi(\boldsymbol{r}_i)}\mathrm{d}\boldsymbol{r}_3\cdots\mathrm{d}\boldsymbol{r}_N\,, \qquad (7.154)
\end{aligned}$$

which is the probability density of finding particle 1 at $\boldsymbol{r}$ *and* particle 2 at $\boldsymbol{r}'$ regardless of the coordinates of other particles. Since the pair of particles 1 and 2 is no different from any other pair, (7.150) gives

$$n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}')=N(N-1)\langle\delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N\,. \qquad (7.155)$$

Given the physical content of (7.151) and (7.154), we see that the ratio

$$\frac{\langle\delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'}{\langle\delta(\boldsymbol{r}-\boldsymbol{r}_1)\rangle_N\mathrm{d}\boldsymbol{r}} \qquad (7.156)$$

is the conditional probability that particle 2 is within the volume element $\mathrm{d}\boldsymbol{r}'$ taken around $\boldsymbol{r}'$ given that particle 1 is inside $\mathrm{d}\boldsymbol{r}$ taken around $\boldsymbol{r}$. Because particles are identical, this probability is no different for any other particle (particle 3 through particle N in place of particle 2). Thus, on average, the number of particles within $\mathrm{d}\boldsymbol{r}'$ is given by

$$(N-1)\frac{\langle\delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'}{\langle\delta(\boldsymbol{r}-\boldsymbol{r}_1)\rangle_N\mathrm{d}\boldsymbol{r}}=\frac{n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}')}{n_N(\boldsymbol{r})}\mathrm{d}\boldsymbol{r}'\,. \qquad (7.157)$$

In other words, $n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}')/n_N(\boldsymbol{r})$ is the number density of particles at $\boldsymbol{r}'$ when there is a particle at $\boldsymbol{r}$. This is the physical content of $n_N^{(2)}$ we seek. We have the factor $N-1$ instead of N because the particle fixed at $\boldsymbol{r}$ is not available to occupy $\boldsymbol{r}'$.

If the condition that a particle must be at $\boldsymbol{r}$ is disregarded, then the density at $\boldsymbol{r}'$ is simply $n_N(\boldsymbol{r}')$. Dividing (7.157) by $n_N(\boldsymbol{r}')$, therefore, we isolate the effect of the particle at $\boldsymbol{r}$ on the density at $\boldsymbol{r}'$:

$$g_N(\boldsymbol{r},\boldsymbol{r}'):=\frac{n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}')}{n_N(\boldsymbol{r})n_N(\boldsymbol{r}')}\,. \qquad (7.158)$$

This definition of the **radial distribution function** $g_N(\boldsymbol{r},\boldsymbol{r}')$ should be compared with (7.134) for the grand canonical ensemble. (Our definition of $g_N(\boldsymbol{r},\boldsymbol{r}')$ follows the convention adopted in Ref. [9]. The choice is not unique, however. For example, g_N in Ref. [8] is $(N-1)/N$ times our g_N. The latter definition is perhaps more convenient for a *homogeneous* system, but it leads to a somewhat different interpretation of g_N.)

Let us now consider a qualitative behavior of g_N in a homogeneous system in the absence of any external field. In this case,

$$n_N(\boldsymbol{r}) = n_N(\boldsymbol{r}') = \frac{N}{V} =: n \tag{7.159}$$

is a constant. Since every point in the system is equivalent to any other, we have

$$g_N(\boldsymbol{r},\boldsymbol{r}') = g_N(\boldsymbol{0},\boldsymbol{r}'-\boldsymbol{r}) = g_N(\boldsymbol{r}'-\boldsymbol{r}) \,, \tag{7.160}$$

where we dropped the explicit reference to $\boldsymbol{0}$. We shall also assume that the system is isotropic so that g_N and $n_N^{(2)} = n^2 g_N$ depend only on $r := \|\boldsymbol{r}'-\boldsymbol{r}\|$. (Notice that $r \neq \|\boldsymbol{r}\|$ here. Fortunately, we do not have to consider $\|\boldsymbol{r}\|$ in the remainder of this section.)

For an ideal gas, the presence of a particle at $\boldsymbol{r}$ does not affect the probability density of finding another at $\boldsymbol{r}'$, which is therefore $(N-1)/V$ with -1 accounting for the particle fixed at $\boldsymbol{r}$ and hence cannot simultaneously occupy $\boldsymbol{r}'$. Division by n yields

$$g_N(r) = 1 - \frac{1}{N} \,, \tag{7.161}$$

which is essentially unity for a macroscopic system. Alternatively, we notice that

$$\langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N = \langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\rangle_N \langle \delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N \tag{7.162}$$

for an ideal gas. Thus, (7.157) reduces to

$$\frac{n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}')}{n_N(\boldsymbol{r})} = (N-1)\langle \delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N = \left(1-\frac{1}{N}\right) n_N(\boldsymbol{r}') \,, \tag{7.163}$$

from which we obtain (7.161).

In the case of a low-density gas, it is rare for a given particle to have another nearby, and having two particles nearby is extremely rare. Thus, a particle fixed at $\boldsymbol{r}$ serves as the sole source of an external field $v(\boldsymbol{r}'-\boldsymbol{r})$ for another at $\boldsymbol{r}'$, implying that

$$\frac{n_N^{(2)}(r)}{n_N} \propto e^{-\beta v(r)} \,, \tag{7.164}$$

where we assumed that v depends only on the distance r between the two particles. Typically, $v(r)$ vanishes with increasing r. At the same time, g_N should approach the value for an ideal gas. This is sufficient to fix the proportionality constant in (7.164) and leads to

$$g_N(r) = \left(1-\frac{1}{N}\right) e^{-\beta v(r)} \,. \tag{7.165}$$

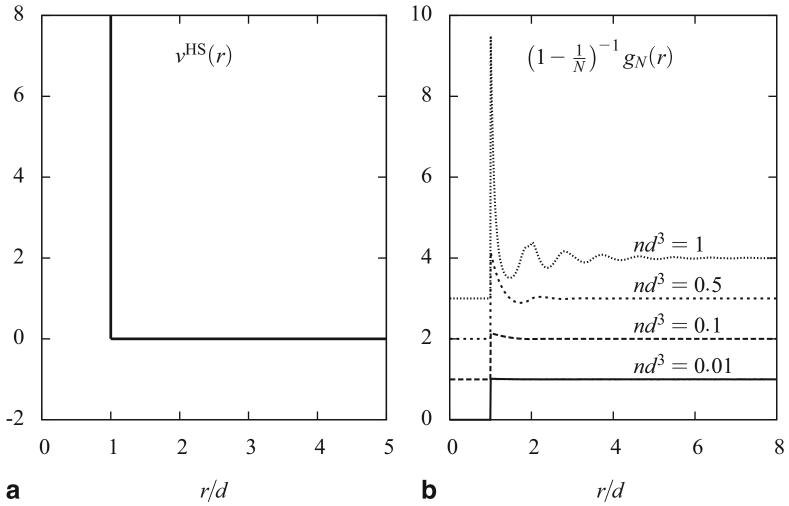

Fig. 7.2 **a** Hard-sphere potential and **b** its radial distribution functions g_N from Monte Carlo simulations at different densities $nd^3 = 0.01$, $nd^3 = 0.1$, $nd^3 = 0.5$, and $nd^3 = 1$. In view of (7.161), g_N is multiplied by $(1-1/N)^{-1}$. For clarity, the plots for $nd^3 = 0.1$, $nd^3 = 0.5$, and $nd^3 = 1$ are shifted upward by 1, 2, and 3, respectively. Note that g_N of a hard-sphere fluid does not have any temperature dependence since $v^{\text{HS}}(r)/k_BT$ is independent of T. The system was taken as a cubic box of volume $8000d^3$ under periodic boundary conditions.

As an example, consider the **hard-sphere potential** defined by

$$v^{\text{HS}}(r) = \begin{cases} \infty & \text{if } r < d \\ 0 & \text{otherwise,} \end{cases} \tag{7.166}$$

where the parameter d is called the **hard-sphere diameter**. Equation (7.165) then is the step function:

$$g_N(r) = \left(1 - \frac{1}{N}\right)\theta(r-d) := \begin{cases} 0 & \text{if } r < d \\ 1-\frac{1}{N} & \text{otherwise.} \end{cases} \tag{7.167}$$

That $g_N(r) = 0$ for $r < d$ makes perfect sense because the hard-sphere potential prohibits a pair of particles to get any closer than d. Figure 7.2 shows the pair potential along with the radial distribution function obtained by Monte Carlo simulations at a few values of n. At the lowest density considered, (7.167) indeed is an excellent approximation. At the highest density shown in the figure, g_N exhibits a considerable oscillatory behavior. What is causing this?

