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Collective dynamics in single-particle motion for pure fluids

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Single-particle time correlation function $F_s(k,t)$ of pure fluids is studied within the generalized mode approach. Analytical expression for self-intermediate scattering function, which contains oscillating terms, is obtained for three-variable basis set of single-particle dynamic variables. The meaning of oscillating contributions is discussed, and it is shown, that in low-density fluids the oscillating contributions do not appear. Our approach, developed within the five-variable scheme, is used for the analysis of MD-derived single-particle time correlation function of Lennard-Jones fluid at two densities. It is shown, that the proposed scheme allows us to reproduce perfectly the function $F_s(k,t)$ at the whole range of wavenumbers k studied. The generalized self-diffusion coefficient as a function of k is also calculated.

Key words: *single-particle dynamics, Lennard-Jones fluid, velocity autocorrelation function, diffusion*

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1. Introduction

Single-particle motion in liquids is a rather complex phenomenon, which itself involves a variety of dynamic collective processes. This is the main reason why the single-particle dynamics is well understood so far in hydrodynamic limit only, where the slowest dynamic processes on large spatial scales are dominant and, therefore, some analytical methods can be used for its explanation [1,2].

Self-intermediate scattering function $F_s(k,t)$ and velocity autocorrelation function $\psi(t)$ are considered now to be the most popular tools in studying single-particle motion in liquids both in the theory and in the experiment. $F_s(k,t)$ can be extracted from neutron scattering [1–3] giving us, in particular, in the hydrodynamic limit the information about self-diffusion coefficient D. Beyond the hydrodynamic region, the spatial inhomogeneities in a system, like clusters of atoms or moveless obstacles, affect the shape of function $F_s(k,t)$, and hence an appropriate method is required to analyse the shape of $F_s(k,t)$ at a fixed wavenumber k, which corresponds to some spatial scale.

Recently, in [4] the problem of single-particle dynamics was attacked by comparison of the numerical results obtained by molecular dynamics for liquid lithium with the predictions of several theoretical approaches, widely used in the literature. Namely, the expressions, derived within hydrodynamic theory, Lovesey theory [5], mode-coupling theory as well as kinetic theory, were compared with MD-derived single-particle time correlation functions $F_s(k,t)$ in a wide range of wavenumbers k. In particular, it was shown, that the mode-coupling (*non-local*) approach, developed by Wahnström and Sjögren [6], gave the best agreement with the simulation data at different wavenumbers, but even in this case a noticeable discrepancies from the MD results were observed. The results, found within Lovesey (*local*) theory, exhibited some nonrealistic oscillations at high k.

For the purpose of theoretical studies of *collective* dynamics of liquids in a wide range of k and ω, an approach of generalized collective modes (GCM) has been developed [7–9]. This method is based on the concept of generalized collective excitations and allows one to take into account kinetic effects in liquid dynamics as well as *local* coupling between hydrodynamic and kinetic collective excitations. The GCM method enables us to derive a more general expression, in comparison with hydrodynamic one, for the collective density-density time correlation function $F_{nn}(k,t)$, which already contains the contributions from the so-called kinetic collective excitations (heat waves, optic-like excitations in many-component liquids, relaxing modes connected with structural relaxation, etc.) [10–12]. It was shown that in different k-regions, which correspond to distinct spatial scales, different processes are responsible for leading contributions to $F_{nn}(k,t)$ [or, alternatively, to dynamic structure factor $S(k,\omega)$]. In the recent years the GCM approach has been developed in order to investigate collective dynamics in many-component fluids [13], in magnetic liquids [14,15], in semi-quantum helium [16,17], in dipolar [18,19] and site interacting models of polar [20] fluids.

In this paper we have the aim to apply the main ideas of generalized collective mode approach to the analysis of single-particle time correlation functions $F_s(k,t)$, that would allow us to study an effect of diffusive-like and oscillating modes in single-particle motion. It will be shown, that the many-variable generalized modes approach provides a good description of single-particle dynamics in pure liquids and theoretical results (we will abbreviate time correlation functions derived within the GCM approach as GM-functions) almost coincide with MD-derived time correlation functions $F_s(k,t)$. Another important issue reported here is the study of generalized static diffusion coefficient $D(k) = D(k,\omega = 0)$ in a pure fluid, which follows from the memory function formalism.

