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The role of poles of the structure factor in determining properties of the hard sphere fluid

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Abstract. The distribution function of a fluid is determined by the singularities of its Fourier transform. Whereas the distribution functions at long range are well described by the contributions of those poles closest to the real axis, the short-range behaviour involves contributions from an infinite series of poles. For Percus–Yevick hard spheres in one and three dimensions, the series of discontinuities in the distribution function and its derivatives are shown to derive from the asymptotic distribution of the infinite series of poles in the Fourier transform of the distribution function.

1 Introduction

The structure of a disordered fluid of spherically symmetric particles may be described in terms of the two-particle distribution function $\rho_2(12)$ defined in the canonical ensemble by:

$$\rho_2(12)=[(N-2)!\,Q_N]^{-1}\int d(3)\dots\int d(N)\exp\left\{-\frac{1}{kT}\sum_{1\le i<j\le N}\phi(i,j)\right\} \tag{1.1}$$

where $\phi(i,j)$ is the two-particle potential and Q_N is the canonical partition function. If the system has particle density ρ and no external field then the correlation function $g(r)$, the total correlation function $h(r)$ and the direct correlation function $c(r)$ are related to $\rho_2(12)$ by

$$\rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)=\rho^2g(|\boldsymbol{r}_1-\boldsymbol{r}_2|), \tag{1.2}$$

$$h(r)=g(r)-1 \tag{1.3}$$

and the Ornstein–Zernike (OZ) relation

$$h(|\boldsymbol{r}|)=c(|\boldsymbol{r}|)+\rho\int d^d s\, c(|\boldsymbol{s}|)h(|\boldsymbol{r}-\boldsymbol{s}|) \tag{1.4}$$

where d is the dimensionality of the system. The definition of $c(r)$ via equation (1.4) allows $c(r)$ to be identified as a functional derivative or a sum of graphs. This in turn allows the derivation of other approximate relations between $h(r)$ and $c(r)$, these second relations being called 'closures'. As examples we mention the Percus–Yevick

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(PY) hypernetted chain (HNC) and mean spherical approximation (MSA) closures. The pair of relations between $h(r)$ and $c(r)$ allows the calculation of both.

Numerical and analytic methods of solution of equation (1.4) plus a closure proceed (either explicitly or implicitly) by studying the Fourier transforms

$$\hat{h}(|\boldsymbol{k}|) = \int \mathrm{d}^d\boldsymbol{r}\, \exp(\mathrm{i}\boldsymbol{k}.\boldsymbol{r})h(|\boldsymbol{r}|)$$

$$\hat{c}(|\boldsymbol{k}|) = \int \mathrm{d}^d\boldsymbol{r}\, \exp(\mathrm{i}\boldsymbol{k}.\boldsymbol{r})c(|\boldsymbol{r}|).$$

The function $h(r)$ may then be found as a one-dimensional Fourier transform inverse of $\hat{h}(k)$. The relation of $h(r)$ to $\rho_2(1, 2)$ shows that $h(k)$ is simply related to the structure factor of the system. The transform inverse may be determined from the singularities of $\hat{h}(k)$ in the complex k-plane because in a disordered fluid $\hat{h}(k)$ may be expected to be bounded as $k \to \infty$.

For many systems for which a solution is known, the singularities of $\hat{h}(k)$ are an infinite series of poles. As examples we mention PY hard spheres (Baxter 1968*a*) and PY sticky hard spheres (Baxter 1968*b*), the mean spherical approximation for hard spheres with a potential of the form $\phi(r) = A\exp(-zr)/r$ (Høye and Stell 1976) and the rigorous theory of hard spheres at sufficiently low density (Abraham and Kunz 1977). Another example is the two-dimensional Ising model, though there, only the closest singularity to the real k-axis is known to be a pole (Abraham 1978). The singularities are not always poles: in the MSA for hard spheres with potentials of the form $A\exp(-zr)r^{P-1}$ and p not a positive integer, there are branch points of $\hat{h}(k)$ at $k = \pm \mathrm{i}z$ (Smith 1979). Whichever form the singularities take, the asymptotic form of $h(r)$ for large r is determined by those singularities of $\hat{h}(k)$ in the lower half k plane which are closest to the real k axis.