As the density is increased, a hard-sphere particle at $\boldsymbol{r}$ starts to get surrounded by other hard-spheres that are all pushed toward the particle at $\boldsymbol{r}$. But their centers cannot enter the spherical region of diameter d around $\boldsymbol{r}$, thus leading to formation of a layer as illustrated in Fig. 7.3. This explains the first peak of $g_N(r)$ observed in

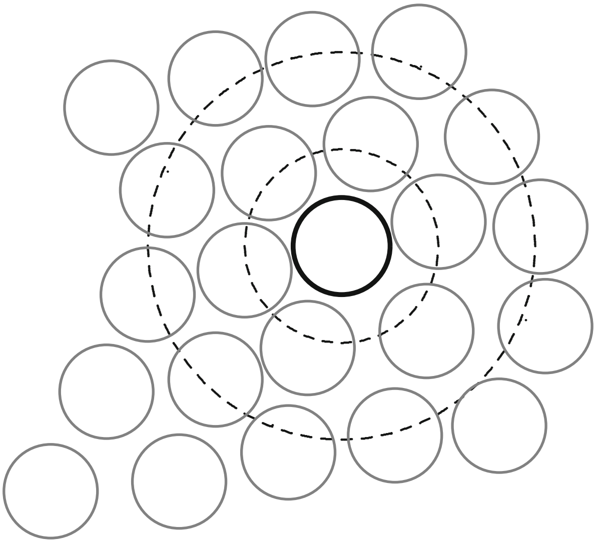

Fig. 7.3 Formation of coordination shells (*gray circles*) around a particle at $\mathbf{r}$ (*black circle*). Radii of the *dashed circles* are d and $2d$.

Fig. 7.2b. These spheres in what we might call the "first coordination shell," in turn, exclude other particles from their cores, leading to formation of the "second coordination shell" and hence to the second peak of $g_N(r)$. Continuing in this way, $g_N(r)$ exhibits an oscillatory behavior with the amplitude of oscillation gradually decreasing with increasing r. For sufficiently large r, (7.162) holds and $g_N(r)$ asymptotes toward $1-1/N$. The important thing to remember is that even a homogeneous fluid has a structure when observed from the perspective of a given particle.

Essentially, the same behavior is observed for other pair potentials having a less harsh but still short-ranged repulsive core.

As an example, let us take the **Lennard–Jones potential**:

$$v^{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{7.168}$$

where the energy parameter ε is positive and σ is called the **Lennard–Jones diameter**. Figure 7.4a illustrates the form of this potential. We note that $v^{\mathrm{LJ}}(\sigma) = 0$ and that v^{LJ} takes its minimum value $-\varepsilon$ at the distance $r_{\min} := 2^{1/6}\sigma$.

It is often more convenient to work with the **truncated and shifted Lennard–Jones potential** defined by

$$v^{\mathrm{tsLJ}}(r) = \begin{cases} v^{\mathrm{LJ}}(r) - v^{\mathrm{LJ}}(r_c) & \text{if } r < r_c \\ 0 & \text{otherwise.} \end{cases} \tag{7.169}$$

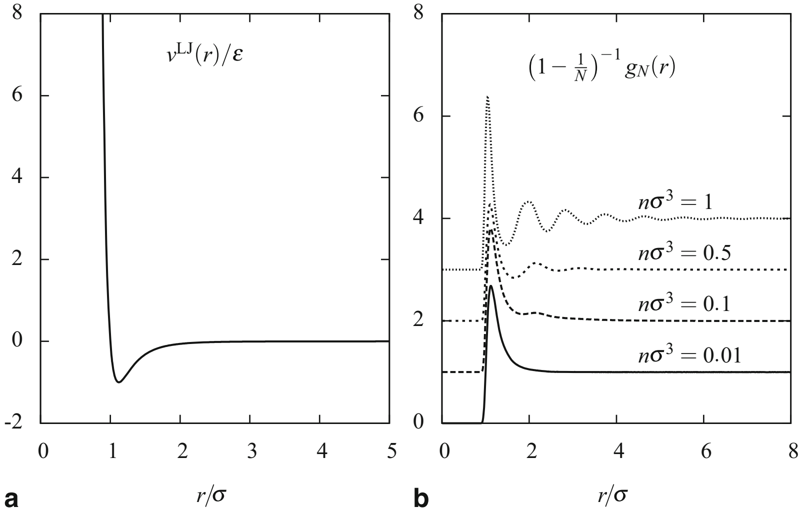

Fig. 7.4 **a** Lennard–Jones potential and **b** the radial distribution functions for its truncated and shifted version ($r_c = 2.5\sigma$) from Monte Carlo simulations at four different densities $n\sigma^3 = 0.01$, $n\sigma^3 = 0.1$, $n\sigma^3 = 0.5$, and $n\sigma^3 = 1$. For clarity, the plots for $n\sigma^3 = 0.1$, $n\sigma^3 = 0.5$, and $n\sigma^3 = 1$ are shifted upward by 1, 2, and 3, respectively. The system temperature was $T = \varepsilon/k_B$. The system was taken as a cubic box of volume $8000\sigma^3$ under periodic boundary conditions.

The radial distribution function for $v^{\mathrm{tsLJ}}(r)$ with $r_c = 2.5\sigma$ is shown in Fig. 7.4b for a few values of density. Equation (7.165) is very accurate for the lowest density value shown in the figure. We can also see the development of the oscillatory behavior with increasing density.

We note that $g_N(r)$ of a hard-sphere fluid captures essential features of $g_N(r)$ of other fluids having a short-ranged repulsive core. This is illustrated in Fig. 7.5, in which we compare $g_N(r)$ of a hard-sphere fluid against that of a Lennard–Jones fluid. At the densities indicated, they look fairly similar with the higher density results showing closer resemblance.

For an open system, fixing a particle at $\boldsymbol{r}$ does not affect the number of particles available at $\boldsymbol{r}'$. Thus, we can simply drop the $1-1/N$ factor from (7.161), (7.165), and (7.167) to obtain the corresponding radial distribution function $g(r)$ for open systems.

Before we conclude this section, we note that $g(r)$ is related to the Fourier transform of the so-called static structure factor, which is directly measurable by means of neutron or X-ray scattering experiments. Approximate theories for $g(r)$ can also be developed (For details of these topics, see Chap. 4 of Ref. [8] or Chap. 5 of Ref. [9], for example.) As we shall see in Sect. 7.7, a direct link exists between $g(r)$ and equations of state.

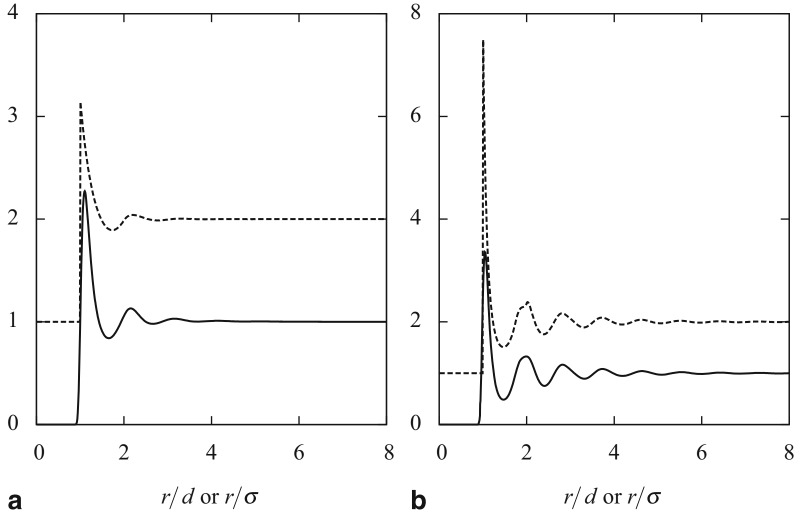

Fig. 7.5 Comparison of the radial distribution functions of the hard-sphere fluid (*dashed line*) and the truncated and shifted Lennard–Jones fluid (*solid line*) at $T = \varepsilon/k_B$. **a** $nd^3 = n\sigma^3 = 0.5$. **b** $nd^3 = n\sigma^3 = 1$. For clarity, the plots for the hard-sphere fluid are shifted upward by one.

7.4.5 *Repulsive Potential*

To construct the density functional by means of (7.148) for a system, in which the pair potential is $v(r)$, we must first choose a reference pair potential. How should we proceed here?

As we have seen in the previous subsection, $g(r)$ is determined primarily by the short-ranged repulsive part of the pair potential $v(r)$. This suggest that the λ dependence of $g_\lambda(r)$ in (7.148) will be small if we take the repulsive part of $v(r)$ as the reference potential.

But, how do we separate $v(r)$ into the repulsive part $v^{\text{rep}}(r)$ and the rest, which we refer to as the attractive tail $v^{\text{att}}(r)$? There is no unique answer to this question, and merits of each method must be judged by the accuracy of the predictions it produces. Here, we mention one particularly useful scheme known as the **Weeks-Chandler-Andersen** (WCA) **separation** [12]. Taking $v^{\text{LJ}}(r)$ as the example, this scheme separates the potential into

$$v^{\text{rep}}(r) = \begin{cases} v^{\text{LJ}}(r) + \varepsilon & \text{if } r \le r_{\text{min}} \\ 0 & \text{otherwise} \end{cases} \quad \text{and} \quad v^{\text{att}}(r) = \begin{cases} -\varepsilon & \text{if } r \le r_{\text{min}} \\ v^{\text{LJ}}(r) & \text{otherwise,} \end{cases} \tag{7.170}$$

leading to the graphs in Fig. 7.6.