2. Generalized mode approach

Let us start from the well-known relation between the self-intermediate scattering function $F_s(k,t)$ and velocity autocorrelation function $\psi(t)$ (see, e.g., [2]):

$$\psi(t) = \frac{1}{3}\langle \mathbf{v}_i(t)\mathbf{v}_i(0)\rangle = \lim_{k\to 0}\left\{-\frac{1}{k^2}\frac{\mathrm{d}^2}{\mathrm{d}t^2}F_s(k,t)\right\}, \tag{1}$$

where $\mathbf{v}_i(t)$ is the velocity of the tagged particle. This expression implies, that in dense fluids, for which velocity autocorrelation function exhibits negative minimum connected with a "cage effect" (back scattering of the particle due to interaction with the cage of its nearest neighbours) [1], the function $F_s(k,t)$ already contains the information, hidden in its shape, about *collective* arrangement of the nearest neighbors. We also note that another well-known hydrodynamic expression [1,2]:

$$F_s(k,t) = \mathrm{e}^{-Dk^2t}, \qquad k \to 0, \tag{2}$$

where D denotes the self-diffusion coefficient, obviously does not contain any oscillating contributions. This means that a leading contribution from oscillating processes to the function $F_s(k,t)$ must be of the order k^2 in small-k limit. It is shown below, that in the simplest three-variable GCM scheme one can easily obtain the expressions for mode contributions to $F_s(k,t)$ which behave in the hydrodynamic limit in full agreement with equations (1) and (2).

One of the advantages of GCM approach is the possibility to represent time-dependent quantities such as time correlation functions via separated contributions from the long-time (or hydrodynamic) and short-time (kinetic-like) processes. Short-time contributions for single-particle time correlation function can be connected to purely relaxing processes or to the processes, describing oscillatory motions of particles. By analogy with the terminology used in our previous studies of collective dynamics in liquids [8–11], we will refer to kinetic-like excitations, being associated with some short-time processes, as *kinetic single-particle modes*. In contrast to hydrodynamic long-time modes, the kinetic ones have the finite lifetime in $k \to 0$ limit, so that they do not contribute significantly to time-dependent quantities in the hydrodynamic region. Mathematically, the relaxing and oscillatory (kinetic and hydrodynamic) modes can be presented by the set of corresponding purely real and complex-conjugated dynamic eigenvalues, respectively, which are the solutions of an eigenvalue-problem for some dynamic matrix, describing the time evolution of the system under consideration.

The starting point for a generalized mode approach is the choice of a basis set of dynamic variables which is further used for solving the generalized Langevin equation (GLE): a chosen basis set of dynamic variables is used to generate a matrix form of GLE; applying GLE scheme one can derive the matrix equation for single-particle time correlation functions; and the highest order memory function, obtained for the chosen basic set, is then taken in Markovian approximation. In order to illustrate our approach let us consider the following basis set of three single-particle operators:

$$\mathbf{A}^{(3)} = \{n(k,t), \dot{n}(k,t), \ddot{n}(k,t)\}, \tag{3}$$

where

$$n(k,t) = \mathrm{e}^{\mathbf{i}\mathbf{k}\mathbf{r}_i(t)}$$

is the dynamic variable of single-particle density (subindex of the tagged particle is dropped in (3) for simplicity) and overdots in (3) denote the order of time derivatives of a relevant operator.

For the basis set $\mathbf{A}^{(3)}$ the corresponding 3×3 generalized hydrodynamic matrix $\mathbf{T}(k)$, which already contains all the dissipation processes (in terminology of the memory function formalism the matrix $\mathbf{T}(k)$ is in fact a sum of the matrix of memory functions and thus the frequency matrix [8,9]) has the following form:

$$\mathbf{T}^{(3)}(k) = F^{(3)}(k)[\tilde{F}^{(3)}(k)]^{-1} = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ [\bar{\omega}_{4,k} - \bar{\omega}_{2,k}]\tau_s^{-1} & \bar{\omega}_{4,k} & [\bar{\omega}_{4,k}\bar{\omega}_{2,k}^{-1} - 1]\tau_s \end{pmatrix}, \quad (4)$$

where $F^{(3)}(k) = F^{(3)}(k,t=0)$ and $\tilde{F}^{(3)}(k) = \tilde{F}^{(3)}(k,z=0)$ denote the matrices of static correlation functions and the Laplace transforms $\tilde{F}^{(3)}(k,z)$ of time correlation functions $F^{(3)}(k,t)$, constructed on the variables (3), at $z=0$, respectively; $\bar{\omega}_{4,k}$ and $\bar{\omega}_{4,k}$ are the normalized frequency moments:

$$\bar{\omega}_{4,k} = \frac{\langle \ddot{n}_k \ddot{n}_{-k}\rangle}{\langle \dot{n}_k \dot{n}_{-k}\rangle} = \Omega_0^2 + \frac{3k_\mathrm{B}T}{m}k^2, \qquad \bar{\omega}_{2,k} = \frac{\langle \dot{n}_k \dot{n}_{-k}\rangle}{\langle n_k n_{-k}\rangle} = \omega_0^2 = \frac{k_\mathrm{B}T}{m}k^2, \quad (5)$$

and the generalized correlation time $\tau_s(k)$ is defined by

$$\tau_s(k) = \int_0^\infty F_s(k,t)\mathrm{d}t. \quad (6)$$

Note that Ω_0 in (5) has the sense of a mean frequency of vibrations for the tagged particle (see, e.g., [3]) and is often recalled as the Einstein frequency, due to the analogy with the crystal model, proposed by Einstein for the lattice vibrations. This is intuitively expected in solid-like picture for an oscillating motion of the tagged particle as a result of the interactions with its nearest neighbours.

The difference between the standard memory function formalism [1,2,5] and the GCM approach is twofold: (i) we consider the basis set (3) of *non-orthogonal* dynamic variables as the theory input. Thus, for any k value, all the time correlation functions, constructed on dynamic variables from the basis set, in general case of the M-variable GCM approach are presented as a weighted sum of exponential functions with complex arguments:

$$F_s^{(M)}(k,t) = \sum_{i=1}^{M} G^\alpha(k)\mathrm{e}^{-z_\alpha(k)t}, \quad (7)$$

where complex numbers $z_\alpha(k)$ are the eigenvalues of generalized dynamic matrix $\mathbf{T}^{(M)}(k)$, and $G_\alpha(k)$ denote the complex (in general case) weight coefficients, evaluated via the associated eigenvectors [8,9]. For further convenience we will make a distinction between purely real eigenvalues [they will be marked as $d_\alpha(k) \equiv \mathrm{Re}\ (z_\alpha(k))$], describing the relaxing processes, and complex-conjugated eigenvalues $z_\alpha(k)$, corresponding to propagating excitations. Therefore, in Fourier space, the self-dynamic structure factor $S_s(k,\omega)$, found within the GCM approach, is just the sum of Lorentzian-like terms for any wavenumber; (ii) within the GCM approach we do not use any parameterizations for correlation time $\tau_s(k)$. The function $\tau_s(k)$ is just taken as the "reference" correlation time, which can be directly evaluated from the MD-derived function $F_s(k,t)$, using the definition (6); so that no fitting parameters are needed. This gives an additional sum rule in our approach [9]. However, for the purpose of an analytical treatment, the k-dependence of $\tau_s(k)$ can be often specified. For instance, in the hydrodynamic limit the explicit expression for $\tau_s(k)$ can be derived. It is also worth emphasizing that the expression for $F_s(k,t)$, obtained within the Lovesey model [5], is easily reproduced within the three-variable GCM scheme with a special choice for $\tau_s(k)$, namely:

$$\tau_s(k) = \frac{2\omega_0^2 + \Omega_0^2}{\omega_0^2}\tau_L(k),$$

where the notations of [4] are used.

To proceed further in our analysis, we note that the normalized fourth-order frequency moment $\bar{\omega}_{4,k}$ [see (5)] tends to the nonzero frequency Ω_0^2 in the limit $k \to 0$. Under this condition it can be easily shown that among three eigenvalues of generalized hydrodynamic matrix $\mathbf{T}(k)$ one obtains one purely real eigenvalue with the asymptotic behaviour:

$$d(k) \to Dk^2, \qquad k \to 0,$$

and two eigenvalues $z^{\pm}(k)$:

$$z^{\pm}(k=0) = \frac{mD\Omega_0^2}{2k_{\mathrm{B}}T}\left(1 \pm \sqrt{1 - \frac{4(k_{\mathrm{B}}T)^2}{m^2D^2\Omega_0^2}}\right), \tag{8}$$

which can be either purely real or complex-conjugated ones, depending on the parameters of the system. Introducing two specific times τ_{dif} and τ_{vib}:

$$\tau_{\mathrm{dif}} = \frac{Dm}{k_{\mathrm{B}}T}, \qquad \tau_{\mathrm{vib}} = \frac{1}{\Omega_0},$$

