Appendix D

SOLUTION OF THE PY EQUATION FOR HARD SPHERES

The PY closure relation for hard spheres is

$$h(r) = -1, \quad r < d \tag{D.1a}$$

$$c(r) = 0, \quad r > d \tag{D.1b}$$

When substituted in the Ornstein–Zernike relation (3.5.12), this approximation yields an integral equation that can be solved in closed form. We follow here the method of Baxter, which is based on a transformation of the Ornstein–Zernike relation via a so-called Wiener–Hopf factorisation of the function $\hat{A}(k)$ defined as

$$\hat{A}(k) = \frac{1}{S(k)} = 1 - \rho\hat{c}(k) = 1 - \frac{4\pi\rho}{k}\int_0^\infty r\sin(kr)c(r)\,\mathrm{d}r \tag{D.2}$$

The three-dimensional Fourier transform of any function f of $r \equiv |\mathbf{r}|$ can be cast in the form

$$\begin{aligned}\hat{f}(k) &= \frac{4\pi}{k}\int_0^\infty r\sin(kr)f(r)\,\mathrm{d}r = 4\pi\int_0^\infty \cos(kr)F(r)\,\mathrm{d}r \\ &= 2\pi\int_{-\infty}^\infty \exp(ikr)F(r)\,\mathrm{d}r\end{aligned} \tag{D.3}$$

where

$$F(r) = \int_r^\infty sf(s)\,\mathrm{d}s = F(-r) \tag{D.4}$$

The second equality in (D.4) follows immediately if the convention that $f(r) = f(-r)$ is followed. Substitution of (D.1b), (D.3) and (D.4) in (D.2) leads to

$$\hat{A}(k) = 1 - 4\pi\rho\int_0^d \cos(kr)S(r)\,\mathrm{d}r = \hat{A}(-k) \tag{D.5}$$

where

$$S(r) = \int_r^d tc(t)\,\mathrm{d}t \tag{D.6}$$

Similarly:

$$\hat{h}(k) = 2\pi \int_{-\infty}^{\infty} \exp(ikr) J(r)\, \mathrm{d}r \tag{D.7}$$

with

$$J(r) = \int_{r}^{\infty} s h(s)\, \mathrm{d}s \tag{D.8}$$

Consider now the behaviour of the function $\hat{A}(k)$ in the complex k-plane and set $k = x + iy$. Because $\hat{A}(k)$, as given by (D.5), is a Fourier transform over a finite interval, it is regular throughout the complex plane. It also has no zeros on the real axis ($y = 0$), since it is the inverse of the static structure factor; the latter is a finite quantity at all wavenumbers. Moreover, according to (D.5), $\hat{A}(k)$ tends uniformly to unity as $|x| \to \infty$ in any strip $y_1 < y < y_2$. Thus there exists a strip $|y| \leqslant \varepsilon$ about the real axis within which $\hat{A}(k)$ has no zeros. The function $\ln \hat{A}(k)$ is therefore regular within that strip and tends uniformly to zero as $|x| \to \infty$. Integrating around the strip and applying Cauchy's theorem, we find that for any $k = x + iy$ such that $|y| < \varepsilon$:

$$\ln \hat{A}(k) = \ln \widehat{Q}(k) + \ln \widehat{P}(k) \tag{D.9}$$

where

$$\ln \widehat{Q}(k) = \frac{1}{2\pi i} \int_{-i\varepsilon-\infty}^{-i\varepsilon+\infty} \frac{\ln \hat{A}(k')}{k' - k}\, \mathrm{d}k' \tag{D.10a}$$

$$\ln \widehat{P}(k) = -\frac{1}{2\pi i} \int_{i\varepsilon-\infty}^{i\varepsilon+\infty} \frac{\ln \hat{A}(k')}{k' - k}\, \mathrm{d}k' \tag{D.10b}$$

Since $\hat{A}(k)$ is an even function of k, (D.10) implies that

$$\ln \widehat{P}(k) = \ln \widehat{Q}(-k) \tag{D.11}$$

From (D.10a) we see that $\ln \widehat{Q}(k)$ is regular in the domain $y > -\varepsilon$. It follows from (D.9) and (D.11) that when $|y| < \varepsilon$:

$$\hat{A}(k) = \widehat{Q}(k)\widehat{Q}(-k) \tag{D.12}$$

The function $\widehat{Q}(k)$ is regular and has no zeros in the domain $y > -\varepsilon$, since it is the exponential of a function that is regular in the same domain. Equation (D.12) is the Wiener–Hopf factorisation of $\hat{A}(k)$.

When $|x| \to \infty$ within the strip $|y| < \varepsilon$, it follows from (D.10a) that $\ln \widehat{Q}(k) \sim x^{-1}$ and hence that $\widehat{Q}(k) \sim 1 - \mathcal{O}(x^{-1})$. The function $1 - \widehat{Q}(k)$ is therefore Fourier integrable along the real axis and a function $Q(r)$ can be defined as

$$2\pi\rho Q(r) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-ikr)\big[1 - \widehat{Q}(k)\big]\, \mathrm{d}k \tag{D.13}$$

Equation (D.10a) shows that if k is real, the complex conjugate of $\widehat{Q}(k)$ is $\widehat{Q}(-k)$, and hence that $Q(r)$ is a real function. The same equation also shows that when $y \geqslant 0$, $\ln \widehat{Q}(k) \to 0$, and therefore $\widehat{Q}(k) \to 1$, as $k \to \infty$. Thus, if $r < 0$, the integration in (D.13) can be closed around the upper half-plane, where $\widehat{Q}(k)$ is regular, to give

$$Q(r) = 0, \quad r < 0 \tag{D.14}$$

The right-hand side of (D.10a) is a different analytic function of k according to whether $y > -\varepsilon$ or $y < -\varepsilon$. The analytic continuation of $\widehat{Q}(k)$ into the lower half-plane is therefore given, not by (D.10a), but by (D.12), i.e.