Having settled on the reference potential, we move on to the evaluation of the excess Helmholtz free energy $F^{\text{exc}}_{\text{int}}[n, v^{\text{rep}}]$ of the reference system. A common approach for an inhomogeneous system consists of two parts. First, we seek for

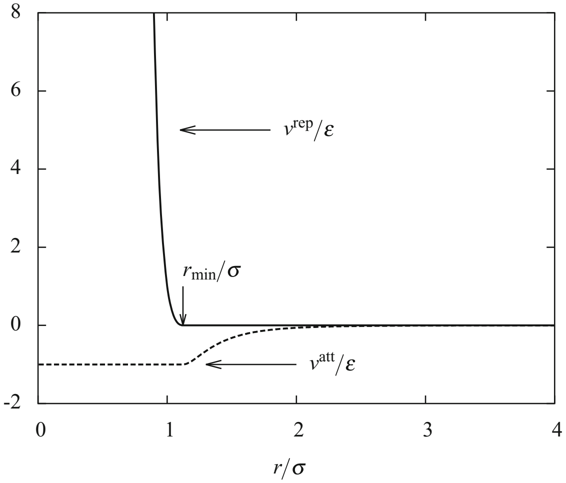

Fig. 7.6 WCA separation of the Lennard–Jones pair potential. *WCA* Weeks–Chandler–Andersen.

a "mapping" from a *homogeneous* reference system to a *homogeneous* hard-sphere (hHS) fluid. This is because properties of a hHS fluid have been studied extensively, and a very accurate formula is available for the excess Helmholtz free energy of a hard-sphere fluid. Second, we devise a method for incorporating the effect of inhomogeneity.

The most general mapping from the reference system to a hard-sphere fluid would involve two parameters, the hard-sphere diameter d and the density n^{eff} of the hard-sphere fluid. However, one commonly set $n = n^{\mathrm{eff}}$ and determine the optimum value of d so as to minimize the error involved in the approximation

$$F^{\mathrm{exc}}_{\mathrm{int}}[n, v^{\mathrm{rep}}] \approx F^{\mathrm{exc}}_{\mathrm{int}}[n, v^{\mathrm{HS}}] \,. \tag{7.171}$$

The optimum value of d is then a function of T and n in general. However, an approximate solution to this optimization problem leads to the expression

$$d = \int_0^\infty \left[1 - e^{-\beta v^{\mathrm{rep}}(r)}\right] \mathrm{d}r \,, \tag{7.172}$$

which is a function of T only. Equation (7.172) is known as the **Barker–Henderson scheme** [1, 12] and is derived in Sect. 7.4.7.

As an illustration, let us consider the truncated and shifted Lennard–Jones potential with $r_c = 2.5\sigma$. After v^{rep} is determined by the WCA separation, we can compute d using (7.172). The result is summarized in Fig. 7.7. The $T \to 0$ limit of d is given by $r_{\mathrm{min}} = 2^{1/6}\sigma$. This makes perfect physical sense because βv^{rep} reduces to the hard-sphere potential with $d = r_{\mathrm{min}}$ in this limit. The observed decrease in d with increasing T is also very reasonable physically since βv^{rep} becomes less harsh for higher temperatures.

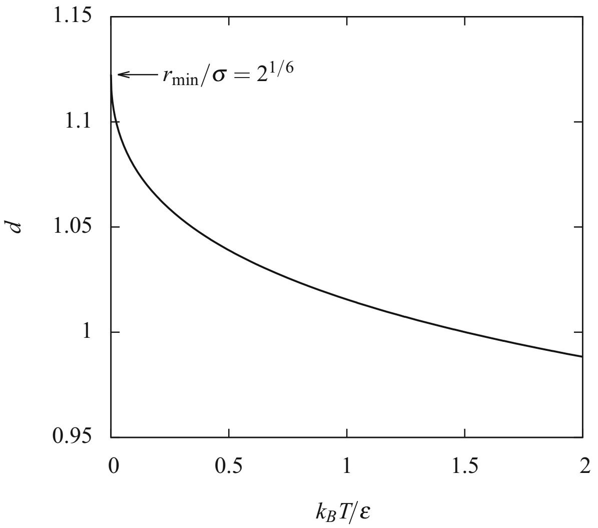

Fig. 7.7 Temperature dependence of the hard-sphere diameter as determined by the Barker–Henderson scheme for the truncated and shifted Lennard–Jones potential ($r_c = 2.5\sigma$).

The simplest approximation to cope with the inhomogeneity is the **local density approximation** (LDA), in which an inhomogeneous system is regarded as a collection of infinitesimally small homogeneous systems. Within LDA, therefore, we write

$$F_{\text{int}}^{\text{exc}}[n, v^{\text{HS}}] \approx \int_V f_{\text{hHS}}^{\text{exc}}(n(\boldsymbol{r}))\mathrm{d}\boldsymbol{r} , \tag{7.173}$$

where $f_{\text{hHS}}^{\text{exc}}(n)$ is the excess Helmholtz free energy per unit volume of a hHS fluid of density n.

If the density changes slowly over many particle diameters, LDA is expected to perform well. For a system exhibiting more rapid spatial variation of density, however, the underlying assumption of LDA does not apply. A common approximation scheme is to replace the local density $n(\boldsymbol{r})$ in (7.173) by the weighted density $\overline{n}(\boldsymbol{r})$ defined by

$$\overline{n}(\boldsymbol{r}) := \int_V w(\boldsymbol{r}, \boldsymbol{r}')n(\boldsymbol{r}')\mathrm{d}\boldsymbol{r}' , \tag{7.174}$$

where $w(\boldsymbol{r}, \boldsymbol{r}')$ is a properly normalized weighting function:

$$\int_V w(\boldsymbol{r}, \boldsymbol{r}')\mathrm{d}\boldsymbol{r}' = 1 . \tag{7.175}$$

Various choices for the weighting function are possible, but the resulting approximation schemes are collectively called the **weighted density approximation** (WDA). For fluids, w is often chosen as

$$w(\|\boldsymbol{r}' - \boldsymbol{r}\|) = \begin{cases} \frac{3}{\pi d^4}(d - \|\boldsymbol{r}' - \boldsymbol{r}\|) & \text{if } \|\boldsymbol{r}' - \boldsymbol{r}\| \leq d \\ 0 \quad \text{otherwise.} \end{cases} \tag{7.176}$$

WDA can be developed even for a crystal, which is regarded as a highly inhomogeneous fluid, and provides an accurate estimate for the melting density of hard-sphere crystals [4, 5].

The explicit form of $f_{\text{hHS}}^{\text{exe}}$ can be deduced from an equation of state. The **Carnahan–Starling formula** [2, 3] is one famous example of highly accurate equations of state of hard-sphere fluids. According to this formula,

$$\frac{\beta P_{\text{hHS}}}{n} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} , \tag{7.177}$$

where

$$\eta := \frac{\pi}{6} d^3 n \tag{7.178}$$

is called the **packing fraction**. Because $\pi d^3/6$ is the volume of a hard-sphere, η represents the volume occupied by the spheres per unit volume of the fluid. Spheres cannot be packed without leaving any gap among them. So, the maximum packing fraction η_{max} is less than unity and is given by

$$\eta_{\text{max}} = \frac{\pi}{3\sqrt{2}} , \tag{7.179}$$

which is realized when the spheres are packed into the face-centered-cubic (fcc) structure.

Exercise 7.9. Confirm (7.179). ///

To find the expression for the excess free energy of a hard-sphere fluids, we recall the Gibbs–Duhem relation for a constant T process:

$$\mathrm{d}P_{\text{hHS}} = n \mathrm{d}\mu_{\text{hHS}} , \quad T \text{ const.} \tag{7.180}$$

Subtracting off the same equation applied to an ideal gas at the same density, we find

$$\mathrm{d}P_{\text{hHS}}^{\text{exc}} = n \mathrm{d}\mu_{\text{hHS}}^{\text{exc}} , \quad T \text{ const.} \tag{7.181}$$

Dividing this equation by dn,

$$\left(\frac{\partial \beta \mu_{\text{hHS}}^{\text{exc}}}{\partial n} \right)_T = \frac{1}{n} \left(\frac{\partial \beta P_{\text{hHS}}^{\text{exc}}}{\partial n} \right)_T . \tag{7.182}$$

Now we integrate this equation from some reference state density n_0 to the density of interest:

$$\beta\mu^{\text{exc}}_{\text{hHS}}(n) - \beta\mu^{\text{exc}}_{\text{hHS}}(n_0) = \int_{n_0}^{n} \frac{1}{n}\left(\frac{\partial \beta P^{\text{exc}}_{\text{hHS}}}{\partial n}\right)_T \mathrm{d}n = \int_{\eta_0}^{\eta} \frac{1}{\eta}\left(\frac{\partial \beta P^{\text{exc}}_{\text{hHS}}}{\partial n}\right)_T \mathrm{d}\eta \,. \tag{7.183}$$

