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Computer "experiments" on classical fluids: Triplet correlations and moments of current correlation functions

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We present here results for the fourth frequency moments of current-correlation functions obtained by simulating a Lennard-Jones system of 256 particles near its triple point. A comparison with the results of Bansal and Pathak based on superposition approximation (SA) for the triplet correlation function $g_3(\vec{r},\vec{r}\,')$ leads us to a conclusion that the errors involved in the calculation of moments due to use of SA are not of much significance, in contrast to what is generally expected.

Frequency moments have long been recognized to play an important role in the study of dynamics of liquids. Recent studies of current correlation functions in liquids are directed at the fourth and sixth frequency moments.[1-5] However, until recently these higher moments were not of practical use because of the multiple integrals requiring knowledge of three-particle correlation function $g_3(\vec{r},\vec{r}\,')$ and were treated as parameters fixed through some physical property of the system.[1] Very recently, Bansal and Pathak[4] (BP) partially surmounted this difficulty by successfully performing the angular integrations associated with three-body terms of these moments. They could then numerically evaluate these moments for liquid argon using the Kirkwood superposition approximation (SA) for g_3,

$$g_3(\vec{r},\vec{r}\,') \simeq g_2(r)g_2(r')g_2(|\vec{r}-\vec{r}\,'|) \tag{1}$$

and a low-order decoupling approximation for the quadruplet correlation function.

The purpose of this paper is twofold: (i) to report our first results for fourth moments obtained by the computer simulation of a Lennard-Jones system, a so-called liquid-argon-like system, and (ii) to compare these molecular-dynamics (MD) results with those obtained by BP and to investigate the uncertainties involved in the calculation of moments due to the use of the SA for g_3.

The calculations reported here were carried out for systems of 108 and 256 particles and based on the following ingredients.

Particles with mass $m = 66.332 \times 10^{-24}$ g (the mass of an argon atom) were assumed to interact in pairs according to the potential $\phi(r) = 4\epsilon \times [(\sigma/r)^{12} - (\sigma/r)^6]$, $\epsilon/k_B = 119.8\,°\mathrm{K}$, $\sigma = 3.405$ Å, r being the distance between the particles and k_B is the Boltzmann constant. The potential was cut at 2.5σ. Using the method described by Verlet,[6] the integration of the equation of motion was carried out for 1200 integration steps of 0.2×10^{-13} sec. The calculations were first performed for a system of 108 particles and then for 256 particles. In the first case, a cubic box of size 5.027σ was used and the average temperature over the total MD run of 1200 steps was found to be $T = 85.5\,°\mathrm{K}$. In the second case, the length of the cube was changed to 6.703σ so as to obtain the same density ($mn = 1.428$ g cm^{-3}) as with 108 particles. The average temperature in this case was $T = 85.8\,°\mathrm{K}$. This state of temperature and density is close to the triple point of liquid argon and the available experimental data[7] for current correlations in liquid argon correspond to this state. Furthermore, this also enables us to directly compare our results with those of BP obtained under similar conditions.

According to our previous work,[4] we define the n^{th} frequency moment of the spectral function of the current correlation function as

$$\langle \omega^n_{l,t} \rangle = K^{l,t}_n + \sum_{i=2} I^{l,t}_{ni} \quad n = 0, 2, 4, \ldots, \tag{2}$$

where the subscripts l and t denote, respectively, the longitudinal and transverse current. $K^{l,t}_n$ denotes the kinetic part and $I^{l,t}_{n2}$, $I^{l,t}_{n3}, \ldots,$ etc., represent the contributions due to static pair and triplet correlation functions, respectively. Explicit expressions for both $\langle \omega^n_{l,t} \rangle$ ($n = 0, 2, 4, 6$) are given in Refs. 8 and 9. Comparing (2) with the exact expression for $\langle \omega^4_l \rangle$, we note that

