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Role of the poles in determining the structure factor of a simple fluid

P T Cummings†§ and J W Perram‡||

† Departments of Mechanical Engineering and Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794, USA

‡ Department of Mechanical Engineering, State University of New York at Stony Brook, Stony Brook, New York 11794, USA

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Abstract. An earlier study of the role of the poles of the function $\hat{h}(k)$ in determining details of its inverse Fourier transform $h(r)$, the total correlation function of the hard sphere fluid, is extended to a consideration of their role in determining the details of the structure factor.

In an earlier paper, Perram and Smith (1980) considered the poles of the function $\hat{h}(k)$, the three-dimensional Fourier transform of the total correlation function $h(r)$ for the hard sphere fluid (HSF) at number density ρ . This function is related to the radial distribution function $g(r)$ (proportional to the probability density of finding the two particles in the fluid separated by distance r) for the HSF by $h(r) = g(r) - 1$. The function $\hat{h}(k)$ has an infinite number of poles in the upper-half complex k -plane, and if we denote the n th pole by $k_n = \lambda_n + i\mu_n$, then symmetry dictates that poles also exist at $\lambda_n - i\mu_n$, $-\lambda_n + i\mu_n$ and $-\lambda_n - i\mu_n$. The large- r asymptotic form of $h(r)$ is clearly given by $\exp(-\mu_1 r) \cos(\lambda_1 r)/r$, and we note that λ_n and μ_n are functions of ρ . Perram and Smith derived a large- n asymptotic formula to describe accurately $\lambda_n + i\mu_n$ for the HSF in the Percus–Yevick (PY) approximation (Percus and Yevick 1958), as well as the corresponding quantities for the hard rod fluid (the one-dimensional analogue of the hard sphere fluid).

It is straightforward to see that

$$h(r) = \sum_{n=1}^{\infty} A_n \frac{\exp(-\mu_n r)}{r} \cos \lambda_n r \quad (1)$$

where A_n is related to the sum of the residues of $\hat{h}(k)$ at $k = \lambda_n + i\mu_n$ and $k = -\lambda_n + i\mu_n$. Perram and Smith examined the role of the poles k_n in determining $h(r)$ by considering the truncated series

$$h_N(r) = \sum_{n=1}^N A_n \frac{\exp(-\mu_n r)}{r} \cos \lambda_n r. \quad (2)$$

Although $h(r)$ is represented accurately for $r \geq 1.2\sigma$, where σ is the hard sphere diameter, for quite small N (depending on the density ρ), $h(r)$ is poorly represented

§ Present address: Department of Chemical Engineering, Thornton Hall, University of Virginia, Charlottesville, Virginia 22901, USA.

|| Permanent address: Matematisk Institut, Odense Universitet, DK 5230 Odense, Denmark.

in the vicinity of $r = \sigma$ for any finite N . This is because $h(r)$ is discontinuous at $r = \sigma$, and is constant ($= -1$) for $r < \sigma$. In fact, Perram and Smith demonstrate that, by taking the limit $N \rightarrow \infty$ in (2) and using their asymptotic formula for the k_n , the discontinuity in $h(r)$ at $r = \sigma$ is correctly obtained.

This present paper is complementary to the earlier Perram and Smith paper in that we focus on the structure factor $S(k)$ given by

$$S(k) = 1 + \rho \hat{h}(k) \tag{3}$$

and examine the role of the poles in determining it. Experimentally, one measures $S(k)$ for real k only, whereas the mathematical expression (3) is valid for any complex k . The remarkable feature of the poles in relation to $S(k)$ is shown in figure 1, where