Using the ideal gas equation of state ($\beta P^{\text{id}} = n$) and (7.177),

$$\beta P^{\text{exc}}_{\text{hHS}} = \beta P_{\text{hHS}} - n = n\frac{4\eta - 2\eta^2}{(1-\eta)^3} \,. \tag{7.184}$$

So,

$$\left(\frac{\partial \beta P^{\text{exc}}_{\text{hHS}}}{\partial n}\right)_T = \frac{4\eta - 2\eta^2}{(1-\eta)^3} + \eta\frac{\mathrm{d}}{\mathrm{d}\eta}\left[\frac{4\eta - 2\eta^2}{(1-\eta)^3}\right] \,. \tag{7.185}$$

We can now carry out the integration in (7.183) and obtain

$$\beta\mu^{\text{exc}}_{\text{hHS}}(n) - \beta\mu^{\text{exc}}_{\text{hHS}}(n_0) = \left[\frac{2}{1-\eta} + \frac{1}{(1-\eta)^2} + \frac{4\eta - 2\eta^2}{(1-\eta)^3}\right]_{\eta_0}^{\eta} \,. \tag{7.186}$$

In the limit of $\eta_0 \to 0$, the fluid approaches the ideal gas and hence $\mu^{\text{exc}}_{\text{hHS}}(n_0) \to 0$. Thus,

$$\beta\mu^{\text{exc}}_{\text{hHS}}(n) = \frac{2}{1-\eta} + \frac{1}{(1-\eta)^2} + \frac{4\eta - 2\eta^2}{(1-\eta)^3} - 3 = \frac{\eta(3\eta^2 - 9\eta + 8)}{(1-\eta)^3} \,. \tag{7.187}$$

Recalling that $F := U - TS = -PV + \mu N$, we finally arrive at

$$\beta f^{\text{exc}}_{\text{hHS}}(n) := \frac{\beta F^{\text{exc}}_{\text{hHS}}}{V} = n\frac{\eta(4-3\eta)}{(1-\eta)^2} \,. \tag{7.188}$$

Even though we introduced a mapping from v^{rep} to the hard-sphere potential, this is only for the purpose of computing $F^{\text{exc}}_{\text{int}}$. Thus, we emphasize that the pair potential of our reference system is still v^{rep} and $v_b - v_a$ in (7.148) is v^{att}, not $v - v^{\text{HS}}$. In various theories of homogeneous fluids with mapping onto hard-spheres, v^{rep} still plays an important role, for example, in approximating the radial distribution function $g_\lambda(r)$.

7.4.6 Radial Distribution Function

The radial distribution function $g(\boldsymbol{r}, \boldsymbol{r}')$ of an inhomogeneous system is not very well known even for a hard-sphere fluid. This is not surprising since $g(\boldsymbol{r}, \boldsymbol{r}')$ depends on three spatial variables even in the simplest case of a flat interface. Consequently, we must adopt a rather drastic approximation for $g_\lambda(\boldsymbol{r}, \boldsymbol{r}')$.

For example, we can take over (7.167), without the $1-1/N$ factor for an open system, and write

$$g_\lambda(\boldsymbol{r},\boldsymbol{r}') \approx \theta(\|\boldsymbol{r}'-\boldsymbol{r}\|-d) \,. \tag{7.189}$$

with d determined by the Barker–Henderson scheme. Alternative approximation is based on (7.165) and is given by

$$g_\lambda(\boldsymbol{r},\boldsymbol{r}') \approx e^{-\beta v^{\mathrm{rep}}(\|\boldsymbol{r}'-\boldsymbol{r}\|)} \,, \tag{7.190}$$

where we recall $v^{\mathrm{rep}} = v_{\lambda=0}$ is the pair potential of the reference system. The simplest approximation is

$$g_\lambda(\boldsymbol{r},\boldsymbol{r}') \approx 1 \,, \tag{7.191}$$

which is exact only for an ideal gas.

We are now in position to write down approximate density functionals. The simplest density functional is based on LDA and (7.191), and is given by

$$\begin{aligned}\Omega[n] = k_BT\int_V n(\boldsymbol{r})[\ln\Lambda^3 n(\boldsymbol{r})-1]\mathrm{d}\boldsymbol{r} + \int_V f^{\mathrm{exc}}_{\mathrm{hHS}}(n(\boldsymbol{r}))\mathrm{d}\boldsymbol{r} - \int_V n(\boldsymbol{r})[\mu-\psi(\boldsymbol{r})]\mathrm{d}\boldsymbol{r}\\ +\frac{1}{2}\int_V\int_V n(\boldsymbol{r})n(\boldsymbol{r}')v^{\mathrm{att}}(\|\boldsymbol{r}'-\boldsymbol{r}\|)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \,,\end{aligned} \tag{7.192}$$

where we dropped the reference to the pair potential v from $\Omega[n,v]$.

Equation (7.192) motivates the following definition for the grand potential density:

$$\begin{aligned}\chi(\boldsymbol{r},n] := k_BTn(\boldsymbol{r})[\ln\Lambda^3 n(\boldsymbol{r})-1] + f^{\mathrm{exc}}_{\mathrm{hHS}}(n(\boldsymbol{r})) - n(\boldsymbol{r})[\mu-\psi(\boldsymbol{r})]\\ +\frac{1}{2}n(\boldsymbol{r})\int_V n(\boldsymbol{r}')v^{\mathrm{att}}(\|\boldsymbol{r}'-\boldsymbol{r}\|)\mathrm{d}\boldsymbol{r}' \,,\end{aligned} \tag{7.193}$$

in terms of which we may write

$$\Omega[n] = \int_V \chi(\boldsymbol{r},n]\mathrm{d}\boldsymbol{r} \,. \tag{7.194}$$

We have already made use of (7.194) in Sect. 6.9. A few illustrative applications of (7.192) will be given in Sects. 7.5 and 7.6.

7.4.7 †*Barker–Henderson Scheme*

The only difference between $F^{\mathrm{exc}}_{\mathrm{int}}[n,v^{\mathrm{rep}}]$ and $F^{\mathrm{exc}}_{\mathrm{int}}[n,v^{\mathrm{HS}}]$ is in the pair potentials. Thus, one possible approach for minimizing the error associated with (7.171) may be to expand $F^{\mathrm{exc}}_{\mathrm{int}}[n,v^{\mathrm{rep}}]$ into the functional Taylor series around $v^{\mathrm{rep}} = v^{\mathrm{HS}}$ and then choose d so that the first-order term becomes identically zero. If this can be done, the error will be in the higher order terms. Glancing at Fig. 7.6, we see immediately that v^{rep} and v^{HS} are very different regardless of how we choose d. In fact, for $r<d$,

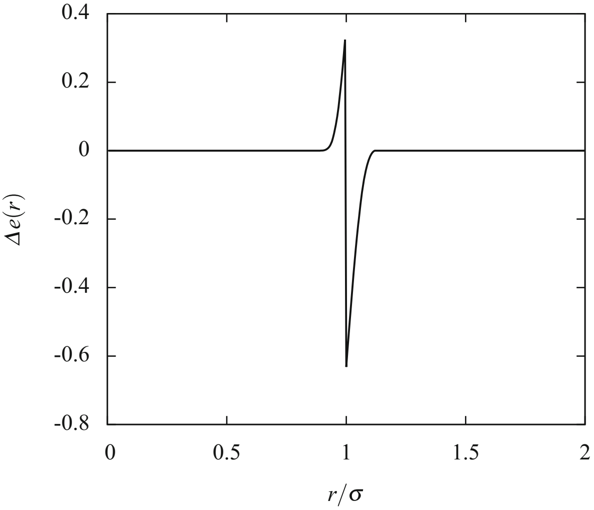

Fig. 7.8 The blip function. We set $\sigma = d$ and $T = \varepsilon/k_B$.

their difference is infinitely large. This implies that the higher order terms probably cannot be neglected.

What we need is a better way to characterize the difference between v^{rep} and v^{HS}. For this purpose, we define

$$e(r) := e^{-\beta v(r)} . \tag{7.195}$$

For the pair potentials at hand,

$$e^{\text{rep}}(r) = e^{-\beta v^{\text{rep}}(r)} \quad \text{and} \quad e^{\text{HS}}(r) = e^{-\beta v^{\text{HS}}(r)} . \tag{7.196}$$

The difference between them

$$\Delta e(r) := e^{\text{rep}}(r) - e^{\text{HS}}(r) \tag{7.197}$$

is known as the **blip function**. The origin of this term is revealed in Fig. 7.8. Unlike $v^{\text{rep}} - v^{\text{HS}}$, Δe remains finite for all values of r.

