Appendix E

SCALED-PARTICLE THEORY

Scaled-particle theory is an approximate interpolation scheme that allows the calculation of the work required to create a spherical cavity in a hard-sphere fluid or, equivalently, to insert a solute sphere of the same radius. From this starting point it is possible to derive the equation of state of the fluid. The theory is easily formulated for mixtures, but we restrict the discussion here to the one-component case.

Consider a fluid of N hard spheres of diameter $d = 2R$ at a number density ρ. Let $W(R_0)$ be the reversible work required to create a spherical cavity of radius R_0 centred on a point $\mathbf{r}$ within the fluid. According to the basic principles of thermodynamic fluctuation theory, the probability that such a cavity will appear as the result of spontaneous fluctuations within the system is

$$p_0(R_0) = \exp\left[-\beta W(R_0)\right] \tag{E.1}$$

This is the same as the probability that there are no spheres whose centres lie within the spherical region of radius $R_0 + R$ around $\mathbf{r}$. That interpretation can be extended to negative values of R_0 in the range $-R \leqslant R_0 \leqslant 0$, in which case the radius of the region of interest is $0 \leqslant R_0 + R \leqslant R$. Since overlap of hard spheres is forbidden, there can be at most one particle in such a region, a situation that occurs with probability

$$p_1(R_0) = \tfrac{4}{3}\pi\rho(R_0 + R)^3 = 1 - p_0(R_0) \tag{E.2}$$

Combination of (E.1) and (E.2) gives

$$W(R_0) = -k_\mathrm{B}T \ln\left[1 - (4\pi\rho/3)(R_0 + R)^3\right], \quad R_0 \leqslant 0 \tag{E.3}$$

In the opposite limit, that of very large cavities, the reversible work required is given by thermodynamics. If P is the pressure of the fluid and $\Delta V_0 = 4\pi R_0^3/3$ is the volume of the cavity, then $W(R_0)$ is the increase in Helmholtz free energy resulting from a reduction equal to ΔV_0 in the volume accessible to the fluid:

$$W(R_0) = P\Delta V_0 = \tfrac{4}{3}\pi P R_0^3, \quad R_0 \gg R \tag{E.4}$$

The assumption now made is that for $R_0 > 0$, $W(R_0)$ is given by a cubic polynomial in R_0, where the term in R_0^3 (the dominant contribution for large cavities) is given by (E.4), i.e.

$$W(R_0) = w_0 + w_1 R_0 + \tfrac{1}{2}w_2 R_0^2 + \tfrac{4}{3}\pi P R_0^3, \quad R_0 \geqslant 0 \tag{E.5}$$

The coefficients w_0, w_1 and w_2 are determined by requiring $W(R_0)$ and its first derivative, as given by (E.3) for $R_0 < 0$ and (E.5) for $R_0 > 0$, to be continuous at $R_0 = 0$. The results obtained in this way are

$$\beta w_0 = -\ln(1-\eta), \qquad \beta w_1 = \frac{4\pi\rho R^2}{1-\eta}$$
$$\beta w_2 = \frac{8\pi\rho R}{1-\eta} + \frac{(4\pi\rho R^2)^2}{(1-\eta)^2} \tag{E.6}$$

where η is the hard-sphere packing fraction.

The excess chemical potential of the fluid is the reversible work required to insert a hard sphere of radius $R_0 = R$. Thus, from (E.5) and (E.6):

$$\begin{aligned}\beta\mu^{\text{ex}} &= \beta W(R_0) \\ &= -\ln(1-\eta) + \frac{6\eta}{1-\eta} + \frac{9\eta^2}{2(1-\eta)^2} + \frac{\beta P\eta}{\rho}\end{aligned} \tag{E.7}$$

Then use of the thermodynamic relation $\partial P/\partial\rho = \rho(\partial\mu/\partial\rho)$ leads to the scaled-particle equation of state in the form

$$\frac{\beta P}{\rho} = \frac{1+\eta+\eta^2}{(1-\eta)^3} \tag{E.8}$$

Equation (E.8) is identical to the Percus–Yevick compressibility equation (4.4.12). The corresponding expression for the excess free energy is

$$\frac{\beta F^{\text{ex}}}{N} = -\ln(1-\eta) + \frac{3\eta}{1-\eta} + \frac{3\eta^2}{2(1-\eta)^2} \tag{E.9}$$