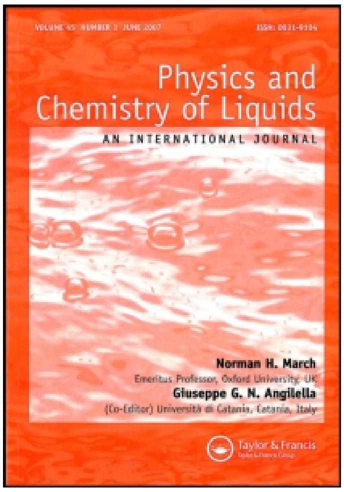

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LETTER

The importance of the three-particle correlation function in the theory of monatomic classical liquids like argon

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The present study was motivated by the work of Fortov *et al.* (2008) on the use of experimental methods of analysis of spatial correlation of dust particles in plasma. Here, we therefore focus on the importance of the three-particle correlation function g_3 in the theory of monatomic classical liquids like argon, in the framework of two-body central forces. We cover (i) the asymptotic relation of g_3 to the Ornstein–Zernike direct correlation function $c(r)$; (ii) the use of g_3 to determine the specific heat difference $c_P - c_V$; and (iii) g_3 related to the pressure dependence of the pair correlation function.

Keywords: force equation; direct correlation function

In very recent work, Fortov *et al.* [1] have made measurements in dusty plasmas to elucidate the range of validity of approximate relations in the statistical mechanics of classical liquids. One area they focus on is the regime of validity of the Kirkwood superposition approximation to the three-particle correlation function, as especially exemplified by Figure 4 in [1].

This study has motivated the present Letter. Here, we shall make the assumption, appropriate to a monatomic classical liquid like argon, that the many-body force field can be written as a sum purely of pair force contributions, characterised by a central potential $\phi(r)$.

Then, as utilised, for instance, in the early work of Johnson and March [2], the so-called force equation, which is the first member of the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy of classical statistical mechanics [3], reads

$$-\frac{\partial U(r_{12})}{\partial \mathbf{r}_1} = -\frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} - \rho \int \frac{g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g(\mathbf{r}_1, \mathbf{r}_2)} \frac{\partial \phi(r_{13})}{\partial \mathbf{r}_1} \, \mathrm{d}\mathbf{r}_3, \tag{1}$$

where ρ is the atomic number density. In Equation (1), $U(r)$ denotes the potential of mean force, related to the pair correlation function $g(r)$ by

$$g(r) = \exp\left(-\frac{U(r)}{k_{\mathrm{B}} T}\right). \tag{2}$$

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Of course, to proceed further with Equation (1), one requires a closure approximation [4,5], the commonest known approximation for g_3 being the Kirkwood proposal that g_3 is a product of three pair function terms. This was tested experimentally by Fortov *et al.* in [1].

Here we note first that, for dense fluids like argon far from the critical point, as was particularly emphasised by Johnson *et al.* [6], it is widely recognised that the Ornstein–Zernike direct correlation function $c(r)$, related to $g(r) - 1 \equiv h(r)$ by

$$h(r) = c(r) + \rho \int h(|\mathbf{r} - \mathbf{r}'|)c(\mathbf{r}')\mathrm{d}\mathbf{r}', \tag{3}$$

is asymptotically related at sufficiently large r to the pair potential $\phi(r)$ by

$$c(r) = -\frac{\phi(r)}{k_\mathrm{B}T}. \tag{4}$$

We next note, in relation to g_3, that the Kirkwood superposition approximation tested experimentally in [1] is also deficient for liquids like argon in that while $c(r)$ is indeed proportional to $-\phi(r)/k_\mathrm{B}T$ at large r, the multiplying constant is significantly different from unity [7,8].

We turn at this point to emphasise a further 'experimental' test of approximations to g_3. This concerns the specific heat difference $c_P - c_V$. Within the central pair potential framework adopted throughout this Letter, this difference was studied by Bratby *et al.* [9]. Their result will immediately be stated below, with the main, largely thermodynamic, steps in the proof being summarised below. Denoting the liquid structure factor, accessible to neutron scattering experiments [10], by $S(q)$, this is related to the pair correlation function $g(r)$ by

$$S(q) = 1 + \rho \int [g(r) - 1] \exp(i\mathbf{q}\cdot\mathbf{r})\mathrm{d}\mathbf{r}. \tag{5}$$