$$I^l_{43} = \frac{n^2}{m^2} \int\int d\vec{r}\, d\vec{r}\,'\, g_3(\vec{r},\vec{r}\,')[1 - 2\cos qx + \cos q(x-x')] \times U_{x\alpha}(r) U_{x\alpha}(r'), \tag{3}$$

where $U_{x\alpha}(r) = \partial^2\phi(r)/\partial x\, \partial r_\alpha$, α denotes the Cartesian components x, y, z, and summation over doubly occurring indices is implied. Using the definition of g_3,

$$n^2 g_3(\vec{r}, \vec{r}') = \frac{1}{N} \sum_{\substack{i \neq j \neq k \\ i, j, k}} \langle \delta(\vec{r} - \vec{r}_{ij}) \delta(\vec{r}' - \vec{r}_{ik}) \rangle \vec{r}_{ij} = \vec{r}_i - \vec{r}_j, \tag{4}$$

I_{43}^l can be rewritten

$$I_{43}^l = \frac{1}{Nm^2} \sum_{i \neq j \neq k} \langle [1 - \cos qx_{ij}(\cos qx_{ik} - 2) + \sin qx_{ij} \sin qx_{ik}] U_{x\alpha}(r_{ij}) U_{x\alpha}(r_{ik}) \rangle. \tag{5}$$

In our MD calculations, we perform these three-particle summations using the following equality,

$$\sum_{\substack{i, j, k \\ i \neq j \neq k}} f(r_{ij}) h(r_{ik}) = \sum_i \left[\left(\sum_{\substack{j \\ j \neq i}} f(r_{ij}) \right) \left(\sum_{\substack{k \\ k \neq j}} h(r_{ik}) \right) - \sum_{\substack{j \\ j \neq i}} f(r_{ij}) h(r_{ij}) \right]. \tag{6}$$

The second term on the right-hand side of Eq. (6) arises due to the inclusion of $j = k$ term in the first term on this side. Here we would like to point out that in a recent paper, Michler *et al.*[10] have also attempted to calculate $\langle \omega_l^4 \rangle$ but for liquid aluminium. Instead of equality (6), they use

$$\sum_{\substack{i, j, k \\ i \neq j \neq k}} f(r_{ij}) h(r_{ik}) = \left(\sum_{\substack{i, j \\ i \neq j}} f(r_{ij}) \right) \left(\sum_{\substack{i, j \\ i \neq j}} h(r_{ij}) \right) - N \sum_{\substack{i, j \\ i \neq j}} f(r_{ij}) h(r_{ij}), \tag{7}$$

which is obviously wrong (see Ref. 10).

Having calculated I_{43}^l, we calculate I_{43}^t in a similar way. The calculation of $I_{42}^{l,t}$ is straightforward. The various contributions are then added according to Eq. (2) to get full moments.

In Fig. 1, we have compared the results of our MD calculations for $I_{43}^{l,t}$ with those obtained by BP. This comparison is made in order to investigate explicitly the errors involved due to the use of the SA for g_3. Clearly, the wave-number dependence of both I_{43}^l and I_{43}^t is well accounted for by the BP results based on the SA. Note that the magnitude of the present results is always smaller as compared to those of BP thereby implying that the SA has overestimated the integrals of $I_{43}^{l,t}$. The average of all the 18 values of I_{43}^l shows that the overestimation due to the SA is within 20%. The same holds true for I_{43}^t. It is, however, interesting to note that the results for the full moments $\langle \omega_{l,t}^4 \rangle$ obtained here and by BP are not very different. These are shown in Fig. 2. The differences are somewhat more at smaller q values ($q < 1.5$ Å^{-1}), where the structure is more and also the errors are expected to be large. But for $q \geq 1.5$ Å^{-1}, the agreement is very good. On the average, these differences are not more than 1.4% in the case of $\langle \omega_l^4 \rangle$ and 1% in the case of $\langle \omega_t^4 \rangle$. The reason for this behavior is that at small q values $K_4^{l,t}$ contributes very little to $\langle \omega_{l,t}^4 \rangle$ and the dominant contribution comes only from $I_{42}^{l,t}$ and $I_{43}^{l,t}$. But as q increases, the $K_4^{l,t}$ contribution increases relative