$$\widehat{Q}(k) = \hat{A}(k)/\widehat{Q}(-k) \tag{D.15}$$

where (D.10a) can be used to evaluate $\widehat{Q}(-k)$. Since $\hat{A}(k)$ is regular everywhere, and $\widehat{Q}(-k)$ is regular and has no zeros for $y < \varepsilon$, we see from (D.15) that $\widehat{Q}(k)$ is also regular for $y < \varepsilon$. Furthermore, since $\widehat{Q}(-k) \to 1$ as $y \to -\infty$, it follows from (D.5) and (D.15) that both $\hat{A}(k)$ and $\widehat{Q}(k)$ grow exponentially as $\exp(ikd) = \exp(ixd)\exp(-yd)$ when y becomes large and negative. Thus, when $r > d$, the integration in (D.13) can be closed around the lower half-plane, giving

$$Q(r) = 0, \quad r > d \tag{D.16}$$

On inversion of the Fourier transform in (D.13), (D.14) and (D.16) together yield

$$\widehat{Q}(k) = 1 - 2\pi\rho \int_0^d \exp(ikr)Q(r)\,\mathrm{d}r \tag{D.17}$$

Substitution in (D.12) of the expressions (D.5) for $\hat{A}(k)$ and (D.17) for $\widehat{Q}(k)$, followed by multiplication by $\exp(-ikr)$ and integration with respect to k from $-\infty$ to $+\infty$, shows that

$$S(r) = Q(r) - 2\pi\rho \int_r^d Q(s)Q(s-r)\,\mathrm{d}s, \quad 0 < r < d \tag{D.18}$$

Equations (3.5.13), (D.2) and (D.12) imply that

$$\widehat{Q}(k)\big[1 + \rho\hat{h}(k)\big] = 1/\widehat{Q}(k) \tag{D.19}$$

where $\hat{h}(k)$ is given by (D.7). We now multiply both sides of (D.19) by $\exp(-ikr)$ and integrate with respect to k from $-\infty$ to $+\infty$. The contribution from the right-hand side vanishes when $r > 0$, since the integration can then be closed around the lower half-plane, where $\widehat{Q}(k)$ is regular, has no zeros and tends to unity at infinity. On substituting (D.7) and (D.17) into the left-hand side of (D.19) and carrying out the integration, we obtain a relation between $Q(r)$ and $J(r)$ for $r > 0$ of the form

$$-Q(r) + J(r) - 2\pi\rho \int_0^d Q(s)J\big(|r-s|\big)\,\mathrm{d}s = 0, \quad r > 0 \tag{D.20}$$

It is clear from (D.6) and (D.18) that $Q(r) \to 0$ as $r \to d$ from below; comparison with (D.16) then shows that $Q(r)$ is continuous at $r = d$.

Equations (D.18) and (D.20) can be expressed in terms of $c(r)$ and $h(r)$, rather than $S(r)$ and $J(r)$, by differentiating them with respect to r. If we use (D.6) and (D.8), and the fact that $Q(d) = 0$, we find after integration by parts that

$$rc(r) = -Q'(r) + 2\pi\rho \int_r^d Q'(s) Q(s-r)\, \mathrm{d}s, \quad 0 < r < d \tag{D.21}$$

and

$$rh(r) = -Q'(r) + 2\pi\rho \int_0^d (r-s) h\big(|r-s|\big) Q(s)\, \mathrm{d}s, \quad r > 0 \tag{D.22}$$

where $Q'(r) \equiv \mathrm{d}Q(r)/\mathrm{d}r$. Equations (D.21) and (D.22) express $h(r)$ and $c(r)$ in terms of the same function, $Q(r)$, and constitute a reformulation of the Ornstein–Zernike relation that is applicable whenever $c(r)$ vanishes beyond a range d, which is precisely the case with the PY closure. Equation (D.22) is an integral equation for $Q(r)$ that is easy to solve for $0 < r < d$, where $h(r) = -1$ and (D.22) therefore reduces to

$$r = Q'(r) + 2\pi\rho \int_0^d (r-s) Q(s)\, \mathrm{d}s, \quad 0 < r < d \tag{D.23}$$

The solution is of the form

$$Q'(r) = ar + b \tag{D.24}$$

with

$$a = 1 - 2\pi\rho \int_0^d Q(s)\, \mathrm{d}s, \qquad b = 2\pi\rho \int_0^d s Q(s)\, \mathrm{d}s \tag{D.25}$$

Given the boundary condition $Q(d) = 0$, (D.24) is trivially integrated to yield $Q(r)$. Substitution of the result in (D.25) gives two linear equations, the solutions to which are

$$a = \frac{1+2\eta}{(1-\eta)^2}, \qquad b = \frac{-3d\eta}{2(1-\eta)^2} \tag{D.26}$$

where η is the hard-sphere packing fraction. Thus $Q(r)$ is now a known function of r and $c(r)$ can therefore be calculated from (D.21); this leads to the results displayed in (4.4.10) and (4.4.11). The isothermal compressibility is obtained from (3.8.8), (D.2) and (D.15) as

$$\beta/\rho\chi_T = \hat{A}(0) = \big[\widehat{Q}(0)\big]^2 \tag{D.27}$$

The function $\widehat{Q}(0)$ is easily calculated from (D.17) and the solution for $Q(r)$, leading ultimately to the PY compressibility equation of state (4.4.12).