which characterize the hydrodynamic processes, connected with the selfdiffusion, and the processes of vibrational nature being strongly dependent on an arrangement of the tagged particle, respectively, one can see from (8) that the oscillating modes appear only if the inequality

$$\tau_{\mathrm{dif}} < 2\tau_{\mathrm{vib}} \tag{9}$$

is fulfilled. In this case one has for the corresponding eigenvalues:

$$z^{\pm}(0) = \tilde{\sigma} \pm \mathrm{i}\tilde{\omega}, \tag{10}$$

with

$$\tilde{\sigma} = \frac{\tau_{\rm dif}}{2\tau_{\rm vib}^2}, \qquad \tilde{\omega} = \Omega_0 \left[1 - \left(\frac{\tau_{\rm dif}}{2\tau_{\rm vib}}\right)^2\right]^{1/2}$$

being the damping coefficient and the frequency of propagating modes. It is seen that the damping coefficient $\tilde{\sigma}$ has a nonzero value at $k = 0$, which is the specific feature of kinetic modes. Note that there is also one additional typical time $\tau_{\rm col}$ which describes, in fact, the mean time between collisions. Its value can be estimated as follows:

$$\tau_{\rm col} = \left(\frac{m}{k_{\rm B} T n^{2/3}}\right)^{1/2},$$

where $n = N/V$ is a number density, so that $\tau_{\rm col}$ characterizes the mean-free-motion path of a particle in noninteracting system. Thus, one can expect that for time intervals smaller than $\tau_{\rm col}$ an effective Gaussian-like behaviour of time correlation functions can be expected.

Eigenvectors, associated with the corresponding eigenvalues, determine the amplitude of a particular mode contribution to the self-intermediate scattering function $F_s^{(3)}(k,t)$ (upper index means three-variable basis set). For the case of complex-conjugated eigenvalues $z^{\pm}(k) = \sigma(k) \pm \omega(k)$, in particular, when the condition (9) is fulfilled, one obtains for any fixed wavenumber k that:

$$F_s^{(3)}(k,t) = A(k){\rm e}^{-d(k)t} + \Big[B(k)\cos\{\omega(k)t\} + C(k)\sin\{\omega(k)t\}\Big]{\rm e}^{-\sigma(k)t} \qquad (11)$$

with the following expressions for amplitudes:

$$A(k) = \frac{\sigma^2(k) + \omega^2(k) - \bar{\omega}_{2,k}}{[d(k) - \sigma(k)]^2 + \omega^2(k)}, \qquad B(k) = \frac{d(k)[d(k) - 2\sigma(k)] + \bar{\omega}_{2,k}}{[d(k) - \sigma(k)]^2 + \omega^2(k)},$$

$$C(k) = \frac{d^2(k)\sigma(k) + d(k)[\omega^2(k) - \sigma^2(k)] - \bar{\omega}_{2,k}[d(k) - \sigma(k)]}{\{[d(k) - \sigma(k)]^2 + \omega^2(k)\}\omega(k)}. \qquad (12)$$

Here we adopted the notations from [10] to mark amplitudes of relaxing contributions as $A(k)$, and amplitudes of symmetric and asymmetric oscillating contributions as $B(k)$ and $C(k)$, respectively. In the hydrodynamic limit $k \to 0$, the amplitude $A(k)$ of diffusive mode $d(k) \approx Dk^2$ tends to unity, while the amplitude of symmetric oscillating contribution can be a negative function of k^2 depending on the ratio between thermal velocity and diffusion coefficient:

$$B(k) \approx k^2 \left[\frac{k_{\rm B}T}{m} - 2D\tilde{\sigma}\right], \qquad k \to 0.$$

Negative amplitudes of oscillating contributions are not a specific feature of single-particle time correlation function $F_s(k,t)$. For the collective dynamics of liquids, a similar result was previously found [21,22] for the contributions of over-damped sound excitations at wavenumbers k, being close to the position of the main peak of a static structure factor. It is worth noting that the complex-conjugated modes can appear for fixed k even if the condition (9) is not satisfied. This point will be discussed more in detail hereinafter together with the numerical results obtained.

