

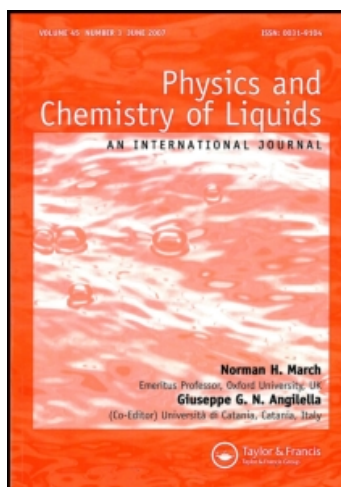
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A New Approach to Study Structure-Force Relations in Liquids

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We have used established relations between a probability density, expressed as a sum of positive integrable functions, to its characteristic function, which must consequently be given by a sum of functions of positive type, to study the asymptotic behaviour—in the limit $k \rightarrow 0$ —of the structure factors of liquids $S(k)$. We have illustrated this new approach by choosing examples for which the asymptotic behavior of $S(k)$ has been obtained using other methods.

We also discuss the suitability of this novel technique to study the relationship between structure and the, implicitly assumed, forces in the Structural Diffusion model.

1 INTRODUCTION

Classical theories of liquids take for granted the existence of well defined potentials of intermolecular interaction, valid within some range of thermodynamic parameters, and consider as their major goal to provide workable functional relations between potentials and molecular correlations. Such an approach has been successfully pursued for a variety of simple ionic and non-ionic liquids for which the potentials may be thought of as reasonably well understood.

Moreover, when the assumption of pairwise additivity of the affective interactions is justified, some precise information about the pair

potential may be obtained by examining the asymptotic behavior of pair correlations.¹ The quantity directly accessible to measurement is the structure factor $S(k)$, and its asymptotic behavior is directly related to that of the radial distribution function $g(r)$. Here asymptotic behavior means the functional form these functions adopt as the limits k (or r) tending to either zero or infinity are taken. It is now generally accepted that these limits convey important information about the forces *provided* that only the assumed pair interaction determines its behavior.

The most successful approach to study the asymptotic behaviour of $S(k)$ is due to Enderby *et al.*² Their work assumes that the Ornstein-Zernike direct correlation function $C(r)$ tends asymptotically to the potential, viz.

$$C(r) \simeq -\beta\phi(r) \quad \text{as } r \rightarrow \infty \quad (1.1)$$

with $\beta \equiv (k_B T)^{-1}$. Replacing (1.1) in the Ornstein-Zernike equation, the method of asymptotic estimates of Fourier transforms³ leads to a number of fruitful relations for the small k -behavior of $S(k)$ and its derivatives.⁴ Alternatively the same results follow by using the same method together with the asymptotic behavior of $g(r)$ ⁵

$$g(r) - 1 \simeq k_B T n^2 K_T \phi(r) + 0[\phi(r)]^2 \quad \text{as } r \rightarrow \infty \quad (1.2)$$

where n is the number density and K_T the isothermal compressibility of the liquid.

The above results have been obtained by following well established procedures which make use of the explicit relationships between structure and forces characterizing the radial distribution theories of liquids.

There is, however, another class of approximate theories of liquids which become very useful when the forces are not known. These may be broadly referred to as quasi-crystalline models, of which we shall be mainly concerned with the Structural Diffusion Model (SDM).⁶ In these models the forces are only implicitly accounted for by the local structure which they impose. This local structure is assumed to be a lattice in the broadest sense of the word and need not be restricted to a crystalline structure.⁷ Recent developments suggest that, using generalized local lattices, the SDM may be useful in studying the structure of amorphous systems.⁷

The extended SDM indicates it is possible to represent $S(k)$ generally as a sum of positive terms,

$$S(k) = \sum_v S_v(k), \quad S_v(k) \geq 0 \quad \text{for all } v, k \quad (1.3)$$

This form may be regarded as a generalization of the stability condition which for isotropic systems has the form⁸

$$S(k) \geq 0 \quad \text{for all } k \quad (1.4)$$

The inequality follows from the definition

$$S(k) = \frac{\langle |n_k|^2 \rangle}{n} \quad (1.5)$$

where n_k is the k th-Fourier component of $\Delta n(r) = n(r) - n$ where $n(r)$ is the local number density and the angular brackets denote an ensemble average.

