7.5: Thermodynamic quantities in terms of g(r)

In the canonical ensemble, the average energy is given by

$$E = -\frac{\partial}{\partial \beta}\ln Q(N,V,\beta)$$

$$\ln Q(N,V,\beta) = \ln Z_N - 3N\ln\lambda(\beta) - \ln N!$$

Therefore,

$$E = \frac{3N}{\lambda}\frac{\partial \lambda}{\partial \beta} - \frac{1}{Z_N}\frac{\partial Z_N}{\partial \beta}$$

Since

$$\lambda = \left[\frac{\beta h^2}{2\pi m}\right]^{1/2}$$

$$\frac{\partial \lambda}{\partial \beta} = \frac{1}{2\beta}\lambda$$

Thus,

$$E = \frac{3}{2}NkT + \frac{1}{Z_N}\int dr_1 \cdots dr_N U(r_1,\cdots,r_N)e^{\beta U(r_1,\cdots,r_N)}$$

$$= \frac{3}{2}NkT + \langle U \rangle$$

In order to compute the average energy, therefore, one needs to be able to compute the average of the potential $\langle U \rangle$. In general, this is a nontrivial task, however, let us work out the average for the case of a *pairwise-additive* potential of the form

$$U(r_1,\cdots,r_N) = \frac{1}{2}\sum_{i,j,i\neq j} u(|r_i - r_j|) \equiv U_{pair}(r_1,\cdots,r_N)$$

i.e., U is a sum of terms that depend only the distance between two particles at a time. This form turns out to be an excellent approximation in many cases. U therefore contains $N(N\text{-}1)$ total terms, and $\langle U \rangle$ becomes

$$\langle U \rangle = \frac{1}{2Z_N}\sum_{i,j,i\neq j}\int dr_1\cdots dr_N u(|r_i - r_j|)e^{-\beta U_{pair}(r_1,\cdots,r_N)}$$

$$= \frac{N(N-1)}{2Z_N}\int dr_1\cdots dr_N u(|r_1 - r_2|)e^{-\beta U_{pair}(r_1,\cdots,r_N)}$$

The second line follows from the fact that all terms in the first line are the exact same integral, just with the labels changed. Thus,

$$\langle U \rangle = \frac{1}{2}\int dr_1 dr_2 u(|r_1 - r_2|)\left[\frac{N(N-1)}{Z_N}\int dr_3\cdots dr_N e^{-\beta U_{pair}(r_1,\cdots,r_N)}\right]$$

$$= \frac{1}{2}\int dr_1 dr_2 u(|r_1 - r_2|)\rho^{(2)}(r_1,r_2)$$

$$= \frac{N^2}{2V^2}\int\int dr_1 dr_2 u(|r_1 - r_2|)p^{(2)}(r_1,r_2)$$

Once again, we change variables to $r = r_1 - r_2$ and $R = \frac{(r_1+r_2)}{2}$. Thus, we find that

$$\langle U \rangle = \frac{N^2}{2V^2}\int dr dR u(r)\tilde{g}^{(2)}(r,R)$$

$$= \frac{N^2}{2V^2}\int dr u(r)\int dR\tilde{g}^{(2)}(r,R)$$

$$= \frac{N^2}{2V^2} \int dr u(r) \tilde{g}(r)$$

$$= \frac{N^2}{2V^2} \int_0^\infty dr 4\pi r^2 u(r) g(r)$$

Therefore, the average energy becomes

$$E = \frac{3}{2} NkT + \frac{N}{2} 4\pi\rho \int_0^\infty dr r^2 u(r) g(r)$$

Thus, we have an expression for E in terms of a simple integral over the pair potential form and the radial distribution function. It also makes explicit the deviation from "ideal gas" behavior, where $E=3NkT/2$.

By a similar procedure, we can develop an equation for the pressure P in terms of $g(r)$. Recall that the pressure is given by

$$P = \frac{1}{\beta} \frac{\partial \ln Q}{\partial V}$$

$$= \frac{1}{\beta Z_N} \frac{\partial Z_N}{\partial \beta}$$

The volume dependence can be made explicit by changing variables of integration in Z_N to

$$s_i = V^{-1/3} r_i$$

Using these variables, Z_N becomes

$$Z_N = V^N \int ds_1 \cdots ds_N e^{-\beta U(V_1^{1/R}, \cdots, V_N^{1/R})}$$

Carrying out the volume derivative gives

$$\frac{\partial Z_N}{\partial V} = \frac{N}{V} Z_N - \beta V^N \int ds_1 \cdots ds_N \frac{1}{3V} \sum_{i=1}^{N} r_i \cdot \frac{\partial U}{\partial r_i} e^{-\beta U(V_1^{1/R}, \cdots, V_N^{1/R})}$$

$$= \frac{N}{V} Z_N + \beta \int dr_1 \cdots dr_N \frac{1}{3V} \sum_{i=1} r_i \cdot F_i e^{-\beta U(r_1, \cdots, r_N)}$$

$$= ds_1 \cdots ds_N \frac{1}{3V} \sum_{i=1}^{N} r_i \cdot ds_1 \cdots ds_N \frac{1}{3V} \sum_{i=1}^{N} r_i \cdot ds_1 \cdots ds_N \frac{1}{3V} \sum_{i=1}^{N} r_i \text{\cdo}$$

Thus,

$$\frac{1}{Z_N} \frac{\partial Z_N}{\partial V} = \frac{N}{V} + \frac{\beta}{3V} \left\langle \sum_{i=1}^{N} r_i \cdot F_i \right\rangle$$