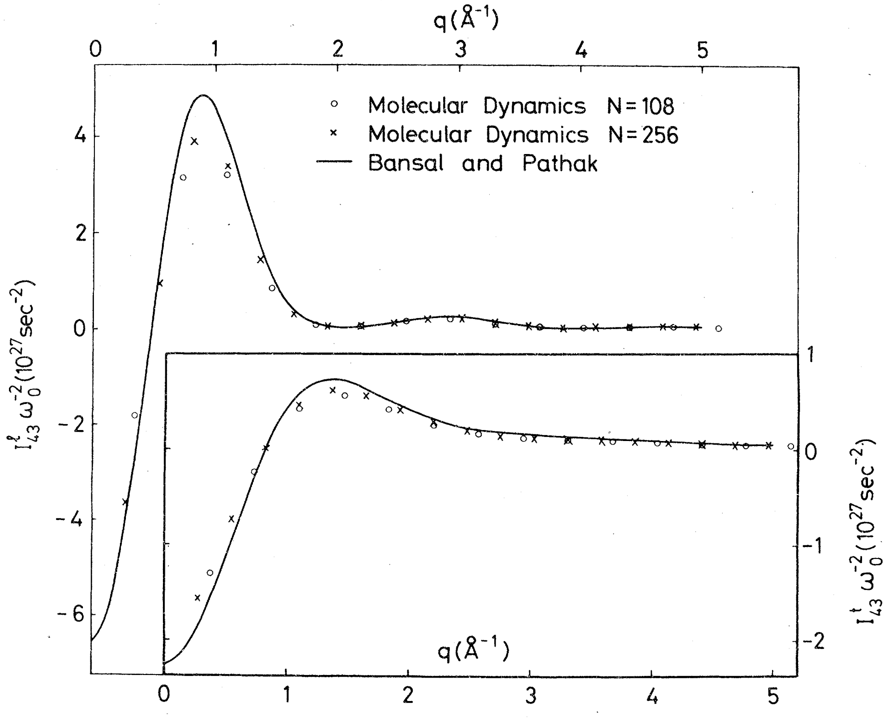

FIG. 1. Wave-number dependence of the contributions to the fourth frequency moments of longitudinal and transverse current correlation functions involving $g_3(\vec{r}, \vec{r}')$. $\omega_0^2 = q^2 k_B T/m$.

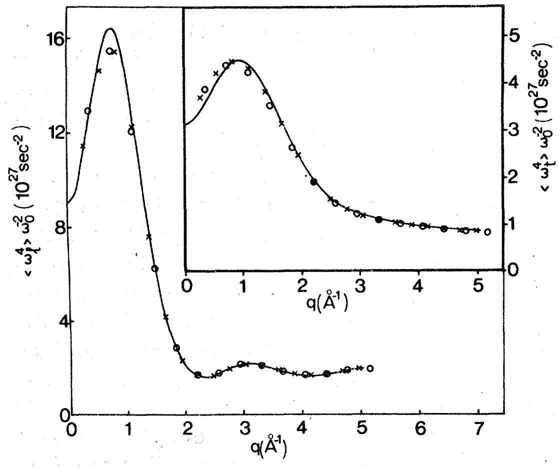

FIG. 2. Wave-number dependence of the fourth frequency moments of longitudinal and transverse current correlation functions. Notation is same as in Fig. 1.

to that of $I_{43}^{l,t}$.