It is seen in (8) that high value of self-diffusion coefficient D can lead to the vanishing of the oscillating contributions. If the condition (9) is not fulfilled (which is a typical situation for gases and for low density liquids) one would obtain two real eigenvalues instead of the pair of complex-conjugated ones. Let us consider this case more in detail. Then, according to (7), the expression for $F_s(k,t)$ does not contain the oscillating contributions, and in the three-variable scheme one gets:

$$F_s^{(3)}(k,t) = \sum_{\alpha=1}^{3} A_\alpha(k)\mathrm{e}^{-d_\alpha(k)t}, \tag{13}$$

where the amplitudes $A_\alpha(k)$ can be written as follows:

$$A_\alpha(k) = \frac{d_\gamma(k)d_\nu(k) - \bar{\omega}_{2,k}}{[d_\alpha(k) - d_\gamma(k)][d_\alpha(k) - d_\nu(k)]} \tag{14}$$

with $\alpha \neq \gamma \neq \nu$. This means that only the relaxing contributions form the shape of $F_s(k,t)$: the purely hydrodynamic contribution corresponds to the eigenvalue $d_1(k) = Dk^2$, describing the self-diffusion process, while the purely kinetic processes with the lifetimes of the order $\tau_2 \approx d_2^{-1}$ and $\tau_3 \approx d_3^{-1}$ are associated with the other two modes $d_2(k)$ and $d_3(k)$, respectively. It is easy to show, that in the limit of small wavenumbers k, the amplitudes of short-time kinetic relaxing modes $d_2(k)$ and $d_3(k)$ [see equation (14)] are proportional to k^2, while the amplitude $A_1(k)$ of the hydrodynamic mode $d_1(k)$ tends to 1. This is in complete agreement with the predictions of the hydrodynamic theory.

To understand the meaning of oscillating contributions to $F_s(k,t)$, associated with the propagating modes (10) found in the $k \to 0$ limit, let us apply the relation (1) to the expression (11) with amplitudes (12). It is easy to show, that the contribution from the hydrodynamic mode $d_2(k)$ to velocity autocorrelation function $\psi(t)$ goes to zero in the limit $k \to 0$, and only the last two terms in (11) form, in fact, the shape of this function when k is small, so that one obtains:

$$\psi^{(3)}(t) = \left\{\tilde{B}\cos\tilde{\omega}t + \tilde{C}\sin\tilde{\omega}t\right\}\mathrm{e}^{-\tilde{\sigma}t}, \tag{15}$$

where the tilted amplitudes $\tilde{B}$ and $\tilde{C}$ are given by the expressions:

$$\tilde{B} = \frac{k_\mathrm{B}T}{m}\ , \quad \tilde{C} = D\frac{\tilde{\omega}^2 + \tilde{\sigma}^2}{\tilde{\omega}} - \frac{k_\mathrm{B}T}{m}\frac{\tilde{\sigma}}{\tilde{\omega}} = \frac{k_\mathrm{B}T}{m}\frac{\tilde{\sigma}}{\tilde{\omega}}. \tag{16}$$

One can easily check that

$$\psi(0) = \frac{k_\mathrm{B}T}{m} \quad \text{and} \quad \int_0^\infty \psi(t)\mathrm{d}t \equiv D.$$

It can be also shown that two additional explicit relations for the derivatives of function $\psi(t)$ at $t = 0$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\psi(t=0) = 0, \qquad \frac{\mathrm{d}^2}{\mathrm{d}t^2}\psi(t=0) = \Omega_0^2$$

are also fulfilled for the case considered. Note that the last four relations may be considered as a particular example of more general expressions known as the sum rules for the function $F_s(k,t)$. It can be shown (see, e.g., [9]) that the expression (7), found for $F_s(k,t)$ in a more general case of the M-variable GCM scheme, reproduces explicitly the first $(2M-1)$ frequency moments at any fixed k value. This results, because of (1), in the correct values of frequency moments for velocity autocorrelation function $\psi(t)$, found within the same approach, up to the order $(2M-4)$ inclusive.

What have we learned from this simple analytical treatment performed within the three-variable GCM scheme? First, the appearance of the oscillating terms in $F_s(k,t)$, which determine, in fact, the shape of velocity autocorrelation function in the small k limit, depends on the ratio of two characteristic times $\tau_{\rm dif}$ and $\tau_{\rm vib}$. Free-particle motion is expected to be dominant only in a short time limit ($t \ll \tau_{\rm col}$ and for large values of k. In dense liquids, the vibrational (*collective*) component of motion becomes more important due to "cage effect" and this results in the oscillating behaviour of velocity autocorrelation function $\psi(t)$. In the function $F_s(k,t)$ the contributions from the propagating kinetic-like modes are not visible in the hydrodynamic limit, because the amplitude of diffusive mode $d_1(k)$ is dominant [as it follows from (12) the ratios of corresponding amplitudes $B(k)/A(k)$ and $C(k)/A(k)$ are proportional to k^2]. Second, within this simple treatment, all the qualitative features of single-particle dynamics are described correctly, so that we can expect to achieve the quantitative agreement in higher mode approximations. Note that most of the results presented above were previously obtained within the memory function formalism (see, e.g., [1]). This point was mainly considered in order to testify the GCM approach to the problem of single-particle dynamics and to establish a relation to the theoretical models developed previously.

