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Structure and Forces in Simple Liquid Metals

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This paper is based on the exact force equation for a classical monatomic liquid with pairwise interactions.

This is handled by expanding the triplet correlation function $g^{(3)}$ in Legendre polynomials to yield

$$g'(r) + g(r) \frac{\varphi'(r)}{k_B T} = - \frac{4\pi\rho}{3k_B T} \int_0^\infty s^2 \varphi'(s) Q_1(r, s) ds \quad (i)$$

where $g(r)$ is the radial distribution function, $\varphi(r)$ the pair potential, ρ is the number density, while Q_1 is the $l = 1$ term in the Legendre polynomial expansion of $g^{(3)}$.

From molecular dynamics data for some simple liquids, we have calculated the left-hand-side of Eq. (i). This has been used to draw some conclusions about the usefulness of the Kirkwood superposition approximation in extracting forces from structure. Used in the right way, the Kirkwood approximation yields a quantitative estimate of the three-body term in the force equation for Na, but is much less useful for argon.

1 INTRODUCTION

Since the work of Johnson and March,^{1,2} there has been a good deal of interest in whether it is possible, in a monatomic liquid, to invert the customary procedure of classical statistical mechanics, in which a pair potential $\varphi(r)$ is specified, and a radial distribution function $g(r)$ calculated from it, and to extract $\varphi(r)$ from the measured structure factors. This area was reviewed

some time ago by Enderby and March.³ Work was done on Lennard–Jones fluids by Krumhansl and Wang,⁴ employing molecular dynamics, and recent relevant work is that of Haymet *et al.*⁵ These workers devised a self consistent approach to the calculation of pair and triplet functions, but, in common with the work of Krumhansl and Wang, they have recently tested the above treatment at liquid state densities against new molecular dynamical results of the Lennard–Jones (12, 6) fluid. For high temperature, they find, by using a topological reduction of the diagrammatic expansion of the triplet correlation function appearing in the basic force equation (2.2) below, good agreement with the triplet function found from molecular dynamics.⁶ However, for lower densities, their approach is not in quantitative agreement with the molecular dynamics approach.

Although, independently, as a part of the programme of work reported in our present paper, we also studied the case of Lennard–Jones fluids, we shall only briefly refer to our own findings at the end of the paper, in view of the recent extensive work on this class of fluids. Rather, we shall focus attention on a simple liquid metal, Na, here, though it will be useful subsequently to compare and contrast the results with those for liquid argon.

Returning to the proposal of Johnson and March for extracting force laws from structure data, two points are now generally agreed by workers in the area:

i) It is essential that structure data is available over a wide range of momentum transfer q , the small angle scattering data being of primary importance in pinning down the more interesting long-range features of the pair potentials. This is still a difficulty, though Greenfield *et al.*⁷ have shown that the X-ray method on Na and K can make accurate small angle scattering data available; see also the very recent work of Waseda.⁸

ii) Related to the discussion of Lennard–Jones fluids above, but more generally now, great care is needed with the treatment of the three-particle distribution function. Thus, it is clear that, while the type of approximation made for this central quantity must take cognizance of the range of the forces, and is therefore certain to be different for liquid argon on the one hand, and liquid Na on the other, the non-critical use of, for instance, the Kirkwood superposition as closure, leading to the Born–Green theory of structure, must be transcended, at the present level of sophistication of liquid structure theories. Thus, for hard core-like interactions, with short-range tails, as in liquids like argon, the Born–Green theory of structure is poor, and we have now considerably more accurate structural theories.

The present work is a contribution essentially in the area (ii) above. Since we have the problem (i), we shall in the present paper mainly make use of computer experiments on simple liquids.

The outline of the paper is as follows. In Section 2 we outline the method of attack on the problem of what information can be gained about the triplet correlation function from molecular dynamics. As pointed out by Hutchinson,⁹ the force equation, which is our main tool here, involves only one term (the p or $l = 1$ component) in the expansion of the triplet function in Legendre polynomials (Eq. (2.3) below). Therefore it must not be expected that full information on the triplet function $g^{(3)}$ can be extracted by our procedure, which uses only $g(r)$ and $\varphi(r)$ as described below.