Given (1.3), it is possible to exploit a theorem relating a probability distribution to its characteristic function.⁹ This enables us to obtain $g(r)$ explicitly via a sum of functions, $F_v(r)$, of positive type.

Returning to the SDM, each term in (1.3) has an explicit form related to the local structure of the liquid. In addition, the asymptotic form of (1.3) can be obtained directly so as to give us information on the forces which are implied by the local structure.

This work attempts to address some aspects of the problem of the structure-forces relations. By exploiting techniques hitherto not used in this context, we wish to draw attention to certain mathematical properties implied by (1.3). We believe that these could be advantageously used in the analysis of structural data and the construction of theoretical representations thereof.

In Section 2 we present the basic definitions and results. In the first part of Section 3 we present a few illustrative examples using the techniques referred to above, which allow us to cross-check that we recover the known results on the asymptotic behaviour of $S(k)$ obtained by using the more conventional analysis. In the second part of Section 3 we discuss the relevance of this technique to provide further insights in the understanding of the asymptotic behaviour of $S(k)$ in the SDM. We complete the paper with a brief discussion of our results.

2 THE STRUCTURE FACTOR REGARDED AS A SUM OF DISTRIBUTIONS

2.1 Distributions and characteristic functions

We introduce below some results from the theory of probability concerned with characteristic functions we shall need in this work. We refer the reader to Chapters 7 and 9 of Gnedenko's book⁹ for a general presentation based on the notion of a probability distribution $F(x)$. In

one dimension this is a nondecreasing function having the boundary value $F(-\infty) = 0$ and satisfying

$$\int dF(x) = 1 \quad (2.1)$$

Henceforth we adopt the more conventional custom used in physics of introducing a positive probability density $p(x)$ via $dF(x) = p(x) dx$, defined for every x , with the understanding that at a point where $F(x)$ experiences a finite jump, $p(x)$ is proportional to a Dirac delta function, $\delta(x)$. In addition we relax condition (2.1) and require only that $p(x)$ is integrable, i.e. that its integral over the entire space is finite,

$$\int p(x) dx < \infty \quad (2.1')$$

in which case $p(x)$ can always be normalized to give the value one for the integral in (2.1').

The characteristic function of a probability distribution $F(x)$ (or for a probability density $p(x)$) is defined by

$$f(t) = \int e^{itx} dF(x) = \int e^{itx} p(x) dx \quad (2.3)$$

This function has the following properties:

- i) is a continuous function of the real argument t ;
- ii) for any set of real numbers t_1, \dots, t_n and complex numbers ξ_1, \dots, ξ_n

$$\sum_{j,k=1}^n f(t_k - t_j) \xi_j^* \xi_k \geq 0 \quad (2.3)$$

A function $f(t)$, defined in the interval $-\infty < t < \infty$, satisfying properties (i) and (ii) is called⁹ a 'positive semi-definite function' or a 'function of positive type'. These properties are satisfied by $f(t)$, as defined in (2.2), irrespective of the 'normalization condition' (2.1).

2.2 Pair distributions in terms of characteristic functions

The Fourier transform of $S(k)$ is related to a pair correlation function $F(r)$ defined by

$$F(r) = \delta(r) + nh(r) \quad (2.4)$$

Here $h(r) = g(r) - 1$ is the total correlation function, while the presence of Dirac's δ -function indicates the inclusion of the self-correlation term. This is consistent with the Meyer-bond fugacity expansion of the total

correlation function, a representation which has been used to define pair and higher order correlation functions³ as well as pair and higher order structure factors.¹⁰

The structure factor is now given by

$$S(k) = \int F(r)e^{ik \cdot r} dr \quad (2.5)$$

and, conversely,

$$F(r) = \frac{1}{(2\pi)^3} \int S(k)e^{-ik \cdot r} dk \quad (2.6)$$

Since as stated in Section 1, $S(k)$ is positive, it is tempting to view it as a probability density and hence have $F(r)$ as a positive semi definite function. However $S(k)$ does not fulfil the requirement of integrability (2.1'), for—given (2.5)—we have

$$\int S(k) dk = (2\pi)^3 F(0)$$

and by (2.4) this integral diverges.