In our further study, to analyze MD-derived self-intermediate scattering function $F_s(k,t)$, the five-variable scheme of GCM approach is used. This scheme can be considered as an extension of our previous analytical treatment with the set of five single-particle dynamic variables:

$$\mathbf{A}^{(5)} = \{n(k,t), \dot{n}(k,t), \ddot{n}(k,t)\ \dddot{n}\ (k,t), \ddddot{n}\ (k,t)\}, \tag{17}$$

chosen as the basis one. Thus, additional short-time dynamic processes can be taken into account in an appropriate way (in comparison with the case $\mathbf{A}^{(3)}$ considered before) which has to result in a more precise short-time analysis of the numerical results beyond the hydrodynamic region.

3. Results and discussion

We performed MD simulations in standard microcanonical ensemble for a system of 1000 particles in a cubic box for Lennard-Jones fluid at the temperature $T^* = 1.706$ for two densities: high $n^*_{\rm h} = 0.845$ and low $n^*_{\rm l} = 0.601$ ones. The parameters of LJ potential were taken as for liquid Ar: $\sigma_{\rm LJ} = 3.405$ Å and $\varepsilon = 119.8$ K.

The smallest wavenumbers achieved in MD for low- and high-density fluids were $k_{\mathrm{min}}^{\mathrm{l}} = 0.1557$ Å^{-1} and $k_{\mathrm{min}}^{\mathrm{h}} = 0.1745$ Å^{-1}, respectively. The time evolution of one-particle variables and their time derivatives (see basis set $\mathbf{A}^{(5)}$) was observed during production runs over $1.2 \cdot 10^5$ steps. Fifteen values of wavenumbers k in the range from k_{min} to 4.3 Å^{-1} were considered in our MD study. Additional averaging over all the possible directions of wavevectors with the same absolute value was performed.

3.1. Single-particle time correlation functions

Self-intermediate scattering functions $F_s(k,t)$, obtained in MD, and the relevant GM-functions $F_s^{(5)}(k,t)$ found for low- and high-density fluids under consideration are shown in figures 1(a-c) and 2(a-c), respectively. One can see, that for small wavenumbers, the shape of $F_s(k,t)$ can be well described by hydrodynamic single-exponential expression (2), while for intermediate values of k, the functions $F_s(k,t)$ decay much faster and obviously do not resemble a single-exponential function. It is easy to see, that the MD-derived time-correlation functions in figures 1 and 2 always tend to unity with zero value of the first order time derivative as time t goes to zero, which was expected because of time inverse symmetry. Thus, for very small t, the precursor of free-particle Gaussian-like behaviour is observed. Otherwise, the hydrodynamic expression (2) reflects correctly only long-time properties and does not reproduce the right short-time behaviour. The GM-functions (7), which generalize the hydrodynamic expression (2), do have the proper short- and long-time behaviour. Depending on the number of dynamic variables taken into the basis set, the GM functions, as it was mentioned before, reproduce explicitly the first frequency moments (up to the order $(2M-2)$ within the M-variable scheme) of dynamic structure factor $S_s(k,\omega)$ or, equivalently, the corresponding time derivatives of the function $F_s(k,t)$ at $t = 0$. Hence, the three-term GM expressions (11) and (13) have an identical short-time behaviour with MD-derived time correlation functions $F_s(k,t)$ up to the fourth order time derivatives and, in addition, the zeroth time moment due to identity of correlation times $\tau_s(k)$. The GM-function $F_s^{(5)}(k,t)$, obtained by using the five-variable basis set (17) and shown in figures 1 and 2 by dashed lines, gives the correct values for the first nine frequency moments (up to the eighth order inclusive). Moreover, the integral property (6) also has a correct value within the scheme used.

From figures 1 and 2 one can conclude, that in a wide range of k considered, the five-term GM-functions very well reproduce the results found for a self-intermediate scattering function $F_s(k,t)$ of a LJ fluid. In a small time region, the free-particle Gaussian-like t-dependence is mimicked by the finite number of exponential terms (five in our case) keeping the correct values for the first eight time derivatives. For a larger t the crossover to exponential behaviour is observed.