Let us consider, once again, a pair potential. We showed in an earlier lecture that

$$\sum_{i=1}^{N} r_i \cdot F_i = \sum_{i=1} \sum_{j=1, j \neq i}^{N} r_i \cdot F_{ij}$$

where F_{ij} is the force on particle i due to particle j. By interchaning the i and j summations in the above expression, we obtain

$$\sum_{i=1}^{N} r_i \cdot F_i = \frac{1}{2} \left[\sum_{i,j,i \neq j} r_i \cdot F_{ij} + \sum_{i,j,i \neq j} r_j \cdot F_{ij} \right]$$

However, by Newton's third law, the force on particle i due to particle j is equal and opposite to the force on particle j due to particle i:

$$F_{ij} = -F_{ji}$$

Thus,

$$\sum_{i=1}^{N} r_i \cdot F_i = \frac{1}{2}\left[\sum_{i,j,i\neq j} r_i \cdot F_{ij} - \sum_{i,j,i\neq j} r_j \cdot F_{ij}\right] = \frac{1}{2}\sum_{i,j,i\neq j}(r_i - r_j)\cdot F_{ij} \equiv \frac{1}{2}\sum_{i,j,i\neq j} r_{ij}\cdot F_{ij}$$

The ensemble average of this quantity is

$$\frac{\beta}{3V}\left\langle \sum_{i=1}^{N} r_i \cdot F_i \right\rangle = \frac{\beta}{6V}\left\langle \sum_{i,j,i\neq j} r_{ij}\cdot F_{ij}\right\rangle = \frac{\beta}{6VZ_N}\int dr_1 \cdots dr_N \sum_{i,j,i\neq j} r_{ij}\cdot F_{ij} e^{-\beta U_{pair}(r_1,\cdots,r_N)}$$

As before, all integrals are exactly the same, so that

$$\frac{\beta}{3V}\left\langle \sum_{i=1}^{N} r_i \cdot F_i \right\rangle = \frac{\beta N(N-1)}{6VZ_N}\int d_1 \cdot r_N r_{12}\cdot F_{12} e^{-\beta U_{pair}(r_1,\cdots,r_N)}$$

$$= \frac{\beta}{6V}\int dr_1 dr_2 r_{12}\cdot F_{12}\left[\frac{N(N-1)}{Z_N}\int dr_3\cdots dr_N e^{-\beta U_{pair}(r_1,\cdots,r_N)}\right]$$

$$= \frac{\beta}{6V}\int dr_1 dr_2 r_{12}\cdot F_{12}\rho^{(2)}(r_1,r_2)$$

$$= \frac{\beta N^2}{6V^3}\int dr_1 dr_2 r_{12}\cdot F_{12} g^{(2)}(r_1,r_2)$$

Then, for a pair potential, we have

$$F_{12} = -\frac{\partial U_{pair}}{\partial r_{12}} = -u'(|r_1 - r_2|)\frac{(r_1 - r_2)}{|r_1 - r_2|} = -u'(r_{12})\frac{r_{12}}{r_{12}}$$

where $u'(r) = du/dr$, and $r_{12} = |r_{12}|$. Substituting this into the ensemble average gives

$$\frac{\beta}{3V}\left\langle \sum_{i=1}^{N} r_i \cdot F_i \right\rangle = -\frac{\beta N^2}{6V^3}\int dr_1 dr_2 u'(r_{12}) r_{12} g^{(2)}(r_1,r_2)$$

As in the case of the average energy, we change variables at this point to $r = r_1 - r_2$ and $R = \frac{(r_1+r_2)}{2}$. This gives

$$\frac{\beta}{3V}\left\langle \sum_{i=1}^{N} r_i \cdot F_i \right\rangle = -\frac{\beta N^2}{6V^3}\int dr dR u^t(r) r \tilde{g}^{(2)}(r,R)$$

$$= -\frac{\beta N^2}{6V^2}\int dr u^t(r) r \tilde{g}(r)$$

$$= -\frac{\beta N^2}{6V^2}\int_0^\infty dr 4\pi r^3 u^t(r) g(r)$$

Therefore, the pressure becomes

$$\frac{P}{kT} = \rho - \frac{\rho^2}{6kT}\int_0^\infty dr 4\pi r^3 u^t(r) g(r)$$

which again gives a simple expression for the pressure in terms only of the derivative of the pair potential form and the radial distribution function. It also shows explicitly how the equation of state differs from the that of the ideal gas $\frac{P}{kT} = \rho$.

From the definition of $g(r)$ it can be seen that it depends on the density ρ and temperature T: $g(r) = g(r;\rho,T)$. Note, however, that the equation of state, derived above, has the general form

$$\frac{P}{kT} = \rho + B\rho^2$$

which looks like the first few terms in an expansion about ideal gas behavior. This suggests that it may be possible to develop a general expansion in all powers of the density ρ about ideal gas behavior. Consider representing $g(r;\rho,T)$ as such a power series:

$$g(r;\rho,T)=\sum_{j=0}^{\infty}\rho^j g_j(r;T)$$

Substituting this into the equation of state derived above, we obtain

$$\frac{P}{kT}=\rho+\sum_{j=0}^{\infty}B_{j+2}(T)\rho^{j+2}$$

This is known as the **virial equation of state**, and the coefficients $B_{j+2}(T)$ are given by

$$B_{j+2}(T)=-\frac{1}{6kT}\int_0^{\infty}dr4\pi r^3u^t(r)g_j(r;T)$$

are known as the *virial coefficients*. The coefficient $B_2(T)$ is of particular interest, as it gives the leading order deviation from ideal gas behavior. It is known as the second virial coefficient. In the low density limit, $g(r;\rho,T)\approx g_0(r;T)$ and $B_2(T)$ is directly related to the radial distribution function.