Now, we proceed to evaluate the functional derivative of $F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}]$ with respect to e^{rep}. Since $F_{\text{int}}^{\text{id}}$ is independent of $v^{\text{rep}}(r)$,

$$\frac{\delta F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}]}{\delta v^{\text{rep}}(\boldsymbol{r}, \boldsymbol{r}')} = \frac{\delta F_{\text{int}}[n, v^{\text{rep}}]}{\delta v^{\text{rep}}(\boldsymbol{r}, \boldsymbol{r}')} . \tag{7.198}$$

From (7.76) and (7.144), we observe that

$$F_{\text{int}}[n, v] = \Omega[n, v] + \int_V [\mu - \psi(\boldsymbol{r})]\, n(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} . \tag{7.199}$$

Recalling (7.134), we find

$$\frac{\delta F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}]}{\delta v^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}')} = \frac{1}{2} n^{(2)}(\boldsymbol{r},\boldsymbol{r}') \;, \tag{7.200}$$

Note that we replaced the distance r between a pair of particles by their coordinates $\boldsymbol{r}$ and $\boldsymbol{r}'$. It follows from (7.41) that

$$\delta F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}] = \frac{1}{2} \int_V \int_V n^{(2)}(\boldsymbol{r},\boldsymbol{r}') \delta v^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}') \mathrm{d}\boldsymbol{r} \mathrm{d}\boldsymbol{r}' \;. \tag{7.201}$$

From (7.196), we have

$$v^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}') = -k_B T \ln e^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}') \;, \tag{7.202}$$

and hence

$$\delta v^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}') = -\frac{k_B T}{e^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}')} \delta e^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}') \;. \tag{7.203}$$

Using this expression in (7.201), we have

$$\delta F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}] = -\frac{k_B T}{2} \int_V \int_V \frac{n^{(2)}(\boldsymbol{r},\boldsymbol{r}')}{e^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}')} \delta e^{\text{rep}}(\boldsymbol{r},\boldsymbol{r}') \mathrm{d}\boldsymbol{r} \mathrm{d}\boldsymbol{r}' \;. \tag{7.204}$$

We now change the variables from $(\boldsymbol{r},\boldsymbol{r}')$ to $(\boldsymbol{r},\boldsymbol{R})$, where $\boldsymbol{R} := \boldsymbol{r}' - \boldsymbol{r}$. The pair potential, by assumption, is a function of $R := \|\boldsymbol{R}\|$. For a *homogeneous and isotropic* system, the same applies to $n^{(2)}$ as well. Thus,

$$\begin{aligned}\delta F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}] &= -\frac{k_B T}{2} \int_V \int_V \frac{n^{(2)}(R)}{e^{\text{rep}}(R)} \delta e^{\text{rep}}(R) \mathrm{d}\boldsymbol{r} \mathrm{d}\boldsymbol{R} \\ &= -\frac{k_B T}{2} V \int_V \frac{n^{(2)}(R)}{e^{\text{rep}}(R)} \delta e^{\text{rep}}(R) \mathrm{d}\boldsymbol{R} \;,\end{aligned} \tag{7.205}$$

where we note that the determinant of the Jacobian matrix for the change of variables from $(\boldsymbol{r},\boldsymbol{r}')$ to $(\boldsymbol{r},\boldsymbol{R})$ is unity. Using $\boldsymbol{r}$ in place of $\boldsymbol{R}$, we arrive at[45]

$$\frac{\delta F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}]}{\delta e^{\text{rep}}(\boldsymbol{r})} = -\frac{k_B T}{2} V \frac{n^{(2)}(r)}{e^{\text{rep}}(r)} = -\frac{k_B T}{2} n^2 V \frac{g^{\text{rep}}(r)}{e^{\text{rep}}(r)} \;. \tag{7.206}$$

Evaluating this expression for $e^{\text{rep}}(r) \equiv e^{\text{HS}}(r)$,

$$\left.\frac{\delta F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}]}{\delta e^{\text{rep}}(\boldsymbol{r})}\right|_{v^{\text{rep}}=v^{\text{HS}}} = -\frac{k_B T}{2} n^2 V y^{\text{HS}}(r) \;, \tag{7.207}$$

where we defined

$$y(r) := \frac{g(r)}{e(r)} \;. \tag{7.208}$$

We observe that $y(r)$ may be regarded as the correction factor to the low-density approximation (7.165) without the $1-1/N$ factor. Thus, the functional Taylor series expansion of $F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}]$ around $e^{\text{rep}}(r) \equiv e^{\text{HS}}(r)$ is given by

$$F_{\text{int}}^{\text{exc}}[n, v^{\text{rep}}] = F_{\text{int}}^{\text{exc}}[n, v^{\text{HS}}] - \frac{1}{2} k_B T n^2 V \int_V y^{\text{HS}}(r) \Delta e(r) \mathrm{d}\boldsymbol{r} + \text{h.o.} \tag{7.209}$$

The desired equation for d is therefore,

$$\int_V y^{\text{HS}}(r) \Delta e(r) \mathrm{d}\boldsymbol{r} = 4\pi \int_0^\infty y^{\text{HS}}(r) \Delta e(r) r^2 \mathrm{d}r = 0 \, . \tag{7.210}$$

From Fig. 7.8, we see that the blip function is nonzero only around $r = d$, suggesting that $r^2 y^{\text{HS}}(r)$ in (7.210) may be replaced by $d^2 y^{\text{HS}}(d)$ without significantly affecting the value of the integral. (We note that $y(r)$ is a continuous function of r even for a discontinuous $v(r)$, such as the hard-sphere pair potential. For an explicit demonstration of this fact, see Sect. 5.3 of Ref. [9].) With this approximation, (7.210) reduces to

$$\int_0^\infty \Delta e(r) \mathrm{d}r = \int_0^\infty \left[e^{\text{rep}}(r) - e^{\text{HS}}(r) \right] \mathrm{d}r = 0 \, , \tag{7.211}$$

which may be rewritten as

$$\int_0^\infty \left[e^{\text{rep}}(r) - 1 \right] \mathrm{d}r = \int_0^\infty \left[e^{\text{HS}}(r) - 1 \right] \mathrm{d}r = -d \, . \tag{7.212}$$

But, this is just (7.172).

7.5 Hard-Sphere Fluid Under Gravity

As the first example illustrating the use of (7.192), let us look at something simple: a hard-sphere fluid in a container under gravity. In this case, we have

$$v^{\text{att}}(\boldsymbol{r}) \equiv 0 \, . \tag{7.213}$$

Taking the z-axis vertically upward from the bottom of the container, the external field due to gravity is given by

$$\psi(\boldsymbol{r}) = m_w g z \, , \tag{7.214}$$

where m_w and g are the mass of a hard-sphere and the gravitational acceleration, respectively.

Using these expressions in (7.192), we see that

$$\Omega[n] = k_BT \int_V n(\boldsymbol{r}) \left[\ln \Lambda^3 n(\boldsymbol{r}) - 1\right] \mathrm{d}\boldsymbol{r} + \int_V f^{\text{exc}}_{\text{hHS}}(n(\boldsymbol{r}))\mathrm{d}\boldsymbol{r} + \int_V n(\boldsymbol{r})(m_w gz - \mu)\mathrm{d}\boldsymbol{r} \,. \tag{7.215}$$

The equilibrium density profile is determined by (7.47), which now reads

$$\frac{\delta\Omega}{\delta n(\boldsymbol{r})} = k_BT \ln \Lambda^3 n(\boldsymbol{r}) + \mu^{\text{exc}}_{\text{hHS}}(n(\boldsymbol{r})) + (m_w gz - \mu) = 0 \,. \tag{7.216}$$

Since $k_BT \ln \Lambda^3 n(z)$ is the ideal gas contribution to the chemical potential, this equation may be rewritten as

$$\mu = k_BT \ln \Lambda^3 n(\boldsymbol{r}) + \mu^{\text{exe}}_{\text{hHS}}(n(\boldsymbol{r})) + m_w gz = \mu_{\text{hHS}}(n(\boldsymbol{r})) + m_w gz \,, \tag{7.217}$$

indicating that the intrinsic part of the chemical potential and the external field, added together, must be constant throughout the system in equilibrium.

Equation (7.216) indicates that $n(\boldsymbol{r})$ depends only on z. We can readily solve the equation for z (but not for $n(z)$):

$$z = \frac{1}{m_w g}\left[\mu - \mu^{\text{exc}}_{\text{hHS}}(n(z)) - k_BT \ln \Lambda^3 n(z)\right] \,. \tag{7.218}$$

If we denote the density at $z = 0$ by n_0,

$$0 = \frac{1}{m_w g}\left[\mu - \mu^{\text{exc}}_{\text{hHS}}(n_0) - k_BT \ln \Lambda^3 n_0\right] \,, \tag{7.219}$$

which can be subtracted from (7.218) to give

$$z = \frac{1}{m_w g}\left[\mu^{\text{exc}}_{\text{hHS}}(n_0) - \mu^{\text{exc}}_{\text{hHS}}(n(z)) + k_BT \ln \frac{n_0}{n(z)}\right] \,. \tag{7.220}$$

With n_0 set to the maximum possible value of $\sqrt{2}/d^3$, which corresponds to the hard-spheres packed into the fcc structure, (7.220) leads to the density profile shown in Fig. 7.9. Despite its appearance, Fig. 7.9 does *not* imply vapor–liquid coexistence for the hard-sphere fluid. The attractive part of the pair potential is needed for such a phase behavior.