In this paper, we show how the behaviour of $h(r)$ for small r can be determined, in part, by all the singularities of $\hat{h}(k)$ together. We have in mind, in particular, the discontinuities present in $h(r)$ for any system whose interaction potential is such that the Boltzmann factor is discontinuous. Our purpose in doing this is partly an intrinsic interest in the role of the poles of the structure factor of a system in determining $h(r)$ at short range, but also because we hope it will allow us to develop a method for numerically determining solutions of equation (1.5) and an approximate closure. This appears possible because, as we shall see, we require only the very simplest approximations to the position and residues of the infinite set of poles of $\hat{h}(k)$ to calculate the discontinuities in $h(r)$ exactly. It appears possible to find accurate numerical information on the closest few poles of $\hat{h}(k)$ to the real k axis for a wide range of problems, thus allowing the calculation of an $h(r)$ which is accurate except near discontinuities. The behaviour at discontinuities may then be calculated from the asymptotic nature of the infinite set of the poles of $\hat{h}(k)$. This asymptotic nature can often be calculated in a very simple way for surprisingly complicated systems.

In § 2 we study one-dimensional hard rods via the (exact) PY method. We find expansions for the poles and residues of $\hat{h}(k)$ and show how the first terms in the expansions for these poles and residues determine the discontinuity in $h(r)$ at the hard-rod width. In § 3 we repeat the analysis for PY hard spheres. Section 4 discusses the accuracy of the expansions and also show how $h(r)$ is accurately modelled by the contribution of a small number of poles of $\hat{h}(k)$, suggesting that our proposed solution method is of some use.

2. One-dimensional hard rods

In one dimension, the Ornstein–Zernike relation takes the form

$$h(x)=c(x)+\rho\int_{-\infty}^{\infty}\mathrm{d}y'\,c(|y'|)h(|x-y'|) \tag{2.1}$$

with $h(|x|)=-1$ for $0<|x|<1$ and $c(|x|)=0$ for $|x|>1$. Although Chen (1975) has presented the details of the application of Baxter's (1968a) method to this problem, we give here, for the guidance of the reader, a quick resumé of the principal results. Fourier transformation of (2.1) and a little subsequent rearrangement gives

$$1+\rho\hat{h}(k)=1/\hat{A}(k)\equiv[1-\rho\hat{c}(k)]^{-1} \tag{2.2}$$

where, in this case, $\hat{h}(k)$ and $\hat{c}(k)$ are simple one-dimensional exponential Fourier transforms of $h(|x|)$ and $c(|x|)$ respectively. A careful analysis of $\ln\hat{A}(k)$ shows that

(i) $$\hat{A}(k)=\hat{Q}(k)\hat{Q}(-k) \tag{2.3}$$

where $\hat{Q}(k)$ is an entire function free of zeros in the upper half k plane.

(ii) $$\hat{Q}(k)=1+\mathrm{O}(1/k) \tag{2.4}$$

as $|k|\to\infty$ with $\operatorname{im} k\geqslant 0$.

(iii) $1-\hat{Q}(k)$ has an inverse Fourier transform which is only non-zero in $0<x\leqslant 1$.