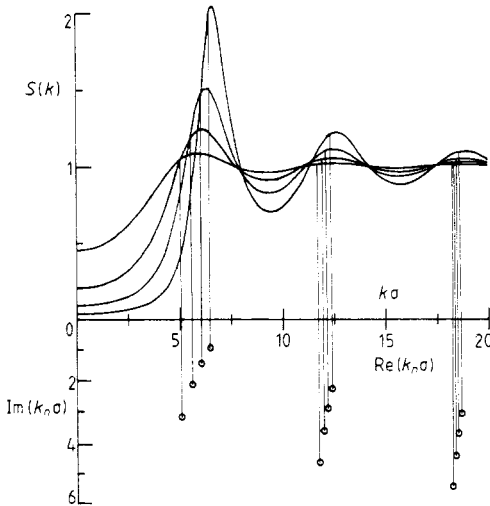


Figure 1. In the bottom half of the figure, the first three poles of $\hat{h}(k)$ for the HSF in the PY approximation are shown as circles. The four sets of poles correspond to densities $\eta = 0.1, 0.2, 0.3$ and 0.4 . As η increases, the poles move closer to the real- k axis. Also shown is the structure factor $S(k)$ at the corresponding densities. The correlation between $\text{Re}(k_n)$, where k_n is the n th pole of $h(k)$, and the position of the n th peak in $S(k)$ is indicated by drawing vertical lines $k = \text{Re}(k_n)$, $n = 1, 2, 3$ from the poles to $S(k)$ at the same density.

the structure factor $S(k)$ is shown for the HSF at a selection of densities, and the $\lambda_n + i\mu_n$ are shown for $n = 1, 2, 3$. (The results displayed in the figures are given in terms of the dimensionless density $\eta = (\pi/6)\rho\sigma^3$.) There is a strong and clear correlation between $\lambda_n = \text{Re}(k_n)$ and k_n^{max} , the position of the n th peak in $S(k)$. In fact, $\lambda_n \cong k_n^{\text{max}}$, with the agreement improving as the density increases. Since $\hat{h}(k)$ is a holomorphic function of the complex variable k (see Copson 1935), the Cauchy-Riemann equations imply that a turning point (maximum or minimum) in the plane $\text{Im}(k) = 0$ corresponds to a saddle point in the complex k -plane. Thus, the peaks in $S(k)$ for real k are saddle points; this is confirmed in figures 2 to 4 which illustrate $|S(k)|$, $\text{Re}(S(k))$ and $\text{Im}(S(k))$ for density $\eta = 0.4$.

This observation, although very simple and to some extent obvious once pointed out, has not (apparently) been noted previously. It proves to be an illuminating observation since we believe that it explains to some extent the well known insensitivity