7.6 Vapor–Liquid Coexistence

As a less trivial example, let us examine vapor–liquid equilibrium in a truncated and shifted Lennard–Jones fluid. For simplicity, we set the external field to zero in (7.192). For this potential, WCA separation gives

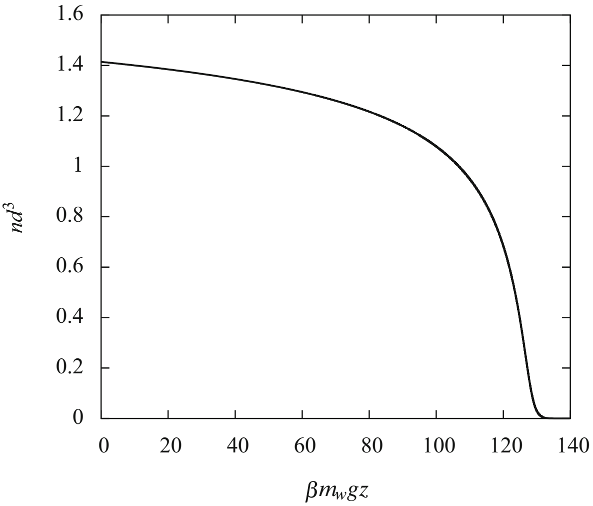

Fig. 7.9 Equilibrium density profile of hard-sphere fluids under gravity. The graph was obtained by assuming maximum packing fraction at $z = 0$.

$$v^{\mathrm{att}}(r) = \begin{cases} -\varepsilon - v^{\mathrm{LJ}}(r_c) & \text{if } r \le r_{\min} \\ v^{\mathrm{LJ}}(r) - v^{\mathrm{LJ}}(r_c) & \text{if } r_{\min} < r \le r_c \\ 0 \quad \text{otherwise.} \end{cases} \tag{7.221}$$

The repulsive potential $v^{\mathrm{rep}}(r)$ is still given by (7.170). In fact, $v^{\mathrm{rep}}(r)$ for $r \le r_{\min}$ is $v^{\mathrm{tsLJ}}(r)$ minus its minimum value at $r_{\min} = 2^{1/6}\sigma$, both of which received the same upward shift by $v^{\mathrm{LJ}}(r_c)$ when defining $v^{\mathrm{tsLJ}}(r)$ in terms of $v^{\mathrm{LJ}}(r)$. In our numerical computation below, we set $r_c = 2.5\sigma$.

7.6.1 Phase Diagram

It is convenient to work with the Helmholtz free energy. Since $F = \Omega + \mu N$ and $\psi(\boldsymbol{r}) \equiv 0$, (7.192) gives

$$\begin{aligned} F[n] = k_B T \int_V n(\boldsymbol{r})[\ln \Lambda^3 n(\boldsymbol{r}) - 1]\mathrm{d}\boldsymbol{r} + \int_V f^{\mathrm{exc}}_{\mathrm{hHS}}(n(\boldsymbol{r}))\mathrm{d}\boldsymbol{r} \\ + \frac{1}{2}\int_V \int_V n(\boldsymbol{r})n(\boldsymbol{r}')v^{\mathrm{att}}(\|\boldsymbol{r}' - \boldsymbol{r}\|)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \,. \end{aligned} \tag{7.222}$$

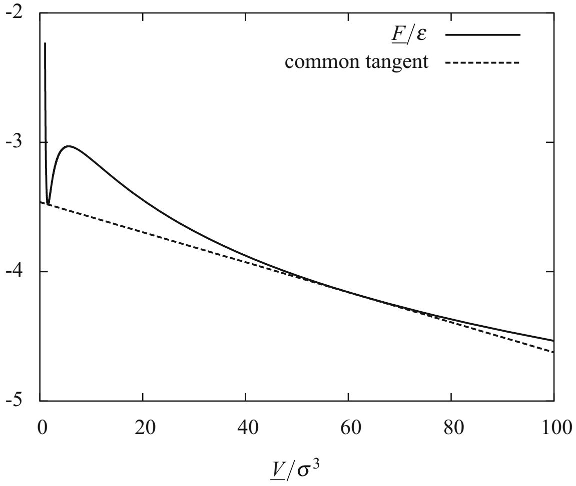

Fig. 7.10 $\underline{F}$ versus $\underline{V}$ plot at $T = 0.8\varepsilon/k_B$.

The Helmholtz free energy of a homogeneous phase follows from (7.222) simply by setting $n(\boldsymbol{r})$ to a constant n:

$$f := \frac{F}{V} = k_B T n[\ln \Lambda^3 n - 1] + f^{\text{exc}}_{\text{hHS}}(n) + \frac{1}{2}\alpha^{\text{att}} n^2 , \tag{7.223}$$

which is then a fundamental equation of the homogeneous fluid. Here, α^{att} is a constant defined by

$$\alpha^{\text{att}} := \frac{1}{V}\int_V\int_V v^{\text{att}}(\|\boldsymbol{r}' - \boldsymbol{r}\|)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' = \frac{1}{V}\int_V\int_V v^{\text{att}}(R)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{R} = \int_V v^{\text{att}}(R)\mathrm{d}\boldsymbol{R} , \tag{7.224}$$

where we defined $\boldsymbol{R} := \boldsymbol{r}' - \boldsymbol{r}$ and $R := \|\boldsymbol{R}\|$. We also made use of the fact that the determinant of the Jacobian matrix for the change of variables from $(\boldsymbol{r}, \boldsymbol{r}')$ to $(\boldsymbol{r}, \boldsymbol{R})$ is unity. Given the fundamental equation (7.223), we can obtain expressions for P and μ:

$$P = k_B T n + P^{\text{exc}}_{\text{hHS}} + \frac{1}{2}\alpha^{\text{att}} n^2 \tag{7.225}$$

and

$$\mu = k_B T \ln \Lambda^3 n + \mu^{\text{exc}}_{\text{hHS}} + \alpha^{\text{att}} n . \tag{7.226}$$

Exercise 7.10. Verify (7.225) and (7.226). ///

Figure 7.10 shows the dependence of $\underline{F} := F/N$ on $\underline{V} := V/N$ at $T = 0.8\varepsilon/k_B$. At this temperature, a portion of the $\underline{F}$ versus $\underline{V}$ plot is concave down and the curve has a common tangent. We recall from Sect. 2.16.1 that we can read off P and μ of a fluid by drawing a tangent line to the $\underline{F}$ versus $\underline{V}$ plot. In particular, its slope and the intercept on the $\underline{F}$-axis are, respectively, $-P$ and μ of the fluid at the point of tangent.

Therefore, the existence of a common tangent implies the equilibrium between two phases, vapor and liquid in this case. The precise values for the densities of the coexisting phases are found as the nontrivial solution (for which $n^l \neq v^v$) of the coupled equations:

$$P(T,n^v) = P(T,n^l) \quad \text{and} \quad \mu(T,n^v) = \mu(T,n^l), \tag{7.227}$$

where the superscripts v and l refer to vapor and liquid phases, respectively. The locus of the coexisting bulk phase densities (traced by varying T) is called a **binodal line**.

The onset of instability is determined by

$$\left(\frac{\partial P}{\partial n}\right)_T = 0\,, \tag{7.228}$$

the locus of which defines the spinodal line. A bulk phase inside the region enclosed by this line is unstable with respect to an infinitesimal density fluctuation and undergoes phase separation by a mechanism called **spinodal decomposition**. (See 5.2.2.) Metastable phases reside in the regions between the binodal and spinodal lines with the lower density part corresponding to supersaturated vapor and the higher density part to superheated (or stretched) liquid. The mechanism of phase separation of a metastable phase is **nucleation**.

Finally, (7.228) and

$$\left(\frac{\partial^2 P}{\partial n^2}\right)_T = 0 \tag{7.229}$$

determine the critical point.

Results of these computations are shown in Fig. 7.11 and are compared against the results of the Gibbs ensemble simulations [11]. We see that our theory predicts qualitatively correct behavior, though it fails at a quantitative level especially for the liquid phase densities. A further refinement is expected to be possible by using a more accurate mapping scheme between the reference system (with v^{rep}) and hard-sphere fluids as well as a better approximation for $g_\lambda(r)$.

The critical point is not particularly well predicted by DFT. This is a generic feature of DFT, which does not adequately account for the effect of fluctuations that become increasingly important near the critical point. In fact, we see shortly that DFT is a form of a mean-field approximation discussed in Sect. 5.2.