(iv) $$\rho q(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-\mathrm{i}kx)[1-\hat{Q}(k)]\,\mathrm{d}k = -\rho/(1-\rho) \qquad 0<x<1. \tag{2.5}$$

(v) $$h(x)=q(x)+\rho\int_0^1 h(|x-y'|)q(y')\,\mathrm{d}y' \tag{2.6}$$

It is readily shown that the solution of equation (2.6) is the solution of the differential-difference equation

$$h'(x)+\frac{\rho}{1-\rho}h(x)=\frac{\rho}{1-\rho}h(x-1), \qquad x>1 \tag{2.7}$$

with $h(x)=-1$ on $0<x<1$, and

$$h(1+)=\rho/(1-\rho). \tag{2.8}$$

Elementary integration also shows that

$$\hat{Q}(k)=1-\frac{\mathrm{i}\rho}{1-\rho}\,\frac{\exp \mathrm{i}k-1}{k}. \tag{2.9}$$

Values of $h(x)$ for $x\geqslant 1$ may be obtained numerically using either standard methods for the solution of equation (2.7) or a simple algorithm for equations of the type of (2.6) (Perram 1975).

Using equation (2.3) in equation (2.2) and taking the inverse transform we find

$$\rho h(x)=\sum\exp(-\mathrm{i}k_n x)[\hat{Q}'(k_n)\hat{Q}(-k_n)]^{-1} \tag{2.10}$$

for $x>0$, where the sum is over the zeros k_n of

$$\hat{Q}(k)=0. \tag{2.11}$$

If equation (2.11) could be solved analytically, equation (2.10) would represent a closed-form analytic expression for $h(x)$. Equation (2.9) does not appear to be soluble in closed form, so we develop an expansion of its roots for large $|k|$. The equation may be shown to have exactly one root in the lower half k plane in each strip $(2n-1)\pi < \mathrm{Re}(k) < (2n-\frac{1}{2})\pi$ for $n \geq 1$ and for each such $k_n = \sigma_n - \mathrm{i}\tau_n$ there is another root $-k_n^* = -\sigma_n - \mathrm{i}\tau_n$ so that equation (2.10) may be written

$$\rho h(x) = \sum_{n=1}^{\infty} \{\exp(-\mathrm{i}k_n x)[\hat{Q}'(k_n)\hat{Q}(-k_n)]^{-1} + \exp(\mathrm{i}k_n^* x)[\hat{Q}'(-k_n^*)\hat{Q}(k_n^*)]^{-1}\}, \qquad x > 0. \tag{2.12}$$

The roots of equation (2.9) may be expanded for large $|k|$ and we find

$$k_n \sim (2n-\tfrac{1}{2})\pi - \frac{\lambda \ln(2n-\frac{1}{2})\pi\lambda] - 1}{(2n-\frac{1}{2})\pi\lambda} - \tau\left(\frac{\lambda + 1 - \lambda \ln[(2n-\frac{1}{2})\pi\lambda]}{[(2n-\frac{1}{2})\pi\lambda]^3}\right) - \mathrm{i}\{\ln[(2n-\tfrac{1}{2})\pi\lambda] + \tau/[(2n-\tfrac{1}{2})\pi\lambda]^2\} \tag{2.13}$$

where

$$\tau = \tfrac{1}{2}\lambda^2\{\ln[(2n-\tfrac{1}{2})\pi\lambda]\}^2 - (\lambda + \lambda^2)\ln[(2n-\tfrac{1}{2})\pi\lambda] + \lambda + \tfrac{1}{2} \tag{2.14}$$

and

$$\lambda = (1-\rho)/\rho. \tag{2.15}$$

The expansion in equation (2.13) may be expected to be most inaccurate for $n = 1$. We expect the accuracy to vary with ρ via the dependence on λ and $\ln \lambda$. Thus for ρ very small, or close to one we expect the results to be less accurate than the results for intermediate ρ. In table 1 we list exact values of $\mathrm{Re}(k_n)/\pi$ and $\mathrm{Im}(k_n)$ (Cummings 1978, private communication) together with estimates of $\mathrm{Re}(k_n)$ and $\mathrm{Im}(k_n)$ from

Table 1. Exact and asymptotic estimates of k_n. 1st two columns: exact numerical results. 2nd two columns: 1st two terms in $\mathrm{Re}(k_n)$ and equation (2.13). 3rd two columns: all of equation (2.13).