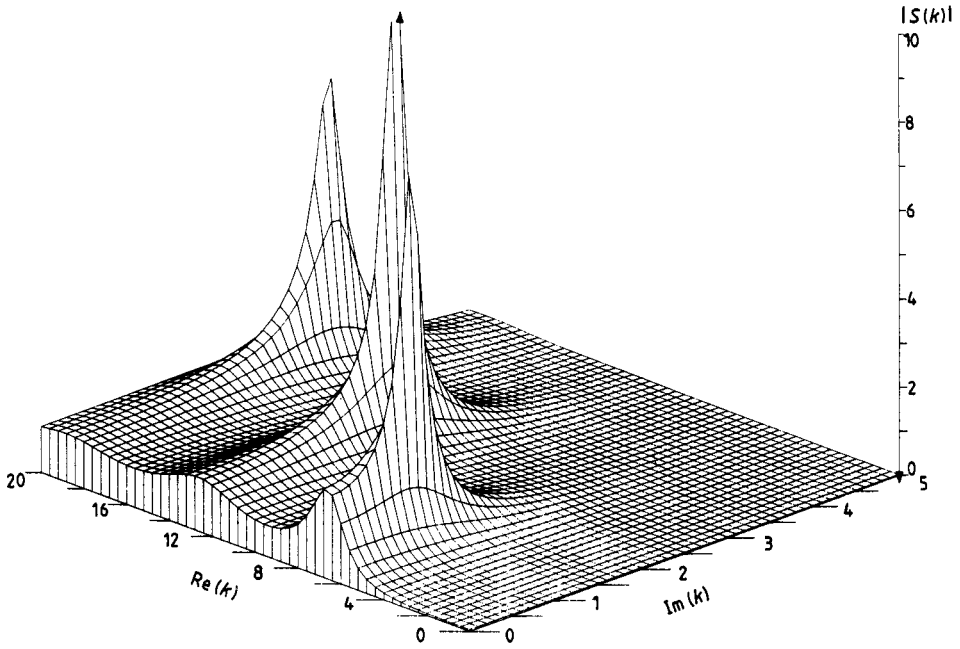


Figure 2. The function $|S(k)|$ for the HSF in the PY approximation at $\eta = 0.4$ as a function of complex k . Along $Re(k)$, $|S(k)|$ reduces to the usual structure factor, since the latter is measured experimentally for real k only and is itself real.

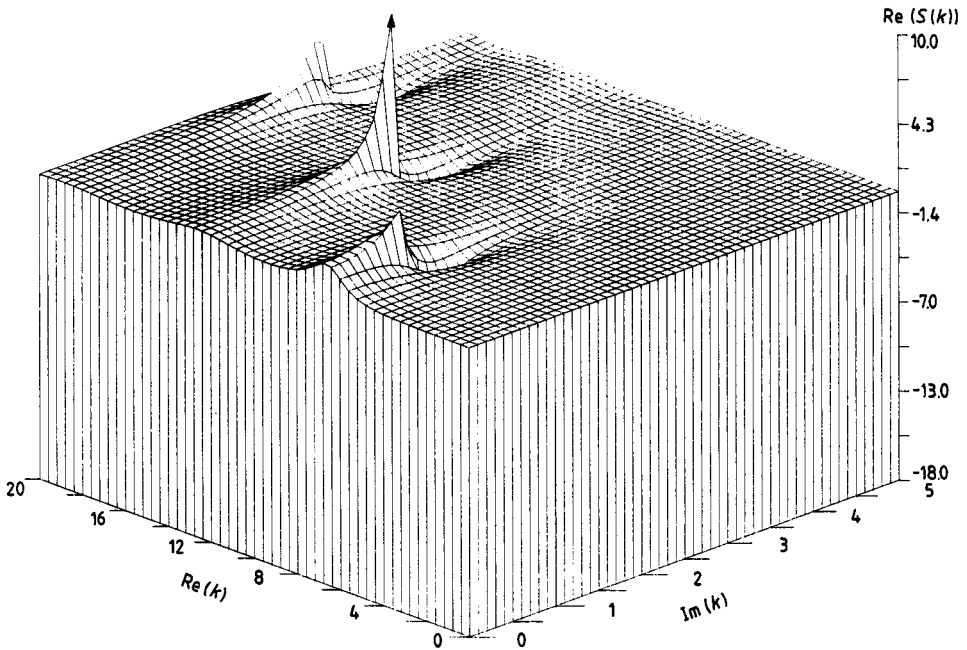


Figure 3. The function $Re(S(k))$ for the HSF in the PY approximation at $\eta = 0.4$ as a function of complex k . Along $Re(k)$, $Re(S(k))$ reduces to the usual structure factor.