2 FORCE EQUATION IN TERMS OF p HARMONIC OF TRIPLET CORRELATION FUNCTION

If we introduce the potential of mean force $U(r)$ in a classical monatomic liquid through the relation

$$g(r) = \exp\left(\frac{-U(r)}{k_B T}\right) \quad (2.1)$$

then it is easy to write down the force equation as

$$-\frac{\partial U(r_{12})}{\partial \mathbf{r}_1} = -\frac{\partial \varphi(r_{12})}{\partial \mathbf{r}_1} - \rho \int \frac{\partial \varphi(r_{13})}{\partial \mathbf{r}_1} \frac{g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g(r_{12})} d\mathbf{r}_3 \quad (2.2)$$

where we can see that the first term on the right-hand side is the direct force between particles 1 and 2 separated by distance r_{12} while in the remaining term the force on particle 1 due to a particle at \mathbf{r}_3 is weighted by the probability that a particle is at \mathbf{r}_3 if there are certainly particles at \mathbf{r}_1 and \mathbf{r}_2 , namely $g^{(3)}/g(r_{12})$.

We stress that Eq. (2.2) is an exact member of the Born-Green-Yvon hierarchy, only dependent on the assumption of pairwise interactions. Following Hutchinson,⁹ we now write, with $r_{13} = s, r_{23} = t, r_{12} = r$, and with θ the angle between the vectors r_{13} and r_{12} ,

$$g^{(3)}(r, s, \theta) = \sum_{l=0}^{\infty} Q_l(r, s) P_l(\cos \theta) \quad (2.3)$$

and evidently, using the orthogonality properties of the Legendre polynomials, we obtain

$$Q_1(r, s) = \frac{3}{2} \int_0^\pi g^{(3)}(r, s, \theta) \cos \theta \sin \theta d\theta. \quad (2.4)$$

But it is now easy to show that the same orthogonality properties cut out all the terms in the triplet correlation function except the term with $l = 1$, to yield

$$g'(r) + \frac{g(r)}{k_B T} \varphi'(r) = -\frac{4\pi\rho}{3k_B T} \int_0^\infty s^2 \varphi'(s) Q_1(r, s) ds \quad (2.5)$$

This equation is the focal point of the present work; for convenience we define the left-hand side as $f(r)$, i.e.

$$f(r) = g'(r) + \frac{g(r)}{k_B T} \varphi'(r). \quad (2.6)$$

This is as far as we can get without either (a) analytical approximation to $g^{(3)}$, or in the form (2.5) to Q_1 , or (b) use of experimental data. As already mentioned, we shall use here not real experimental data but the results of computer experiments. The way we do this, and some results, are set out immediately below in Section 3.

3 USE OF MOLECULAR DYNAMICS DATA

The point we exploit here is that, whereas in an X-ray or neutron experiment we have available merely the structure factor $S(q)$, over a still limited range of q , and therefore, in principle, $g(r)$ by Fourier transform, in molecular dynamical simulation we have both the input force $-\varphi'(r)$ and by computer calculation the corresponding $g(r)$. Thus we can calculate the left-hand-side of Eq. (2.5), or using the definition (2.6) we can calculate the quantity $f_{MD}(r)$. Clearly, this information is giving us, at very least, from Eq. (2.5), a precise if limited way of testing approximations to $Q_1(r, s)$ in Eq. (2.5), and this is the point of view adopted below.

3.1 Use of molecular dynamical simulation results on liquid Na¹⁰

The potential of Taylor¹¹ has been used to calculate the curve in Figure 1 for the force $-\varphi'(r)$ along the connection line between two particles. For comparison, we have plotted the mean force $-U'(r)$ derived from the calculation of $g(r)$ with the Taylor potential, in the manner described below. The different points plotted for $-U'(r)$ are for two different truncation distances of the Taylor potential, the dots corresponding to a truncation of the force at 7.3 Å and the + signs to a distance of 10.03 Å. The curve for $\varphi'(r)$ and the results for $U'(r)$ are at first sight pretty similar, but there is more structure in the mean force than in the pair force. We emphasize that this situation is strictly for the model potential adopted; it is not proven that this is precisely the situation in liquid Na. The data are, specifically, for a density $\rho = 2.41 \cdot 10^{22} \text{ cm}^{-3}$ and for $T \simeq 400 \text{ K}$. The mean force $-U'(r)$ plotted is simply $k_B T \cdot g'(r)/g(r)$, the pair function $g(r)$ being that generated by the Taylor potential inserted into the molecular dynamics programme.