η	$\mathrm{Re}(k_n)/\pi$	$-\mathrm{Im}(k_n)$	$\mathrm{Re}(k_n)/\pi 0$	$-\mathrm{Im}(k_n)0$	$\mathrm{Re}(k_n)/\pi 1$	$-\mathrm{Im}(k_n)1$
$n = 1$						
0·2	1·313 652	2·985 99	1·3185	2·936	1·3232	2·978
0·5	1·463 321	1·532 09	1·4628	1·550 19	1·463 38	1·532 23
0·8	1·687 204	0·465 447	1·759	0·164	1·594	0·668
$n = 3$						
0·2	5·426 658	4·249 13	5·426 57	4·2358	5·427 30	4·249 03
0·5	5·465 856	2·849 01	5·465 92	2·8494	5·465 92	2·849 01
0·8	5·545 692	1·481 80	5·5465	1·4632	5·5794	1·4825
$n = 6$						
0·2	11·468 428	4·978 30	11·458 38	4·973 37	11·458 55	4·978 30
0·5	11·477 195	3·587 66	11·477 21	3·587 07	11·477 21	3·587 66
0·8	11·515 795	2·203 39	11·515 85	2·200 79	11·515 87	2·203 40

equation (2.13) for $n = 1, 3, 6$ and $\rho = 0{\cdot}2, 0{\cdot}5, 0{\cdot}8$. The results are best at $\rho = 0{\cdot}5$ with the accuracy improving with increasing n. It may be noted that the expansions for $\mathrm{Im}(k_n)$ are much more accurate than for $\mathrm{Re}(k_n)$ in all cases.

As we anticipate that the discontinuities in $h(x)$ are determined by the gross features of the distribution of the poles of $\hat{h}(k)$ we consider the asymptotic forms

$$k_{n,A} = (2n-\tfrac{1}{2})\pi - \mathrm{i}\ln[(2n-\tfrac{1}{2})\pi\lambda] \tag{2.16}$$

and

$$h_A(a) = \frac{(-i)}{\rho}\sum_{n=1}^{\infty}\{\exp(-\mathrm{i}k_{n,A}x)[\hat{Q}'_A(k_n)\hat{Q}_A(-k_n)]^{-1} + \exp(\mathrm{i}k^*_{n,A}x)[\hat{Q}'_A(-k^*_n)\hat{Q}_A(k^*_n)]^{-1}\}, \tag{2.17}$$

where the functions $\hat{Q}'_A(k_n)$, $\hat{Q}_A(-k_n)$ are the leading order terms in the asymptotic expansion of $\hat{Q}'(k_n)$, $\hat{Q}(-k_n)$ for large $|k|$. We now show that $h_A(x)$ has precisely the discontinuity of $h(x)$ at $x = 1$. Thence, the discontinuity in the nth derivative of $h_A(x)$ at $x = n+1$ is equal to the nth derivative of $h(x)$.

For large $|k|$, equation (2.9) shows that

$$\exp(\mathrm{i}k_n) \sim -\mathrm{i}\lambda k_n. \tag{2.18}$$

A little calculation then shows

$$\hat{Q}'(k_n)\hat{Q}(-k_n) = -\mathrm{i}[1 + \mathrm{O}k_n^{-1}]$$

so that

$$\hat{Q}'_A(k_n)\hat{Q}_A(-k_n) = -\mathrm{i}. \tag{2.19}$$

Substitution of this result and the leading order real and imaginary parts of k_n from equation (2.13) into equation (2.17) then gives

$$h_A(x) = \frac{1}{\rho}\sum_{n=1}^{\infty}[(2n-\tfrac{1}{2})\pi\lambda]^{-x}\cos(2n-\tfrac{1}{2})\pi x. \tag{2.20}$$

We now study the discontinuity in $h_A(x)$ at $x = 1$. Equation (2.20) readily gives

$$h_A(1+) - h_A(1-) = \frac{1}{1-\rho}\lim_{\epsilon\to 0}\frac{2}{\pi}\sin 2n\pi\epsilon. \tag{2.21}$$