Then the difference $c_P - c_V$ has the exact form

$$\begin{aligned}\frac{c_P - c_V}{k_\mathrm{B}S(0)} = \Bigg\{ 1 - \frac{2\pi\rho}{3k_\mathrm{B}T}\int g(r)r^3\frac{\partial\phi}{\partial r}\mathrm{d}\mathbf{r} \\ - \frac{\rho}{2k_\mathrm{B}TS(0)}\left[\int g(r)\phi(r)\mathrm{d}\mathbf{r} + \rho\int [g_3(\mathbf{r},\mathbf{s}) - g(r)g(s)]\phi(r)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{s}\right]\Bigg\}^2.\end{aligned} \tag{6}$$

Bratby *et al.* [9] derived Equation (6) starting from the usual thermodynamic relation [11]:

$$c_P - c_V = -\frac{T}{N}\left(\frac{\partial P}{\partial T}\right)_V^2\left(\frac{\partial V}{\partial P}\right)_T. \tag{7}$$

Furthermore [11],

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{8}$$

Hence, after a little manipulation, one finds

$$c_P - c_V = S(0)\left[\frac{P}{\rho k_B T} + \frac{1}{\rho k_B T}\left(\frac{\partial E}{\partial V}\right)_T\right]^2 k_B. \tag{9}$$

The long wavelength limit $S(0)$ of the structure factor $S(q)$ is known from fluctuation theory to be given by

$$S(0) = \rho k_B T \kappa_T, \tag{10}$$

where κ_T is the isothermal compressibility.

For pair potentials $\phi(r)$ independent of the density ρ, which is a good approximation for a liquid like argon, a useful form of $(\partial E/\partial V)_T$ appearing in Equation (9) is given by

$$\left(\frac{\partial E}{\partial V}\right)_T = -\frac{\rho^2}{2}\int \frac{\partial}{\partial \rho}[\rho g(r)]\phi(r)\mathrm{d}\mathbf{r}. \tag{11}$$

But, as referred to in [1], the density dependence of the pair function $g(r)$ is related to g_3 in such a manner that one finds

$$\left(\frac{\partial E}{\partial V}\right)_T = -\frac{\rho^2}{2S(0)}\left[\int g(r)\phi(r)\mathrm{d}\mathbf{r} + \rho\int [g_3(\mathbf{r},\mathbf{s}) - g(r)g(s)]\phi(r)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{s}\right]. \tag{12}$$

These equations suffice, after some rearrangement, to establish the desired result in Equation (6).

Bratby *et al.* [9] calculated results for $c_P - c_V$ from Equation (6), with some approximations, including the Kirkwood form discussed in [1] in some detail. Their conclusion was that Equation (6) is important as an extremely sensitive test of the quality of assumptions about the three-particle correlation function g_3. Thus, taking experimental data for $c_P - c_V$ and $S(0)$ for argon, the integral terms on the right-hand side of Equation (6) are individually some orders of magnitude greater than $(c_P - c_V)/S(0)$ from experiment. Massive cancellations occur therefore, making Equation (6) important in the present context. To complete this discussion of specific heats, it is relevant to note from the study of Schofield [10] that c_P and c_V separately involve both g_3 and the four-particle correlation function g_4.

We turn more briefly to the third point we wish to stress, as it is also noted in the study of Fortov *et al.* [1]. It is that the three-particle correlation function g_3 is related to the pressure dependence of the pair correlation function $g(r)$, as also already implied by Equations (11) and (12). Since there are few theoretical examples of this, we refer finally on this point to the two-dimensional one-component plasma studied particularly by Jancovici [12]. For one particular coupling strength, $g(r)$ is calculable in exact analytic form, and Senatore *et al.* [13] have discussed g_3 using the above-mentioned relation.

In summary, the experimental study of Fortov *et al.* [1] on dusty plasma has motivated this Letter. The importance of the three-particle correlation function g_3, within a central pair potential framework appropriate to a classical liquid like argon has been stressed in three areas. First, any realistic approximation to g_3, inserted into the force Equation (1), must recover, far from the critical point, the large r asymptotic relation (4) between the direct correlation function $c(r)$ and the pair potential $\phi(r)$. The Kirkwood approximation to g_3 unfortunately does not satisfy this necessary condition for a currently useful form of g_3. Secondly, the difference in specific heats given in Equation (6) is stressed as a further sensitive test of approximations to g_3. Thirdly, as already emphasised in [1], the pressure dependence of the pair correlation function $g(r)$ is connected by an integral relation with the three-particle correlation function g_3.

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