Figure 2 shows $f(r)$ defined in Eq. (2.6), calculated from the molecular dynamics data, the dots corresponding to data from the system with the

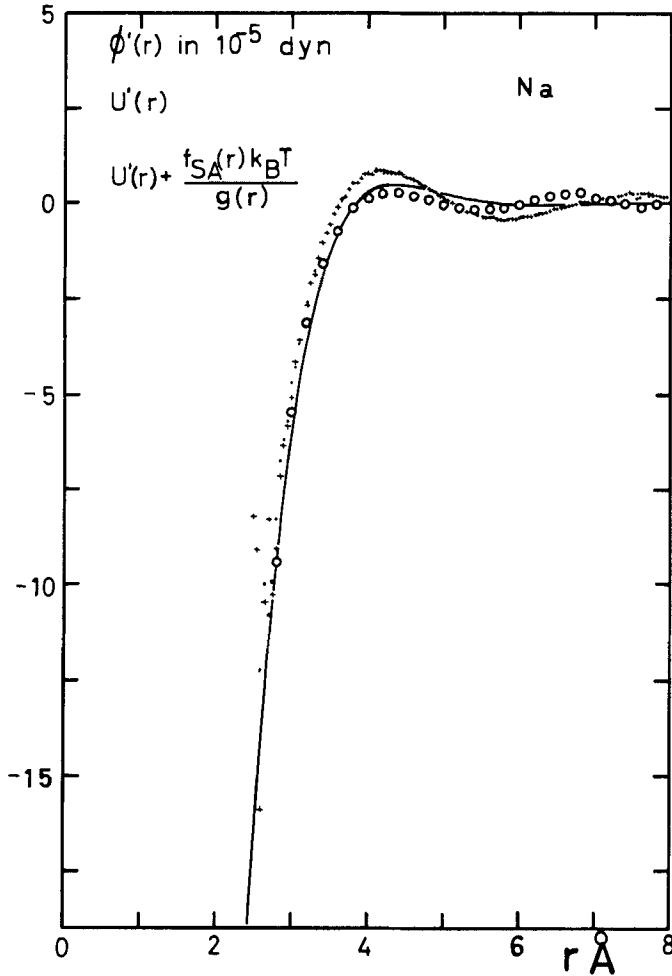


FIGURE 1 The pair force $\phi'(r)$ (—), the mean force $U'(r)$ (· and +) and the 'recovered' pair force (○) by the use of the Kirkwood approximation as described in the text for liquid 'computer sodium'. The pair distribution function has its main maximum at $r \approx 3.63 \text{ \AA}$ and the pair potential its main minimum at $r \approx 3.85 \text{ \AA}$. The data for $U'(r)$ show that the evaluation procedure for $g(r)$ and its first derivative in the small r -region could be improved.