Since $2/\pi\,\Sigma_{n=1}^{\infty} 1/n \sin 2n\pi\epsilon$ is a Fourier series for the function

$$f(\epsilon) = \begin{cases} 1-\epsilon/2, & 0<\epsilon<\tfrac{1}{2} \\ -1+|\epsilon|/2, & -\tfrac{1}{2}<\epsilon<0 \end{cases} \tag{2.22}$$

we have

$$h_A(1+) - h_A(1-) = \frac{1}{1-\rho}, \tag{2.23}$$

which agrees precisely with the discontinuity in $h(x)$ at $x = 1$, as may be seen from equation (2.8) and the fact that $h(1-) = -1$.

3. Percus–Yevick hard spheres

For this system we define

$$\hat{h}(k) = 2\pi \int_{-\infty}^{\infty} \exp(\mathrm{i}kr) J(|r|)\, \mathrm{d}r \tag{3.1}$$

and

$$\hat{c}(k) = 4\pi \int_0^1 \cos kr\, S(r)\, \mathrm{d}r \tag{3.2}$$

where

$$J(r) = \int_r^{\infty} sh(s)\, \mathrm{d}s; \qquad S(r) = \int_r^{\infty} sc(s)\, \mathrm{d}s \tag{3.3}$$

with $h(s) = -1$ for $0 \leq s < 1$ and $c(s) = 0$ for $s > 1$. The analogue of equation (2.2) is then

$$1 + \rho\hat{h}(k) = 1/\hat{A}(k) = [\hat{Q}(k)\hat{Q}(-k)]^{-1} \tag{3.4}$$

as has been shown by Baxter (1968b). The function $\hat{Q}(k)$ is analytic and free of zeros in the upper half k plane and

$$\hat{Q}(k) = 1 - 2\pi\rho \int_0^1 \exp(\mathrm{i}kr) q(r)\, \mathrm{d}r \tag{3.5}$$

and

$$q(r) = \begin{cases} \dfrac{1+2\eta}{2(1-\eta)^2}(r^2 - 1) - \dfrac{3\eta}{2(1-\eta)^2}(r-1), & 0 < r < 1 \\ 0 & \text{otherwise} \end{cases} \tag{3.6}$$

where $\eta = \frac{1}{6}\pi\rho$. For $r > 0$, Fourier inversion of equation (3.4) gives

$$2\pi\rho J(r) = -\mathrm{i} \sum_{\substack{\text{poles} \\ k}} \frac{\exp(-\mathrm{i}kr)}{\hat{Q}(k)\hat{Q}(-k)}. \tag{3.7}$$

The analogue of equation (2.6) for this system is

$$J(r) = q(r) + 12\eta \int_0^1 q(t) J(|r-t|)\, \mathrm{d}t. \tag{3.8}$$

Differentiation of (3.8) gives

$$rh(r) = -q'(r) + 12\eta \int_0^1 (r-t) h(|r-t|) q(t)\, \mathrm{d}t \tag{3.9}$$

whence one may deduce

$$h(1+) - h(1-) = q'(1-) = \tfrac{1}{2}(2+\eta)(1-\eta)^{-2} \tag{3.10}$$

and a similar discontinuity in each $h^{(n)}(r)$ at $r = n+1$. We now show that the asymptotic form of the residue series in equation (3.7) gives precisely this discontinuity.