7.6.2 *Interfacial Properties*

For our choice of the density functional, (7.47) leads to

$$\mu = k_B T \ln \Lambda^3 n(\boldsymbol{r}) + \mu_{\mathrm{hHS}}^{\mathrm{exc}}(n(\boldsymbol{r})) + \int_V n(\boldsymbol{r}')v^{\mathrm{att}}(\|\boldsymbol{r}' - \boldsymbol{r}\|)\mathrm{d}\boldsymbol{r}'\,. \tag{7.230}$$

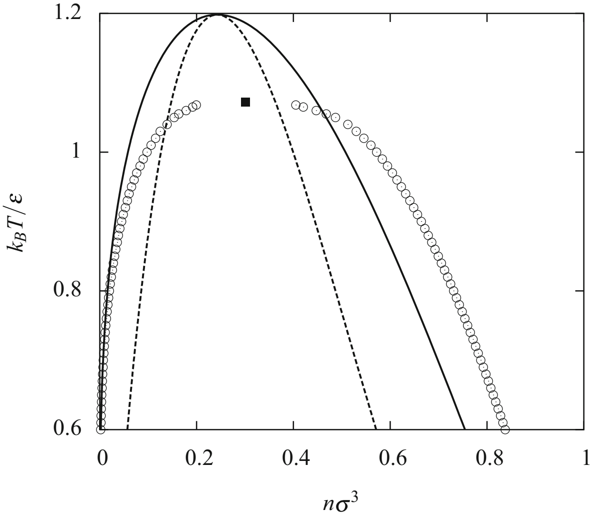

Fig. 7.11 Phase diagram of the truncated and shifted Lennard–Jones fluid ($r_c = 2.5\sigma$). The binodal (*solid line*) and the spinodal (*dashed line*) lines, both from the density functional theory. The coexisting densities (⊙) and the critical point (■), both from Gibbs ensemble simulation involving the total of 1000 particles.

For given T and μ, this equation determines the equilibrium density profile $n^{\text{eq}}(\boldsymbol{r})$. Comparing (7.217) and (7.230), we see that the last term of (7.230) represents the effective field at $\boldsymbol{r}$ that is being generated by the particles in the system. Thus, the density functional we constructed, in essence, is a fluid-phase version of the **mean-field approximation** we saw in Sect. 5.2.

Figure 7.12 exhibits equilibrium density profiles at the vapor–liquid coexistence for a few values of T. Using this information, we computed the surface tension γ_∞ for a range of temperatures using (7.193) and (6.92). The results are shown in Fig. 7.13 and is compared against the predictions of Monte Carlo simulations. Despite the failure of DFT in accurately predicting the critical point and the liquid phase densities at coexistence, the DFT predictions of γ_∞ are in reasonably good agreement with the simulation results. In both cases, γ_∞ decreases monotonically and eventually vanishes at the critical point where the distinction between the vapor and the liquid phases disappears.

The location of the surface of tension is determined by (6.98) and is shown by the curve labeled as z_s in Fig. 7.12. The intersection between the curve and the density profile at a given temperature gives z_s at that T. Similarly for other curves labeled as z_{95} and z_{05}. The former denotes the position at which the density $n^{\text{eq}}(z)$ decreases from its bulk liquid value n^l by 5% of $n^l - n^v$. Likewise, z_{05} is the position at which $n^{\text{eq}}(z)$ decreases to $n^v + 0.05(n^l - n^v)$.

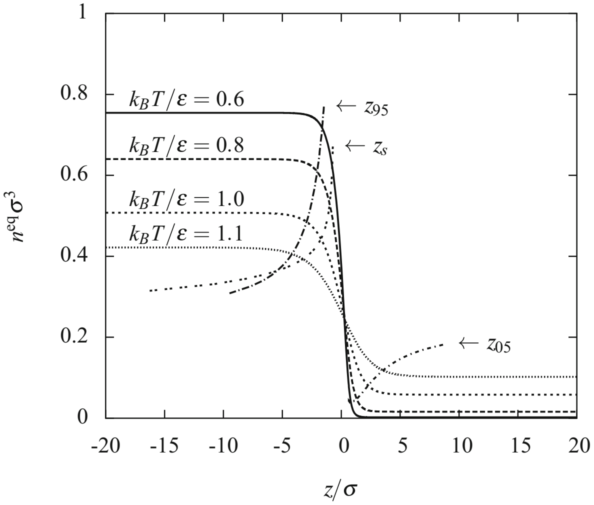

Fig. 7.12 Density profiles across flat interfaces for the truncated and shifted Lennard–Jones fluid ($r_c = 2.5\sigma$).

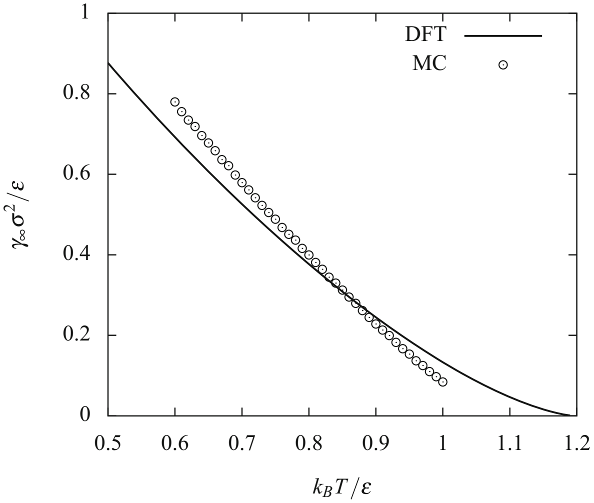

Fig. 7.13 Surface tension versus temperature for the truncated and shifted Lennard–Jones fluid ($r_c = 2.5\sigma$). Monte Carlo (*MC*) simulation employed 8000 particles in a rectangular box (dimension $20\sigma \times 20\sigma \times 80\sigma$) under periodic boundary conditions.

The thickness of the interfacial region may be conveniently characterized by $z_{05} - z_{95}$. Our DFT prediction indicates that $z_{05} - z_{95} = 2.11\sigma$ at $k_BT/\varepsilon = 0.5$. The interface becomes more diffuse with increasing temperature. For example, $z_{05} - z_{95} = 5.22\sigma$ at $k_BT/\varepsilon = 1.0$.

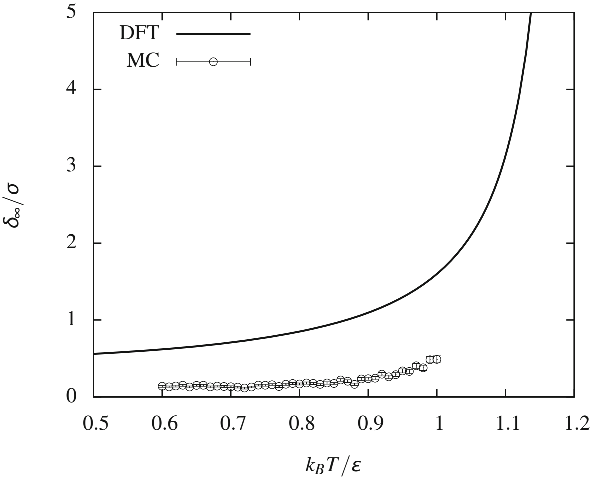

Fig. 7.14 Tolman length versus temperature for the truncated and shifted Lennard–Jones fluid ($r_c = 2.5\sigma$). Monte Carlo (*MC*) simulation employed 8000 particles in a rectangular box (dimension $20\sigma \times 20\sigma \times 80\sigma$) under periodic boundary conditions.

At low temperatures, $z_{95} < z_s < z_{05}$ in agreement with Gibbs's conclusion that the surface of tension should be located within the interfacial region. At temperatures very close to the critical temperature, the interface becomes very diffuse and the arbitrary cut-off at z_{95} does not mark the end of the interfacial region. At $k_BT/\varepsilon \gtrsim 1.14$, for example, $z_s < z_{95}$.

According to DFT, the Tolman length δ_∞ is 0.56σ at $k_BT/\varepsilon = 0.5$ and increases with increasing T. At $k_BT/\varepsilon = 1$ for example, $\delta_\infty = 1.6\sigma$. As shown in Fig. 7.14, the same trend is observed also in Monte Carlo simulations. However, the DFT predictions are considerably larger than the results from the simulations. In this regard, we note that a recent very-large-scale molecular dynamics study casts some doubts on the ability of DFT and small-scale simulations, such as the one included in Fig. 7.14, to accurately predict δ_∞ [10].

7.7 ‡Equations of State from the Radial Distribution Function

In this section, we shall establish a connection between thermodynamic properties of a homogeneous system and the radial distribution function. Since we are interested only in homogeneous systems, the external field is set to zero.