However if $S(k)$ can be represented as a sum of positive integrable functions, viz.

$$S(k) = \sum_v S_v(k) \quad (2.7)$$

such that $S_v(k) > 0$ and $\int S_v(k) dk = \text{finite}$, all the conditions for $S(k)$ to be a probability density are satisfied. Whence $F(r)$ is a sum of positive semi definite functions

$$F(r) = \sum_v F_v(r) \quad (2.8)$$

with

$$F_v(r) = \frac{1}{(2\pi)^3} \int S_v(k)e^{ik \cdot r} dk \quad (2.9)$$

Note that we must have always

$$F_v(0) > 0, |F_v(r)| \leq F_v(0)$$

and, since $F(r)$ contains a $\delta(r)$ function, $\sum_v F_v(0)$ diverges.

There are two main reasons why we have chosen $S(k)$ to be a sum of distributions, as given by Eq. (2.7). The first is that we are now in a position to take full advantage of these properties of distribution laws outlined in the preceding subsection. The second is that such a

representation is the most convenient to study the asymptotic behaviour of $S(k)$ in its relation to the SDM. Indeed, as we have indicated in the Introduction, our approach has been largely suggested and motivated by the latter.

3 ASYMPTOTIC BEHAVIOUR OF $S(k)$ AND THE SDM

3.1 Illustrative examples

We present below three examples which illustrate the use of the approach discussed in the preceding section. We must stress that the results we obtain are not asymptotic; for each assumed $F_v(r)$ there is a corresponding probability density $S_v(k)$. Each term in the sum (2.7) satisfies the same distribution law. The advantage of considering the asymptotic behaviour of $S(k)$, namely that of taking the limit $k \rightarrow \infty$, is that comparison can be made with results obtained using different methods, and also—via those results—to the relationship between the asymptotic behaviour of $S(k)$ and the affective pair potential $\phi(r)$.

Example I Assume

$$F_v(r) = C_v e^{-\lambda_v r} \quad (3.1)$$

Using (2.5)

$$S_v(k) = \frac{8\pi\lambda_v}{(\lambda_v^2 + k^2)^2} \quad (3.2)$$

On taking the limit $k \rightarrow 0$ it follows from Eq. (3.2) that $S_v(k)$ may be written as an expansion in even powers of k , which has been referred to as the analytic expansion of $S(k)$.⁴ Moreover this asymptotic behaviour of $S(k)$ corresponds to the case when the potential $\phi(r) \rightarrow 0$ as $r \rightarrow \infty$ faster than any power r^{-n} , $n > 3$.⁴

Example II Assume

$$F_v(r) = C_v e^{-\lambda_v r} \frac{\sin b_v r}{b_v r} \quad (3.3)$$

and, using (2.5)

$$S_v(k) = C_v \frac{8\pi\lambda_v}{[\lambda_v^2 + (b_v - k)^2][\lambda_v^2 + (b_v + k)^2]} \quad (3.4)$$

This example differs from the first by the addition of the $\sin b_v r/b_v r$ term, and was investigated by Verlet¹¹ in the context of his molecular

dynamics studies of a Lennard-Jones fluid. However, on taking the limit $k \rightarrow 0$, the asymptotic behaviour of $S(k)$ may also be written as an expansion in even powers of k . This result, in agreement with other studies,⁴ shows that all that is required to obtain the correct small k -behaviour of $S(k)$ are the asymptotes of the total correlation function of large r ; the damped oscillations will contribute to the coefficients of the expansion but not its functional form. Whence the pair potential $\phi(r)$ giving rise to the asymptotic behaviour deduced from (3.4) must also asymptotically vanish, at large r , faster than r^{-n} ($n > 3$).