Using equation (3.5, 6) the equation for the k_n may be written

$$\hat{Q}(k) = 1 - \frac{\exp(ik)}{\mu k^2} - \frac{i\exp(ik)}{\mu k^3} + \frac{6i}{\lambda k} - \frac{18}{k^2\lambda^2} + \frac{2i}{\mu k^3} = 0 \tag{3.11}$$

where

$$\mu = \frac{(1-\eta)^2}{6\eta(2+\eta)}; \qquad \lambda = \frac{1-\eta}{\eta}. \tag{3.12}$$

Asymptotic expansions for roots of (3.11) appear to be best calculated by writing

$$k_n = k_{n,0} + k_n \tag{3.13}$$

where $k_{n,0}$ are solutions of

$$\mu k_0^2 = \exp(ik_0). \tag{3.14}$$

This procedure yields

$$k_n = k_{n,0} + \frac{6-\lambda}{\lambda k_{n,0}} + \frac{i(5/2\lambda - 12)}{k_{n,0}^2} + O[(\ln n/n)^3] \tag{3.15}$$

where

$$k_{n,0} = 2n\pi\left[1 - \frac{\ln(2n\pi\sqrt{\mu})}{n^2\pi^2}\left(1 - \frac{\frac{1}{3}\ln^2(2n\pi\sqrt{\mu}) - \frac{3}{2}\ln(2n\pi\sqrt{\mu}) + 1}{n^2\pi^2}\right)\right]$$
$$- 2i\ln(2n\pi\sqrt{\mu})\left(1 + \frac{\frac{1}{2}\ln(2n\pi\sqrt{\mu}) - 1}{n^2\pi^2}\right) \tag{3.16}$$

for the roots of $\hat{Q}(k) = 0$ for which $\text{Re}(k) > 0$. If k_n is a root, then so is $-k_n^*$.

As for the one-dimensional system, we introduce $J_A(r)$ by

$$12\eta J_A(r) = -i\sum_{n=1}^{\infty}\{\exp(-ik_{n,A}r)[\hat{Q}'_A(k_n)\hat{Q}_A(-k_n)]^{-1}$$
$$+ \exp(ik_{n,A}^*r[\hat{Q}'_A(-k_n^*)\hat{Q}_A(k_n^*)]^{-1}\}. \tag{3.17}$$

Fairly simple manipulations with equation (3.11) show that

$$\hat{Q}'_A(k_n)\hat{Q}_A(-k_n) = -i[1 + O(k_n^{-1})] \tag{3.18}$$

and we use the asymptotic form

$$k_{n,A} = 2n\pi - 2i\ln(2n\pi\sqrt{\mu}). \tag{3.19}$$

These equations then give

$$12\eta J_A(r) = 2\sum_{n=1}^{\infty}(4n^2\pi^2\mu)^{-r}\cos 2n\pi r. \tag{3.20}$$

This is continuous at $r = 1$, as it should be. But, using $rh_A(r) = -J'_A(r)$ we obtain, on differentiating equation (3.20), letting $r \to 1+$, $1-$ and using equation (2.21) again

$$h_A(1+) - h_A(1-) = \tfrac{1}{2}(2+\eta)(1-\eta)^{-2} \tag{3.21}$$

This is exactly the discontinuity in $h(r)$ noted in equation (3.10).

In table 2 we list exact values for the real and imaginary parts of k_1 (Perry and Throop 1972) and the values of k_1, k_3 and k_5 calculated from equations (3.15; 3.16) for various values of η.

Table 2. Exact and asymptotic values of $\mathrm{Re}(k_1)$ and $\mathrm{Im}(k_1)$ for the hard-sphere system for a range of values of ρR^3, R = hard sphere diameter.

ρR^3	Exact $\mathrm{Re}(k_1)$	$-$Exact $\mathrm{Im}(k_1)$	Asymptotic $\mathrm{Re}(k_1)$	$-$Asymptotic $\mathrm{Im} k_1$
0·1	4·7608	4·0715	4·795	4·065
0·2	5·1156	3·0934	5·1487	3·1197
0·3	5·3982	2·4865	5·427	2·520
0·4	5·6507	2·0338	5·676	2·064
0·5	5·8887	1·6674	5·914	1·688
0·6	6·1204	1·3576	6·148	1·369
0·7	6·3506	1·0894	6·384	1·077
0·8	6·5828	0·8549	6·626	0·818

