S9.A. The Pressure and Compressibility Equations

In this section, we continue the work leading to

$$U(V,\ T,\ N) = \frac{3}{2} N k_B T \ + \frac{1}{2} \frac{N^2}{V} 4\pi \int d q\ q^2 \mathcal{V}(q)\, g_2^N(q,\ V,\ T) \qquad (9.8)$$

and try to express other thermodynamic functions in terms of the radial distribution function $g_2^N(q\,;V,\ T)$.

S9.A.1. The Pressure Equation

The most straight-forward way to get the pressure is to apply the thermodynamic relation

$$P = -\left.\frac{\partial U}{\partial V}\right|_S$$

to (9.8). However, since we have not yet obtained the entropy S, it is better to deal with the Helmholtz free energy and

$$P = -\left.\frac{\partial F}{\partial V}\right|_T = k_B T \left.\frac{\partial}{\partial V} \ln Z_N\right|_T$$

Using [see (9.2c) & (9.7c)]

$$Z_N(V,\ T) = z^N Q_N(V,\ T) \qquad\qquad z = (2\pi m k_B T)^{3/2} = \lambda_T^{-3}$$

we have

$$P = k_B T \left.\frac{\partial}{\partial V} \ln Q_N\right|_T \qquad (9.67a)$$

For a cubic volume of sides $L = V^{1/3}$,

$$\frac{\partial}{\partial V} = \frac{\partial L}{\partial V}\frac{\partial}{\partial L} = \frac{1}{3 V^{2/3}}\frac{\partial}{\partial L} = \frac{L}{3V}\frac{\partial}{\partial L}$$

(9.67a) becomes

$$P = \frac{k_B T L}{3V} \left.\frac{\partial}{\partial L} \ln Q_N\right|_T \qquad (9.67)$$

In terms of the $3N$ Cartesian coordinates $q_1,\ \ldots,\ q_{3N}$, (9.5) becomes

$$Q_N(V,\ T) = \int_0^L d q_1 \ldots \int_0^L d q_{3N}\, e^{-\beta \mathcal{V}_2(\boldsymbol{q}^N)}$$
$$= V^N \int_0^1 d x_1 \ldots \int_0^1 d x_{3N}\, e^{-\beta \mathcal{V}_2(L\,\boldsymbol{x}^N)} \qquad (9.68)$$

where

$$\boldsymbol{x}^N = \left\{ x_j = \frac{q_j}{L};\ j = 1,\ \ldots,\ 3N \right\}$$

are dimensionless Cartesian coordinates.

Using

$$\frac{\partial V^N}{\partial L} = N V^{N-1}\left(3L^2\right) = 3N\frac{V^N}{L}$$

(9.68) gives

$$\frac{\partial Q_N(V,\ T)}{\partial L} = \frac{3N}{L} Q_N + V^N \int_0^1 d x_1 \ldots \int_0^1 d x_{3N} \left[-\beta \frac{\partial \mathcal{V}_2^N(L\,\boldsymbol{x}^N)}{\partial L}\right] e^{-\beta \mathcal{V}_2^N(L\,\boldsymbol{x}^N)} \qquad (9.69)$$

Since $\mathcal{V}_2^N$ contains $N(N-1)/2$ pairs of 2-particle interaction,

$$\frac{\partial\, \mathcal{V}_2^N(L\,\boldsymbol{x}^N)}{\partial L} = \sum_{(i,j)}^{N(N-1)/2} \boldsymbol{x}_{ij} \cdot \frac{\partial\, \mathcal{V}_2(\boldsymbol{q}_{ij})}{\partial\, \boldsymbol{q}_{ij}} \tag{9.70}$$

(9.69) becomes

$$\frac{\partial\, Q_N(V,\,T)}{\partial L} = \frac{3\,N}{L}\,Q_N - \frac{1}{L}\,\beta \sum_{(i,j)}^{N(N-1)/2} \int d\,\boldsymbol{q}^N\, \boldsymbol{q}_{ij} \cdot \frac{\partial\, \mathcal{V}_2(\boldsymbol{q}_{ij})}{\partial\, \boldsymbol{q}_{ij}}\, e^{-\beta \mathcal{V}_2^N(\boldsymbol{q}^N)}$$