7.7.1 ‡Compressibility Equation of State

Upon integration over the volume V of the system, (7.51) yields

$$\int_V n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \left\langle \sum_{i=1}^{N} \int_V \delta(\boldsymbol{r}-\boldsymbol{r}_i)\mathrm{d}\boldsymbol{r} \right\rangle = \left\langle \sum_{i=1}^{N} 1 \right\rangle = \langle N \rangle \,. \tag{7.231}$$

Similarly, integration of $n^{(2)}$ defined by (7.134) gives

$$\int_V \int_V n^{(2)}(\boldsymbol{r},\boldsymbol{r}')\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \int_V \int_V \delta(\boldsymbol{r}-\boldsymbol{r}_i)\delta(\boldsymbol{r}'-\boldsymbol{r}_j)\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \right\rangle = \langle N(N-1) \rangle \,. \tag{7.232}$$

Combining these two equations,

$$\int_V \int_V [n^{(2)}(\boldsymbol{r},\boldsymbol{r}') - n(\boldsymbol{r})n(\boldsymbol{r}')]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' = \langle N^2 \rangle - \langle N \rangle - \langle N \rangle^2 \,. \tag{7.233}$$

In a homogeneous system, $n(\boldsymbol{r}) = n(\boldsymbol{r}') =: n$ is a constant. In addition, our choice for the origin of the coordinate system should be immaterial, leading to

$$n^{(2)}(\boldsymbol{r},\boldsymbol{r}') = n^{(2)}(\boldsymbol{0},\boldsymbol{R}) = n^2 g(\boldsymbol{0},\boldsymbol{R}) = n^2 g(\boldsymbol{R}) \,, \tag{7.234}$$

where $\boldsymbol{R} := \boldsymbol{r}' - \boldsymbol{r}$ and we dropped the explicit reference to $\boldsymbol{0}$. Using $\boldsymbol{r}$ and $\boldsymbol{R}$ as the new integration variables, we rewrite the left-hand side of (7.233) as

$$n^2 \int_V \int_V [g(\boldsymbol{R}) - 1]\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{R} = n^2 V \int_V [g(\boldsymbol{R}) - 1]\mathrm{d}\boldsymbol{R} \,. \tag{7.235}$$

On the other hand, (4.155) gives

$$\langle N^2 \rangle - \langle N \rangle - \langle N \rangle^2 = \langle N \rangle (k_B T n \kappa_T - 1) \,. \tag{7.236}$$

Thus, noting that $\langle N \rangle = nV$, we arrive at

$$k_B T n \kappa_T = 1 + n \int_V [g(\boldsymbol{r}) - 1]\mathrm{d}\boldsymbol{r} \,, \tag{7.237}$$

which is known as the **compressibility equation of state**. For an isotropic system, $g(\boldsymbol{r}) = g(r)$. For an ideal gas, $g(r) = 1$. Thus,

$$k_B T n \kappa_T = 1 \,, \tag{7.238}$$

the validity of which can easily be checked using the ideal gas equation of state.

7.7.2 ‡Virial Equation of State

Under the assumption of pairwise additivity of the intermolecular potential, we obtained a statistical mechanical expression for pressure in a canonical ensemble in Sect. 3.14.1. It is possible to rewrite our result (3.201) in terms of g_N.

For this purpose, we note that

$$\left\langle \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \frac{\mathrm{d}v(r_{ij})}{\mathrm{d}r_{ij}} r_{ij} \right\rangle_N = N(N-1) \left\langle \frac{\mathrm{d}v(r_{12})}{\mathrm{d}r_{12}} r_{12} \right\rangle_N , \tag{7.239}$$

where we introduced the subscript N to indicate ensemble averages in the canonical ensemble. But, in the expression

$$\left\langle \frac{\mathrm{d}v(r_{12})}{\mathrm{d}r_{12}} r_{12} \right\rangle_N = \frac{1}{Z} \frac{1}{\Lambda^{3N} N!} \int \frac{\mathrm{d}v(r_{12})}{\mathrm{d}r_{12}} r_{12} \left[\int e^{-\beta\phi(\boldsymbol{r}^N)} \mathrm{d}\boldsymbol{r}_3, \ldots, \mathrm{d}\boldsymbol{r}_N \right] \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 , \tag{7.240}$$

$\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are just the integration variables that can be replaced, respectively, by $\boldsymbol{r}$ and $\boldsymbol{r}'$ without affecting the value of the integral. When the resulting expression is compared against (7.154) with ψ set to zero, we find

$$\left\langle \frac{\mathrm{d}v(r_{12})}{\mathrm{d}r_{12}} r_{12} \right\rangle_N = \int_V \int_V \frac{\mathrm{d}v(R)}{\mathrm{d}R} R \langle \delta(\boldsymbol{r}-\boldsymbol{r}_1)\delta(\boldsymbol{r}'-\boldsymbol{r}_2)\rangle_N \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' . \tag{7.241}$$

Recalling (7.155) and (7.158) with $n_N(\boldsymbol{r}) = n_N(\boldsymbol{r}')$ replaced by $n = N/V$, we obtain

$$\begin{aligned} N(N-1) \left\langle \frac{\mathrm{d}v(r_{12})}{\mathrm{d}r_{12}} r_{12} \right\rangle_N &= n^2 \int_V \int_V \frac{\mathrm{d}v(R)}{\mathrm{d}R} R g_N(\boldsymbol{r}, \boldsymbol{r}') \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' \\ &= n^2 V \int_V \frac{\mathrm{d}v(R)}{\mathrm{d}R} R g_N(\boldsymbol{R}) \mathrm{d}\boldsymbol{R} . \end{aligned} \tag{7.242}$$

With this expression, (3.201) becomes

$$P = P^{\mathrm{id}} - \frac{1}{6} n^2 \int_V \frac{\mathrm{d}v(r)}{\mathrm{d}r} r g_N(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} , \tag{7.243}$$

which is referred to as the **virial equation of state**. If $v(r) \equiv 0$, this equation reduces to the ideal gas equation of state.

7.8 Frequently Used Symbols

$\mathscr{F}[u]$, a functional $\mathscr{F}$ of a function $u(x)$.
$\delta\mathscr{F}/\delta u(x)$, functional derivative.
$\mathrm{Tr}^{\mathrm{cl}}$, classical trace.

d , hard-sphere diameter.
f , F/V.
$g(\boldsymbol{r},\boldsymbol{r}')$, radial distribution function in a grand canonical ensemble.
$g_N(\boldsymbol{r},\boldsymbol{r}')$, radial distribution function in a canonical ensemble.
k_B , Boltzmann constant, 1.3806×10^{-23} J/K.
$n(\boldsymbol{r})$ density profile in a grand canonical ensemble.
$n_N(\boldsymbol{r})$ density profile in a canonical ensemble.
$n^{\mathrm{eq}}(\boldsymbol{r})$, equilibrium density profile.
$n^{(2)}(\boldsymbol{r},\boldsymbol{r}')$, pair distribution function in a grand canonical ensemble.
$n_N^{(2)}(\boldsymbol{r},\boldsymbol{r}')$, pair distribution function in a canonical ensemble.
$\hat{n}(\boldsymbol{r},\boldsymbol{r}^N)$, density operator.
$\boldsymbol{p}_i$, linear momentum of the ith particle.
r_c , cut-off radius for the truncated and shifted Lennard–Jones potential.
r_{min} , $2^{1/6}\sigma$, the distance at which $v^{\mathrm{LJ}}(r)$ takes its minimum value $-\varepsilon$.
$\boldsymbol{r}_i$, position vector of the ith particle.
$v(\boldsymbol{r},\boldsymbol{r}')$, pair potential, that is, the potential energy due to interaction between two particles, one at $\boldsymbol{r}$ and the other at $\boldsymbol{r}'$.
$v^{\mathrm{att}}(r)$, attractive part of $v(r)$.
$v^{\mathrm{rep}}(r)$, repulsive part of $v(r)$.
$v^{\mathrm{HS}}(r)$, hard-sphere potential.
$v^{\mathrm{LJ}}(r)$, Lennard–Jones potential.
$v^{\mathrm{tsLJ}}(r)$, truncated and shifted Lennard–Jones potential.

F_{int} , intrinsic Helmholtz free energy.
$F_{\mathrm{int}}^{\mathrm{exc}}$, intrinsic excess Helmholtz free energy.
$F_{\mathrm{int}}^{\mathrm{id}}$, intrinsic Helmholtz free energy of an ideal gas.
N , the number of particles.
P , pressure.
P_{hHS} , pressure of a homogeneous hard-sphere fluid.
$P_{\mathrm{hHS}}^{\mathrm{exc}}$, excess pressure of a homogeneous hard-sphere fluid.
T , absolute temperature.
V , volume.
X_i , the ith additional variable needed to specify the state of a system that is not in equilibrium.

β , $1/k_BT$.
ε , energy parameter of the Lennard–Jones potential.
η , packing fraction.
μ , chemical potential.
μ_{hHS} , chemical potential of a homogeneous hard-sphere fluid.
$\mu_{\mathrm{hHS}}^{\mathrm{exc}}$, excess chemical potential of a homogeneous hard-sphere fluid.
ρ , statistical weight.
ρ^{eq} , statistical weight at equilibrium.
σ , Lennard–Jones diameter.
$\phi(\boldsymbol{r}^N)$, potential energy due to intermolecular interaction.
$\psi(\boldsymbol{r})$, external field.

$\Delta e(r)$, blip function.
Λ , thermal wavelength.
Ξ , grand canonical partition function.
Ω , grand potential.
Ω_{int} , intrinsic grand potential.

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