4. Discussion

A feature of the data presented in tables 1 and 2 is the accuracy of the asymptotic expansions used, even for the poles closest to the origin. Comparison of the exact and asymptotic values of k_1 for hard spheres in three dimensions shows that the asymptotic

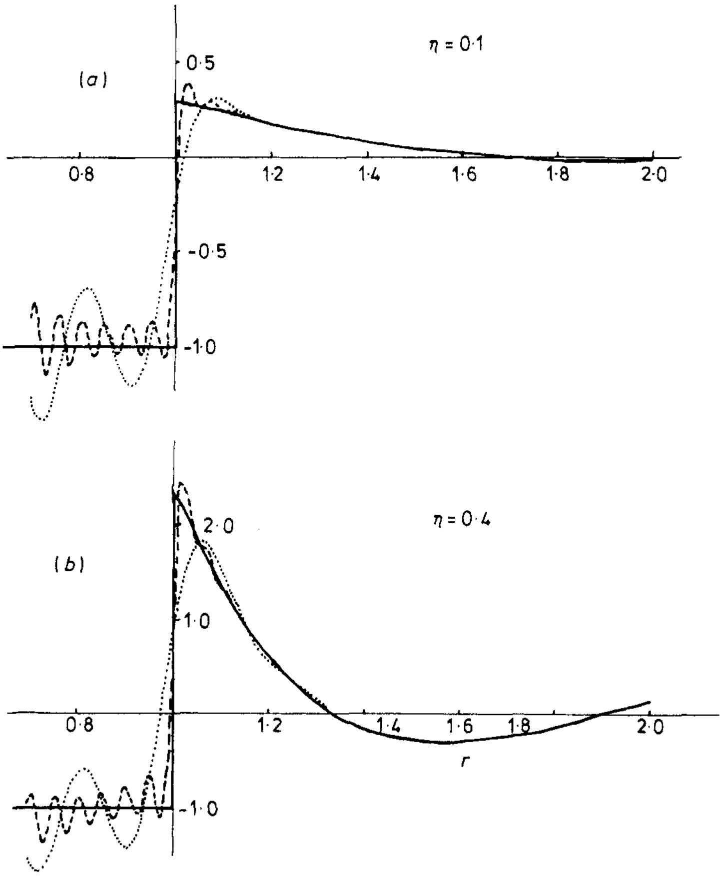

Figure 1. Plot of exact $h(r)$ and $h(r)$ from five poles and twenty poles for $\eta = 0{\cdot}1$ and $0{\cdot}4$, curve, exact results; broken curve, 20 poles; dotted curve 5 poles.

$\mathrm{Re}(k_1)$ is in error by less than 1% for the densities tabulated. The error in $\mathrm{Im}(k_1)$ is less than 4% for the densities tabulated. The error in more distant poles can be expected to be much less, as is shown in table 1 for the one-dimensional hard-rod system.

While an efficient algorithm (Perram 1975) exists for calculating $h(r)$ for the models studied in this paper, this is not true for other more complicated systems. In this paper we have shown how the discontinuous part of $h(r)$ may be derived from a knowledge of the leading term of the zeros of $\hat{Q}(k)$. This suggests that $h(r)$ may be approximately represented as a sum of the discontinuous $h_A(r)$ introduced in §§ 2 and 3 plus a contribution from a small number of poles of $\hat{h}(k)$ which are close to the origin. Alternatively, we may approximate $h(r)$ using a finite number of poles. In figure 1 we plot $h(r)$ exactly and from 5 and 20 poles for $\eta = 0{\cdot}1$ and $\eta = 0{\cdot}4$. It may be seen that for $r > 1{\cdot}2$, the five-pole form is very accurate while the twenty-pole form is accurate for $r > 1{\cdot}1$. For $r < 1$ the pole expansion is inaccurate, reflecting problems with Gibbs' phenomenon. The whole pole series is necessary to give the discontinuity at $r = 1{\cdot}0$ accurately.

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