(9.67) thus becomes

$$\begin{aligned} \frac{P}{k_B\,T} &= \frac{L}{3\,V\,Q_N}\, \frac{\partial\, Q_N}{\partial\, L}\bigg|_T \\ &= \frac{N}{V} - \frac{\beta}{3\,V\,Q_N} \sum_{(i,j)}^{N(N-1)/2} \int d\,\boldsymbol{q}^N\, \boldsymbol{q}_{ij} \cdot \frac{\partial\, \mathcal{V}_2(\boldsymbol{q}_{ij})}{\partial\, \boldsymbol{q}_{ij}}\, e^{-\beta \mathcal{V}_2^N(\boldsymbol{q}^N)} \end{aligned}$$

Since all particle pairs are equivalent,

$$\begin{aligned} \frac{P}{k_B\,T} &= \frac{N}{V} - \frac{\beta\, N(N-1)}{6\,V\,Q_N} \int d\,\boldsymbol{q}^N\, \boldsymbol{q}_{12} \cdot \frac{\partial\, \mathcal{V}_2(\boldsymbol{q}_{12})}{\partial\, \boldsymbol{q}_{12}}\, e^{-\beta \mathcal{V}_2^N(\boldsymbol{q}^N)} \\ &= \frac{N}{V} - \frac{\beta}{6\,V} \int d\,\boldsymbol{q}_1 \int d\,\boldsymbol{q}_2\, \boldsymbol{q}_{12} \cdot \frac{\partial\, \mathcal{V}_2(\boldsymbol{q}_{12})}{\partial\, \boldsymbol{q}_{12}}\, n_2^N(\boldsymbol{q}_{12}\,;\,V,\,T) \end{aligned} \tag{9.71}$$

where (9.4) was used.

Integrating out the CM coordinates then gives

$$\frac{P}{k_B\,T} = \frac{N}{V} - \frac{\beta}{6} \int d\,\boldsymbol{q}\;\; \boldsymbol{q} \cdot \frac{\partial\, \mathcal{V}_2(\boldsymbol{q})}{\partial\, \boldsymbol{q}}\, n_2^N(\boldsymbol{q}\,;\,V,\,T) \tag{9.71a}$$

For central potentials of range $R \ll L$, (9.71) becomes

$$\begin{aligned} \frac{P}{k_B\,T} &= \frac{N}{V} - \frac{4\,\pi\,\beta}{3} \int_0^\infty d\,q\,q^3\; \frac{\partial\, \mathcal{V}_2(q)}{\partial\, q}\, n_2^N(q\,;\,V,\,T) \\ &= \frac{N}{V} - \frac{4\,\pi\,\beta}{3} \left(\frac{N}{V}\right)^2 \int_0^\infty d\,q\,q^3\; \frac{\partial\, \mathcal{V}_2(q)}{\partial\, q}\, g_2^N(q\,;\,V,\,T) \end{aligned} \tag{9.72}$$

where (9.8h) of §9.8 was used. (9.72) is known as the pressure equation.

S9.A.1. The Compressibility Equation

The thermal average for a k-body phase function in the grand canonical ensemble is defined as [c.f.(9.2a)]

$$\langle\, O_k \,\rangle = \frac{1}{Z_\mu} \sum_{N=k}^{\infty} \frac{1}{N!} \int d\,\boldsymbol{p}^N \int d\,\boldsymbol{q}^N\, e^{-\beta\left(H^N - \mu\,N\right)}\, O_k^N(\boldsymbol{q}^k) \tag{9.74a}$$

where the grand partition function $Z_\mu(V,\,T)$ is given by (9.9a-b) and the k-particle operator takes the form

$$O_k^N(\boldsymbol{q}^k) = \sum_{(j_1,\ldots,j_k)}^{C_k^N} O_k(\boldsymbol{q}_{j_1},\;\ldots,\;\boldsymbol{q}_{j_k}) \tag{9.74b}$$

where

$$C_k^N = \frac{N!}{(N-k)!\,k!} = \text{number of distinct clusters of } k \text{ particles}$$

Note that the sum of N in (9.74a) necessarily starts at $N = k$ for a k-body phase function.

