Local density dynamics in a supercritical Lennard-Jones fluid

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Abstract. The collective particle dynamics of supercritical Lennard-Jones fluid is investigated on the basis of molecular dynamic modeling data. The intermediate scattering functions and dynamic structure factor spectra for the wavenumber range \( k \in [0.18; 3.26] \) \( \sigma^{-1} \) were calculated. The characteristics of dynamic structure factor spectra such as the thermal diffusivity and the sound velocity were estimated.

1. Introduction
A detailed description of the collective particle dynamics in a condensed disordered system can be obtained, on the one hand, on the basis of experimental INS/IXS spectroscopy data [1–3]. On the other hand, the study of the dynamics of such a system can be carried out by molecular dynamics simulation with some given potential [4]. In this case, the frequency spectra of time correlation functions of dynamical variables are of the greatest interest [5]. As such a variable, it is convenient to choose the quantity

\[
\rho_k(t) = \sum_{j=1}^{N} \exp(-i \mathbf{k} \cdot \mathbf{r}_j(t)),
\]

which is a spatial Fourier image of the local density function

\[
\rho(\mathbf{r}, t) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j(t)).
\]

Here, \( N \) is the number of particles in the system, \( \mathbf{r}_j(t) \) is the position vector of the \( j \)-th particle at time \( t \) and \( \mathbf{k} \) is the wavevector; dot denotes scalar product. Next, we consider the temporal correlation function of local density fluctuations, the intermediate scattering function

\[
F(\mathbf{k}, t) = \frac{1}{N} \langle \rho_k(t) \rho_{-\mathbf{k}}(0) \rangle,
\]

and its frequency spectrum, the dynamic structure factor [6]

\[
S(\mathbf{k}, \omega) = \int_{-\infty}^{\infty} dt F(\mathbf{k}, t) \exp(i \omega t).
\]

The angle brackets \( \langle \ldots \rangle \) in the expression (3) denote the ensemble averaging, which can be replaced by time averaging in the case of an ergodic system.

In this paper, we present the results of molecular dynamics simulation of a supercritical Lennard-Jones fluid. To investigate the collective microscopic dynamics of this system, the dynamic structure factor and sound dispersion were calculated.
was calculated on the basis of time series of wavevectors computed using the Lennard-Jones potential with a 5.0 σ cutoff radius. As the initial configuration of the system we used a crystal with a FCC lattice with the density ρ = 0.75 σ⁻³. To bring the system to an equilibrium state with the temperature $T = 2.8 \epsilon/k_B$ and the pressure $p = 6.6 \epsilon/\sigma^3$ we used a Nose–Hoover thermostat and barostat with relaxation times of 0.5 τ and 5.0 τ respectively. Next, we simulated the equilibrium system for 5 000 000 steps. To exclude manipulations of the thermostat and barostat on the dynamics, we performed that MD run in the NVE ensemble. While 0.005 τ timestep was used for the isothermal-isobaric simulation, the microcanonical simulation was performed with the smaller timestep of 0.001 τ for better energy conservation. Thus, the simulation time in the NVE ensemble was 5 000 τ.

At the second stage the Fourier components of the local density function (1) were calculated. Acceptable values of wavevector k components for the case when particle trajectories $r_j(t)$ are obtained from MD simulations in a cubic box with periodic boundary conditions are determined from the expression $k = (2\pi/L)(a, b, c)$, where $a, b, c$ are integers and L is the box length. It is important to note that for isotropic disordered systems, the spectral characteristics can be averaged over all possible directions of the wavevector $k_1, k_2, \ldots, k_n$, with the fixed magnitude $k = |k_1| = |k_2| = \ldots = |k_n|$, where $n$ is the number of such directions. In terms of calculations, at this stage each stored MD snapshot is turned into one complex function $\rho_k(t_m)$, where $m$ is the snapshot index. We calculated $\rho_k(t_m)$ time series with a 0.005 τ timestep for 830 wavevectors corresponding to 22 wavenumbers in the $k \in [0.18; 3.26] \sigma^{-1}$ range.

Finally, consider the third and final stage of the calculation. The intermediate scatter function $F(k, t)$ was calculated on the basis of time series $\rho_k(t_m)$ with time averaging. The averaging window is an array of 1 501 elements, which corresponds to a 7.5 τ time interval. Fig. 1(a) shows the obtained scattering functions for 6 wavenumbers. Then, using Filon’s numerical integration method [10], we turned these $F(k, t)$ functions into spectra of the dynamic structure factor $S(k, \omega)$, some of which are shown in Fig. 2(b). All computational procedures corresponding to the second and third stages were performed using the original parallel code.
As can be seen from Fig. 1(b), the high-frequency (Brillouin) components of the spectrum of the dynamic structure factor decay quite rapidly with increasing wave number \( k \) and at \( k \approx 1.5 \sigma^{-1} \) become almost indistinguishable. We plotted the wavenumber dependence of the side peak maximum position for such a range of wavenumbers, when the position of the maximum of the Brillouin peak can be accurately determined. This relationship represents the law of dispersion for the system under study and is shown in Fig. 2(a). Further, the speed of sound \( v_s \) can be estimated using the expression

\[
\omega_c = \lim_{k \to 0} v_s k
\]

from the linear low-\( k \) asymptotic of sound dispersion [11]. To do this, we fit the points from Figure 2(a) with a line whose slope coefficient is the desired speed of sound and is equal to \( v_s = 6.74 \sqrt{\epsilon/\sigma} \). The thermal diffusivity \( D_T \) was calculated using the following relationship [12]

\[
\Delta \omega_R(k) = D_T k^2,
\]

where \( \Delta \omega_R(k) \) is the half-width at half-height of the Rayleigh peak. From the spectrum of the dynamic structure factor \( S(k, \omega) \) at \( k = 0.6728 \sigma^{-1} \), we determined that the thermal diffusivity of the studied system is \( D_T = 2.82 \sigma \sqrt{\epsilon/\sigma} \). We also determined the dependence of the intensity of the zero-frequency spectral component \( S(k, \omega = 0) \) on the wave number \( k \), which is shown in Figure 2(b). This dependence can be used, for example, to determine the sound attenuation coefficient \( \Gamma \) [11].

3. Conclusion
The results of a long-time molecular dynamic simulation of a supercritical Lennard-Jones fluid at the temperature \( T = 2.8 \epsilon/k_B \) and the pressure \( p = 6.6 \epsilon/\sigma^3 \) were presented in this paper. For the considered state of the system it is shown that as the number of waves increases, the side peak of the dynamic structure factor \( S(k, \omega) \) becomes blurred and shifts to the region of high frequencies.

Acknowledgements
The author is grateful to A. V. Mokshin for useful discussions and recommendations. This paper has been supported by the Kazan Federal University Strategic Academic Leadership Program. The author acknowledges the Foundation for the Development of Theoretical Physics and Mathematics “BASIS” (project No. 20-1-2-38-1).
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