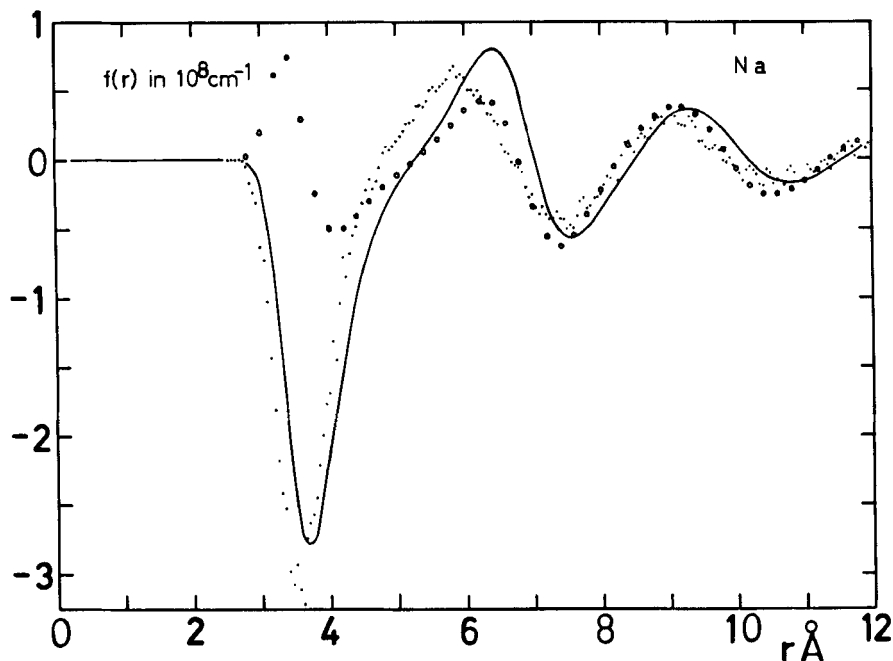


FIGURE 2. Comparison between $f_{MD}(r)$ (· · ·) and $f_{SA}(r)$ (—) for liquid 'computer sodium'. The curve indicated by the open circles is obtained by the use of the mean force $U'(r)$ instead of the pair force in the Kirkwood approximation!

truncation distance $r_c = 7.3 \text{ \AA}$. Beyond this distance $f(r)$ is obtained from the slope of the pair distribution function.

Evidently, there are pronounced features in this curve; a very deep minimum around 3.6 \AA followed by subsidiary maxima and minima.

For comparison, we have now computed the results when the Kirkwood approximation is adopted for $g^{(3)}$, it being understood however that the $g(r)$ used here is the 'exact' $g(r)$ of the molecular dynamics simulation.

The continuous line is calculated then from the approximation

$$f_{SA}(r) = -\frac{\pi\rho g(r)}{k_B T} \int_0^{r_c} g(s)\varphi'(s) \left\{ \int_{|r-s|}^{r+s} tg(t) \frac{r^2 + s^2 - t^2}{r^2} dt \right\} ds. \quad (3.1)$$

The main features of the $f(r)$ curve are clearly given by this approximation. The most serious error introduced is a phase shift, which causes all the maxima and minima to lie at rather too large r , the discrepancies in position being one or two tenths of an \AA . The first minimum is a little too shallow, and the first maximum a little too pronounced, so that the Kirkwood approximation, used

in the manner described above, overemphasizes the structure a little in the $f(r)$ curve.

The other point we feel is significant is the following one. In an actual calculation to try to extract the force law, as proposed in Refs. 1 and 2, one would use the 'exact', i.e. measured $g(r)$ in the Kirkwood decoupled $g^{(3)}$, exactly as we have done here. But one would, in the absence of exact knowledge of the pair potential have to put some trial form into the expression for $f(r)$. One obvious procedure is to put in the mean force derived directly from the experimental $g(r)$.

But the effect of doing this can be gauged from the present model of liquid Na. Thus in the curve marked by open circles in Figure 2 we have calculated $f_{SA}(r)$ with this one modification. The effect is dramatic. One finds now a totally different form of $f(r)$, which has practically a node at the position of the principal minimum of the true $f(r)$.

The final curve we have added to Figure 1 is the plot of $f_{SA}(r)k_B T/g(r) + U'(r)$, with $f_{SA}(r)$ calculated with exact model $g(r)$ and force law.

The conclusion is clearly that it is of vital importance in the three-body term to calculate it with a consistent $g(r)$ and force. If we take the potential of mean force, and the (inconsistent) model $g(r)$, huge errors are introduced.

Of course, we can ask the question: do we really know, in liquid Na metal, from the experimental facts, that the true pair force and the mean force differ by as much as is shown in Figure 1, with the Taylor potential. If we assume, for a moment, that the real force is significantly closer to the potential of mean force than in Figure 1, then Figure 2 makes it tempting to conclude that $f(r)$ may be substantially smaller in magnitude near 3.6 Å in real molten Na than with the Taylor potential.

So the question which remains would be: for real molten Na, do we know that the potential of mean force is *not* an almost self-consistent choice of pair potential. Of course, the potential of mean force, extracted from measured $g(r)$ data, will be temperature dependent. But we know that the liquid metal potential will depend on density, so is this effect merely reflecting the reduced density with increasing temperature?