In analogy to (9.3c), we set

$$\langle O_k \rangle = \frac{1}{k!} \int d\,\boldsymbol{q}^k\, O_k\left(\boldsymbol{q}^k\right) n_k^\mu\left(\boldsymbol{q}^k; V, T\right) \qquad (9.74c)$$

Comparison with (9.74a) then gives

$$n_k^\mu\left(\boldsymbol{q}^k; V, T\right) = \frac{1}{Z_\mu} \sum_{N=k}^{\infty} \frac{1}{(N-k)!} \int d\,\boldsymbol{p}^N \int d\,\boldsymbol{q}_{k+1} \ldots \int d\,\boldsymbol{q}_N\, e^{-\beta\left(H^N - \mu N\right)} \qquad (9.75)$$

as the k-body reduced distribution functions in the grand canonical ensemble.

For a Hamiltonian that depends on the momenta through the kinetic energies only, we can carry out the momentum integrals to get

$$n_k^\mu\left(\boldsymbol{q}^k; V, T\right) = \frac{1}{Z_\mu} \sum_{N=k}^{\infty} \frac{\left(z\, e^{\beta\mu}\right)^N}{(N-k)!} \int d\,\boldsymbol{q}_{k+1} \ldots \int d\,\boldsymbol{q}_N\, e^{-\beta \mathcal{V}^N} \qquad (9.75a)$$

Usually, we are concerned with 1- and 2-body phase functions only. Setting $k = 1$ & 2 in (9.74c) gives

$$\langle O_1 \rangle = \int d\,\boldsymbol{q}\, O_1(\boldsymbol{q})\, n_1^\mu(\boldsymbol{q}; V, T) \qquad (9.73)$$

$$\langle O_2 \rangle = \frac{1}{2} \int d\,\boldsymbol{q}_1 \int d\,\boldsymbol{q}_2\, O_2(\boldsymbol{q}_1, \boldsymbol{q}_2)\, n_2^\mu(\boldsymbol{q}_1, \boldsymbol{q}_2; V, T) \qquad (9.74)$$

Setting $k = 1$ in (9.75a) gives

$$n_1^\mu(\boldsymbol{q}_1; V, T) = \frac{1}{Z_\mu} \sum_{N=1}^{\infty} \frac{1}{(N-1)!} \int d\,\boldsymbol{p}^N \int d\,\boldsymbol{q}_2 \ldots \int d\,\boldsymbol{q}_N\, e^{-\beta\left(H^N - \mu N\right)}$$

Comparing with

$$\langle N \rangle = \frac{1}{Z_\mu} \sum_{N=0}^{\infty} \frac{1}{N!} \int d\,\boldsymbol{p}^N \int d\,\boldsymbol{q}^N\, e^{-\beta\left(H^N - \mu N\right)}\, N$$

we have

$$\langle N \rangle = \int d\,\boldsymbol{q}_1\, n_1^\mu(\boldsymbol{q}_1; V, T) \qquad (9.76)$$

Similarly,

$$n_2^\mu(\boldsymbol{q}_1, \boldsymbol{q}_2; V, T) = \frac{1}{Z_\mu} \sum_{N=2}^{\infty} \frac{1}{(N-2)!} \int d\,\boldsymbol{p}^N \int d\,\boldsymbol{q}_3 \ldots \int d\,\boldsymbol{q}_N\, e^{-\beta\left(H^N - \mu N\right)}$$

$$\rightarrow \qquad \left\langle N^2 \right\rangle - \langle N \rangle = \frac{1}{Z_\mu} \sum_{N=0}^{\infty} \frac{1}{N!} \int d\,\boldsymbol{p}^N \int d\,\boldsymbol{q}^N\, e^{-\beta\left(H^N - \mu N\right)} \left(N^2 - N\right)$$

$$= \int d\,\boldsymbol{q}_1 \int d\,\boldsymbol{q}_2\, n_2^\mu(\boldsymbol{q}_1, \boldsymbol{q}_2; V, T) \qquad (9.77)$$

By deduction,

$$\int d\,\boldsymbol{q}^k\, n_k^\mu\left(\boldsymbol{q}^k; V, T\right) = \langle N(N-1) \ldots (N-k+1) \rangle \qquad (9.77a)$$