To check that the MD program was generating correct configurations, we also computed the second frequency moments $\langle \omega_{l,t}^2 \rangle$, which involve $g(r)$ and derivatives of potential only, and compared the results with those obtained by direct integration using the MD data of Verlet[6] for $g(r)$. It was found that the two results were indistinguishable when plotted on the same graph. Note that the MD calculation of Verlet corresponds to a system of 864 particles whereas we have simulated systems of 108 and 256 particles only. The present results for $\langle \omega_{l,t}^4 \rangle$ obtained from two different experiments with 108 and 256 particles also do not differ much. These differences are of the order of 0.1% for the largest q and 2% for the smallest q investigated here (see Table I). Since it is always difficult to read the numbers from the published graphs, we have tabulated our results for $\langle \omega_{l,t}^4 \rangle$ in Table I.

As a by-product, we also get the second coefficient in the short-time expansion of the normalized velocity autocorrelation function, namely, $B = \langle \dot{V}(0)^2 \rangle / \langle V(0)^2 \rangle$. It comes out to be 1.138×10^{52} sec^{-4}, whereas the result obtained by BP is 3.5% higher (1.178×10^{52} sec^{-4}). Nijboer and Rahman[11] have also estimated B in their MD calculation of liquid argon using a different interaction potential—6-exp function of the Buckingham type. They obtain $B = 0.6648 \times 10^{52}$ sec^{-4}.

From these results, we conclude that the SA generally overestimates the magnitude of triplet correlations. This is consistent with the conclusions of Krumhansl and Wang[12-14] and that of Raveché *et al.*[15] who studied the same system through the Monte Carlo (MC) method. Krumhansl and Wang[12,13] found that the MC g_3 and SA g_3 agree to about 10% at low densities. They used these results in Born-Green equation to yield $\phi(r)$ and found that the MC $\phi(r)$ is in excellent agreement with the exact $\phi(r)$, while the SA $\phi(r)$ is poor. In another paper,[14] they studied the SA at high density and found that the SA predictions for g_3 differ from the MC results by as much as 70%. Similar results are obtained by Mountain and Raveché[16] for liquid neon and Raveché *et al.*[15] for the Lennard-Jones system.

However, our motivation here is not to understand the behavior of g_3 as such, but to check the errors involved in the calculation of moments due to the use of the SA for g_3. It is interesting to note

TABLE I. Molecular-dynamics results for $\langle \omega_{l,t}^4 \rangle$ (in units of $\omega_0^2 \times 10^{27}$ sec^{-2}) as a function q obtained using 256 particles. The results in parentheses correspond to our MD calculations with 108 particles.

q (Å^{-1})	$\langle \omega_l^4 \rangle$	$\langle \omega_t^4 \rangle$	q (Å^{-1})	$\langle \omega_l^4 \rangle$	$\langle \omega_t^4 \rangle$
0.2753	11.2127	3.6093	2.7529	1.8908	1.2680
0.5506	14.3629	4.1093	3.0282	2.0771	1.1348
0.8259	15.1426	4.3432	3.3035	2.0286 (2.0153)	1.0553 (1.0566)
1.1012	12.0110 (11.8134)	4.1965 (4.1494)	3.5788	1.8460	0.9985
1.3764	7.4375	3.7164	3.8540	1.6782	0.9467
1.6517	4.0810	3.0559	4.1293	1.6166	0.8976
1.9270	2.3357	2.4015	4.4046	1.6729 (1.6712)	0.8560 (0.8532)
2.2023	1.6510 (1.6506)	1.8704 (1.8467)	4.6799	1.7837	0.8266
2.4776	1.6198	1.4990	4.9552	1.8790	0.8092

from Fig. 2 that the corrections to the SA are insignificant as regards the calculation of moments even though $I_{43}^{l,t}$ obtained from the MD g_3 and SA g_3 differ by about 20% as stated above. The use of the SA for the calculation of moments can, therefore, be safely recommended. There seem to be no *a priori* reason of not expecting a similar behavior in other simple liquids like liquid aluminium and rubidium. Calculations for these two systems are also in progress and will be reported elsewhere. Finally, we hope that our present results will be of immense help to other theoretical workers in interpreting the experimental data on simple liquids.

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