The MD-derived velocity autocorrelation functions $\psi(t)$ of a LJ fluid, calculated at two densities, are shown in figure 3. For the low-density state (shown by solid line) the function $\psi(t)$ displays a simple decay resembling the behaviour of $F_s(k,t)$ at intermediate wavenumbers. In the case of the high-density state, however, the

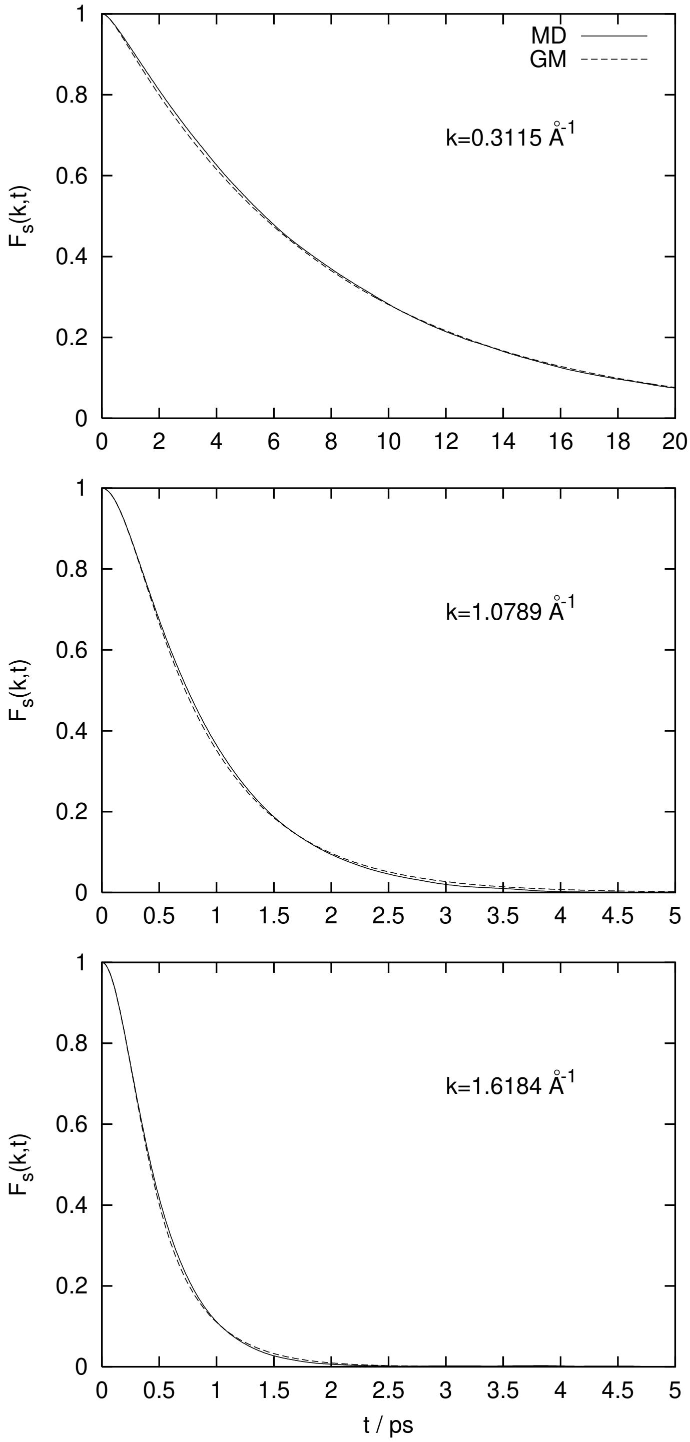

Figure 1. Self-intermediate scattering function $F_s(k,t)$ of a LJ fluid at low-density state: molecular dynamics simulations (solid line) and five-variable GCM scheme (dashed line).