In general, the isothermal compressibility κ_T satisfies [see (7.117) of §7.G]

$$\left\langle N^2 \right\rangle - \langle N \rangle^2 = \frac{k_B\, T}{V} \langle N \rangle^2\, \kappa_T$$

Writing

$$\langle N^2\rangle - \langle N\rangle^2 = \langle N^2\rangle - \langle N\rangle + \langle N\rangle - \langle N\rangle^2$$

$$\frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle} = \frac{\langle N^2\rangle - \langle N\rangle}{\langle N\rangle} + 1 - \langle N\rangle$$

$$\therefore \quad \frac{k_B T}{V}\langle N\rangle \kappa_T - 1 = \frac{\langle N^2\rangle - \langle N\rangle}{\langle N\rangle} - \langle N\rangle$$

$$= \frac{1}{\langle N\rangle}\int d\,\boldsymbol{q}_1 \int d\,\boldsymbol{q}_2\, n_2^\mu(\boldsymbol{q}_1, \boldsymbol{q}_2; V, T) - \langle N\rangle \tag{9.78a}$$

$$= \frac{1}{\langle N\rangle}\int d\,\boldsymbol{q}_1 \int d\,\boldsymbol{q}_2\, [\, n_2^\mu(\boldsymbol{q}_1, \boldsymbol{q}_2; V, T) - n_1^\mu(\boldsymbol{q}_1; V, T)\, n_1^\mu(\boldsymbol{q}_2; V, T)\,] \tag{9.78}$$

For particles interacting via short-range central potentials [c.f.(9.8h)],

$$n_2^\mu(q_{12};\; V, T) = \left(\frac{\langle N\rangle}{V}\right)^2 g_2^\mu(q_{12}; V, T) \tag{9.78b}$$

$$\rightarrow \quad \frac{1}{\langle N\rangle}\int d\,\boldsymbol{q}_1 \int d\,\boldsymbol{q}_2\; n_2^\mu(\boldsymbol{q}_1, \boldsymbol{q}_2; V, T) = \frac{\langle N\rangle}{V^2}\int d\,\boldsymbol{q}_1 \int d\,\boldsymbol{q}_2\, g_2^\mu(q_{12}; V, T)$$

$$= \frac{\langle N\rangle}{V^2}\int d\,\boldsymbol{Q} \int d\,\boldsymbol{q}_{12}\, g_2^\mu(q_{12}; V, T)$$

$$= 4\pi \frac{\langle N\rangle}{V}\int_0^R d\,q\; q^2\, g_2^\mu(q; V, T)$$

where $\boldsymbol{Q}$ is the CM coordinate and

$$V = \frac{4\pi}{3} R^3$$

Setting $\langle n\rangle = \frac{\langle N\rangle}{V}$, (9.78a) thus becomes

$$k_B T \langle n\rangle \kappa_T = 1 + 4\pi\langle n\rangle \int_0^R d\,q\; q^2\, g_2^\mu(q; V, T) - \langle N\rangle$$

$$= 1 + 4\pi\langle n\rangle \int_0^R d\,q\; q^2\, [\, g_2^\mu(q; V, T) - 1] \tag{9.79}$$

which is known as the compressibility equation.

Defining the structure function by

$$h(q) = g_2^\mu(q) - 1 \tag{9.79a}$$

(9.79) becomes

$$k_B T \langle n\rangle \kappa_T = 1 + 4\pi\langle n\rangle \int_0^R d\,q\; q^2\, h_2^\mu(q)$$

$$= 1 + \langle n\rangle \int d\,\boldsymbol{q}\, h_2^\mu(q) \tag{9.80a}$$

Note that [see §7.G]

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} = \frac{1}{V}\left(\frac{\partial\langle N\rangle}{\partial P}\right)_{T,V}\left(\frac{\partial V}{\partial\langle N\rangle}\right)_{T,P} = \frac{1}{\langle n\rangle}\left(\frac{\partial\langle n\rangle}{\partial P}\right)_{T,V}$$

so that (9.80a) can be written as

$$k_B T \left(\frac{\partial \langle n \rangle}{\partial P} \right)_{T,V} = 1 + \langle n \rangle \int d\,\boldsymbol{q}\, h_2^{\mu}(q) \tag{9.80}$$