Example III Here we assume

$$F_v(r) = \frac{\lambda_v^{2\alpha}}{(\lambda_v^2 + r^2)^\alpha}; \quad \alpha > 1 \quad (3.5)$$

Setting $\alpha \equiv \frac{\sigma + 3}{2}$, and integrating (2.5) by parts, we obtain

$$S_v(k) = 2\pi\lambda_v^{\sigma/2+3} \frac{\pi}{\Gamma\left(\frac{\sigma+3}{2}\right)} \left(\frac{k}{2}\right)^{\sigma/2} K_{\sigma/2}(\lambda_v k) \quad (3.6)$$

where $\Gamma(\alpha)$ is the Gamma function and $K_\nu(z)$ the modified Bessel function of the second kind.¹²

The asymptotic limit, $k \rightarrow 0$, deduced from Eq. (3.6), gives $S(k) \sim |k|^\sigma$. The same result arises whenever the assumed effective pair potential behaves like $\phi(r) \sim 1/r^{3+\sigma}$, as $r \rightarrow \infty$, for any positive, odd integer or non-integer σ .⁴

The extension of this example to one which also includes damped oscillations is straightforward. In the analysis of the asymptotic behaviour of $S(k)$ of the above examples two basic assumptions have been made. The first concerns $S_v(k)$ itself. Strictly we have only looked at the asymptotic behaviour of $S_v(k)$, a generic term in the sum given by Eq. (2.7). Here we are assuming that, since each term in the sum has the same functional form and that, hopefully, the terms in the sum belong to a rapidly converging sequence of positive integrable functions, the asymptotic behaviour pertaining to some generic $S_v(k)$ is also that of $S(k)$. The second assumption concerns the relationship between the asymptotic behaviour of $S(k)$ and the effective pair potential which is likely to produce it. The implication here is that the asymptotic behaviour is *solely* determined by $\phi(r)$. This is a problem which goes beyond the specific technique used herein to derive the results shown in the three examples presented in this subsection; we shall return to this point in the concluding section of this work.

3.2 The structural diffusion model (SDM)

In the SDM the local structure parameters which define the local lattice structure are viewed as random functions of space coordinates.⁶ The correlation between a pair of such parameters, spatially separated, are given in terms of Fokker–Planck type of equations leading to expressions for the total correlation function—via Eq. (2.8)—of the form

$$F_v(r) = C_v e^{-b_v^2 W(r)} \frac{\sin b_v r}{b_v r} \quad (3.7)$$

where the b_v 's ($0 < b_1 < b_2, \dots$) denote position vectors of points in the reciprocal lattice, while the width function $W(r)$ is required to satisfy the conditions

$$W(r) \sim Dr \quad \text{as } r \rightarrow \infty \quad (3.8)$$

and

$$W(r) \rightarrow 0 \quad \text{as } r \rightarrow 0$$

In the case of the SDM it may be assumed that the dominant term in Eq. (2.8)—insofar as we are concerned with the asymptotic, $r \rightarrow \infty$, limit of $F(r)$ —is given by

$$F(r) \sim F_1(r) = C_1 e^{-Db_1 r^2} \frac{\sin b_1 r}{b_1 r} \quad \text{as } r \rightarrow \infty \quad (3.9)$$

This result is the same as that discussed in Example II. Hence the small k -behaviour of $S(k)$ will be also described, in this case, by an expansion in even powers of k . There is, however, a problem when it comes to relate this behaviour to the effective pair potential in the fluid. As stated in Section I, within the SDM the forces are only implicitly accounted for by the local structure which they impose. In the low density limit this should lead to an asymptotic behaviour due solely by the forces, which is not necessarily that given in Eq. (3.9), a point which we are currently investigating. However at higher densities, say nearer to the melting point, the local lattice structure should contain information not only on the pair forces but also about collective effects in the liquid which, may in turn, modify the asymptotic behaviour of $F(r)$. Hence it is conceivable that Eq. (3.9), as it stands, is the asymptotic behaviour of $F(r)$ which results from combining the effects of the effective pair potentials and cooperative effects as they are sustained in the liquid state. We return to this point in the next section.