What seems clear for the model we have studied is that, actually at the precise point of solution, the Kirkwood superposition for $g^{(3)}$, with the exact $g(r)$ as input data, and combined in the term in the force equation with the 'exactly consistent' pair potential, is leading for model liquid Na to a pretty useful result for the three-body term needed to extract the force. In order to see whether this is a situation which is specific to a simple liquid metal like Na, we have also carried out some calculations on liquid Ar. We shall not report these in the same detail as done for Na, as a large body of accurate work already exists for liquid argon, as summarized in the Introduction.

3.2 Summary of results for liquid argon

In the case of liquid argon, we made no attempt to use a particularly refined pair potential. The Lennard-Jones potential (12, 6) has been employed by Schofield and Hutchinson (private communication) to obtain the pair function $g(r)$ from molecular dynamics. The results correspond to a density of $0.0214 \text{ atoms}/\text{\AA}^3$ and a temperature of 87.2 K . The value of $f(r)$ given by the superposition approximation is represented by the continuous line in Figure 3, and is to be compared with the molecular dynamics results given by the crosses. It is immediately clear that the result of the superposition approximation is of much poorer quality for Ar than for Na, the molecular dynamics data revealing much more structure in $f(r)$ than is found for the model of liquid Na presented here.

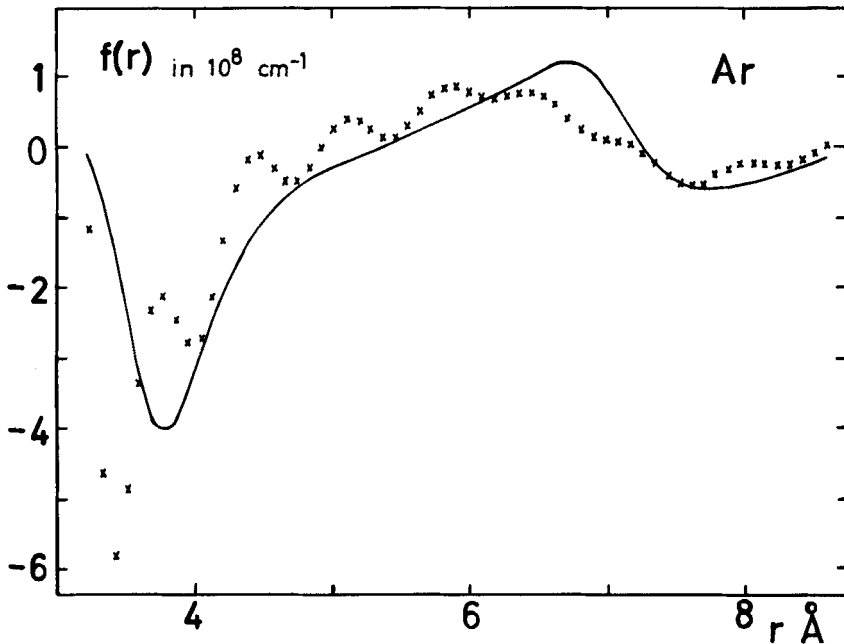


FIGURE 3 Comparison between $f_{MD}(r)$ ($\times \times \times$) and $f_{SA}(r)$ (—) for liquid argon as described by a Lennard-Jones potential.

4 CONCLUSION

What is clear from the above discussion is that, provided one always uses the superposition approximation with the exact $g(r)$ corresponding to the chosen input potential, and treats the three-body term in the force equation with a

consistent $g(r)$ and $\varphi(r)$, then the Kirkwood superposition approximation can be of quantitative value for potentials having the character of liquid Na. On the other hand, this procedure is poor for liquid Ar. This illustrates, quite clearly, that as has been stressed on a number of occasions,¹² it is essential, before asking for an appropriate decoupling procedure for the three-atom correlation function, to ask about the nature of the force law. The present paper leaves little doubt that in simple liquid metals the Kirkwood superposition approximation, when carefully employed, has quantitative merit, in sharp contrast to almost 'billiard ball' liquids like Ar.

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