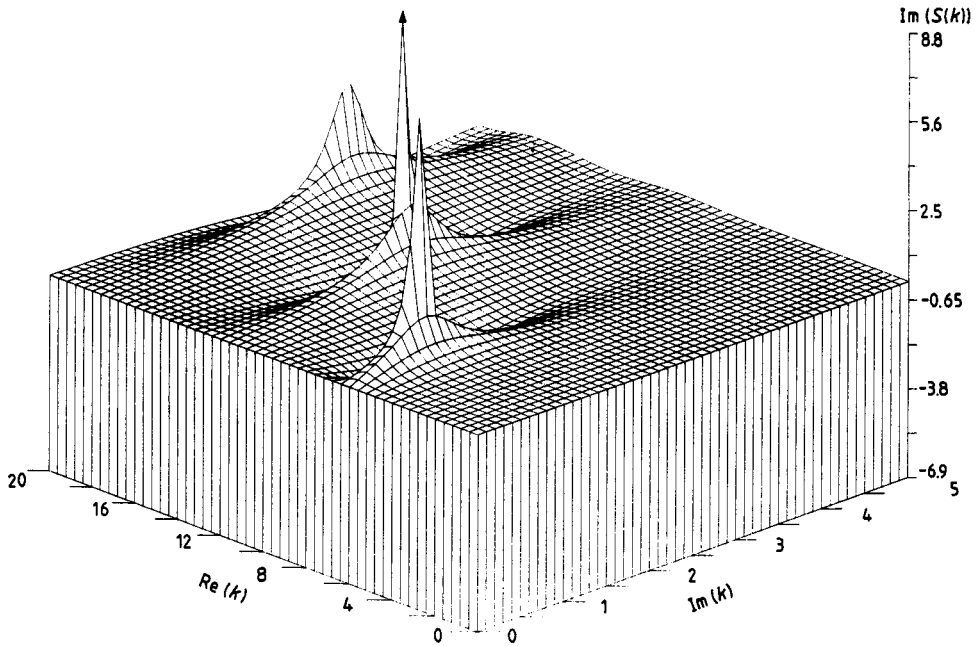


Figure 4. The function $\text{Im}(S(k))$ for the HSF in the PY approximation at $\eta = 0.4$ as a function of complex k . Along both $\text{Re}(k)$ and $\text{Im}(k)$, $\text{Im}(S(k))$ is zero.

of $S(k)$ to details of the potential except in the vicinity of the critical point (where $S(k) \rightarrow \infty$ at $k = 0$). Let us consider a pair potential $u(r)$ with the property

$$u(r) = u_0(r) + u_1(r) \quad (4)$$

where $u_0(r)$ can be thought of as the harsh repulsive part of the potential and $u_1(r)$ the attractive part. (Several prescriptions for the split up of $u(r)$ are presently in use—see Hansen and McDonald 1976.) The poles in $\hat{h}(k)$ for a potential of the form (4) can be considered as having their genesis either in $u_0(r)$ or $u_1(r)$. The identification of the poles related to $u_0(r)$ can be achieved by calculating $S(k)$ for a fluid interacting with potential $u_0(r)$ only: these poles will be similar in position to the HSF poles described above, will be weak functions of temperatures and will depend on ρ in much the same way that the k_n depend on ρ for the HSF.

Among the poles which can be attributed to the attractive part of the potential $u_1(r)$, the key pole is the one which lies along the imaginary axis (see, for example, Stell 1969 and Perram 1983). It is this pole that causes the divergence of $S(k)$ at $k = 0$ at the critical point, since it migrates towards the origin as the fluid approaches the critical point. (This pole occurs roughly at $i\kappa$, where κ is the inverse correlation length that appears in the scaling form of $h(r)$ in the near vicinity of the critical point, and the approach of κ to 0 is described by the critical exponents ε and ν along the critical isotherm and isochore respectively. See, for example, Stell (1969) for a discussion of these exponents.) Thus, provided one is far enough from the critical point that $\kappa > \mu_n$, and at sufficiently high density that the HSF-like poles are close to the real- k axis, then $S(k)$ is seen to be dominated by these HSF-like poles.

The central role of the poles of $\hat{h}(k)$ in determining $S(k)$ suggests that methods of solution of the PY approximation relying on truncated expansions of the form (2)

(Perram 1983) are likely to require quite small values of N to determine $S(k)$ accurately. Conversely, if $h(r)$ contains a substantial discontinuity, $h(r)$ can be expected to be less well represented by such a truncated expansion. (In reference to the practicality of this method of solution of the PY approximation, it is worth noting that the poles reported earlier (Perram and Smith 1980) for the HSF were obtained by a complex Newton–Raphson technique. Using the asymptotic formulae of Perram and Smith (1980) for λ_n and μ_n as the initial guess, the poles are located in at most five iterates for small n , reducing to two iterates for large n . Computations of λ_n and μ_n for n up to 300 have been performed for various densities using this method.)

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