The asymptotic behaviour of $F(r)$, as $r \rightarrow \infty$, provides a useful insight of the class of functions we may choose for $W(r)$ within the SDM, subject to (3.8). In fact, given that $W(r) \simeq 0$ for some neighbourhood of

$r = 0$, say $r < r_0$, inside the unit cell of the reciprocal lattice, the SDM formula (3.7) reproduces the $\delta(r)$ part of $F(r)$, for

$$F(r) = n \sum_{\nu} \frac{\sin b_{\nu} \cdot r}{b_{\nu} \cdot r} = \begin{cases} 0 & \text{for } 0 < r < r_0 \\ \infty & \text{for } r = 0 \end{cases} \quad (3.10)$$

where the sum extends over all reciprocal lattice points.

The construction of width functions $W(r)$, subject to Eq. (3.8) and satisfying Eq. (3.10), requires that they are such that preserve the positive type property of $F_{\nu}(r)$. Amongst the range of possible choices, one inspired by Eq. (3.7) is that $e^{-\lambda W(r)}$ be of positive type for any positive λ . There are necessary and sufficient conditions which $W(r)$ has to satisfy for this to be so, and hence facilitate the choice of appropriate width functions. A further restriction may be imposed by requiring that, in the low density limit, the choice of $W(r)$ is compatible with the asymptotic $r \rightarrow 0$ (or $k \rightarrow \infty$) limit of $F(r)$ ($S(k)$).

4 DISCUSSION

We have used an existing relationship between a probability density, and its characteristic function to discuss a few examples which reproduce known results for the asymptotic behaviour of $S(k)$. These examples illustrate, in our view, the usefulness of the approach presented herein. The number of cases which could be studied is only limited to the ability of constructing the correct class of characteristic functions which also happen to have physical content. Moreover the theorems in probability theory which establish this relationship can be extended to the case of many variables. Hence it also appears to be a promising tool to study the asymptotic behaviour of higher-order structure factors on which, to our knowledge, very little work has been done.¹³

We have also been able, in the light of these results, to scrutinize the asymptotic behaviour of $S(k)$ within the SDM. In our view it is an important step towards relating the structure to the, implicitly assumed, forces in this theory. However in this work we had to stop short of actually relating the asymptotic behaviour of $S(k)$ in the SDM to effective pair potentials.

All the results relating to the asymptotic behaviour of $S(k)$ to forces are based on the assumption that it is solely determined by the assumed pair potential. However, even in systems where the validity of pairwise additivity of the potential could be sensibly assumed, the possibility of the presence of cooperative effects in the small k -regime of $S(k)$ cannot be ruled out. Yet there are no a priori rules prescribing how to separate

out these effects. In a recent work, March and Senatore¹⁴ have empirically assumed that $C(r)$, as $r \rightarrow \infty$, may be written as a sum due to the contribution of the 'potential part' and the 'cooperative part'. While this remains an interesting avenue to explore, such an assumption needs independent corroboration. One possibility, which we are currently exploring, is to find out how the asymptotic behaviour of $S(k)$ changes as the low and high density limits in the fluid are considered. For a simple system the former should be solely determined by the potential, in the latter cooperative effects may play a role. Varying $S(k)$ as a function of density naturally leads to question the role played by the higher correlation functions and finding out whether their asymptotic behaviour convey information on these effects. We believe that, within the approach presented here, such studies are possible.

Only when we have made sufficient progress in understanding the role played by cooperative effects in shaping the asymptotic behaviour of $S(k)$, we shall be in a position to take the final step in relating forces to structure in the SDM.

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