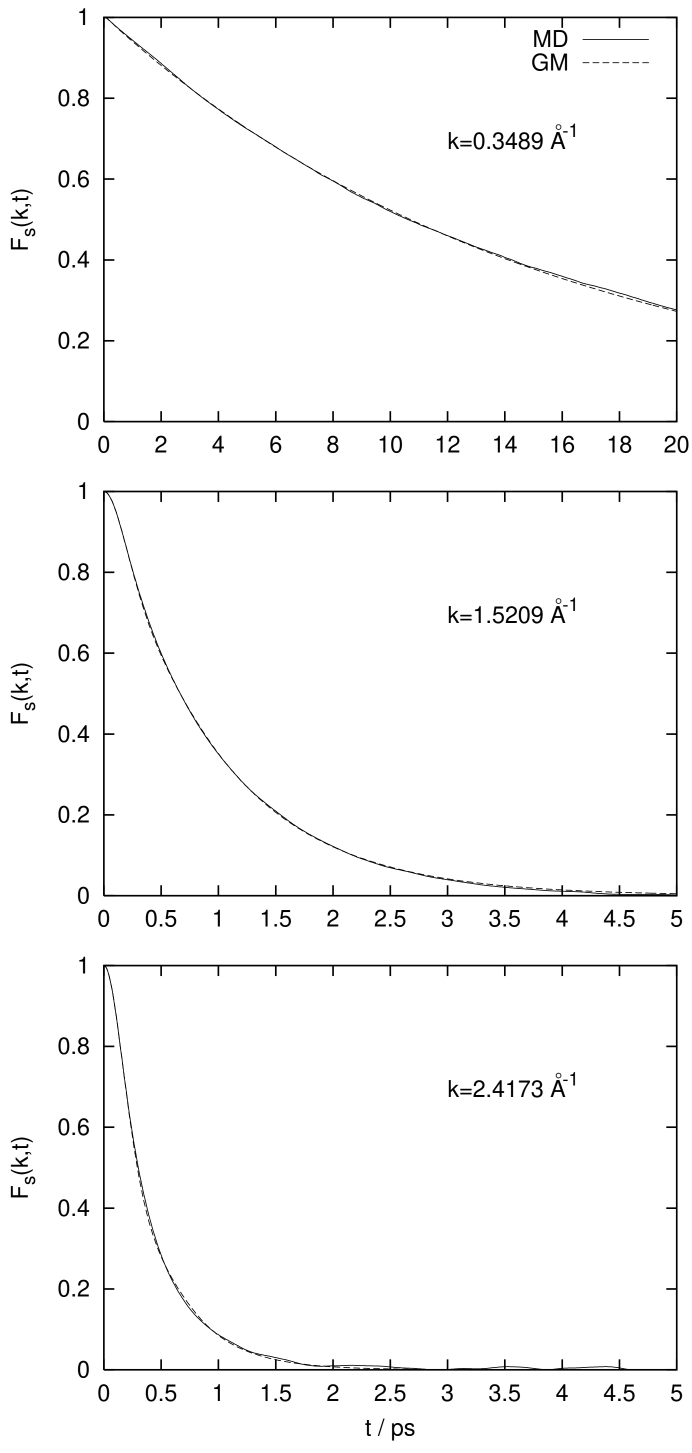

Figure 2. Self-intermediate scattering function $F_s(k,t)$ of a LJ fluid at high-density state: molecular dynamics simulations (solid line) and five-variable GCM scheme (dashed line).

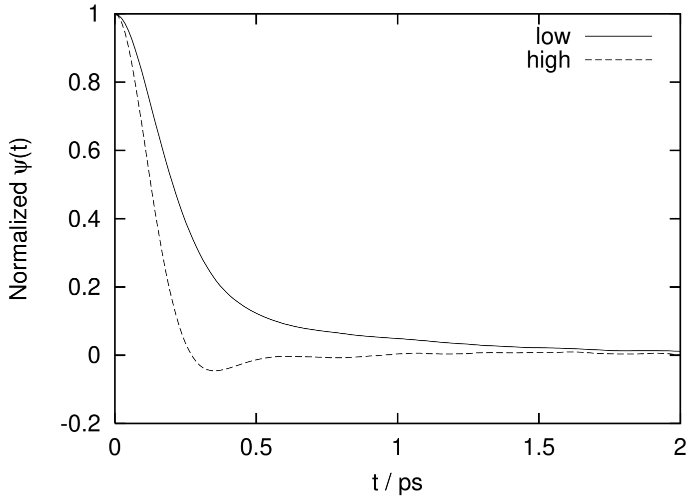

Figure 3. Velocity autocorrelation function of a LJ fluid: low-density (solid line) and high-density (dashed line).

negative minimum appears, which is usually attributed to the so-called "cage effect" [1]. This may be interpreted as the changing of tagged particle's velocity to the opposite direction due to interactions with the nearest neighbours (back scattering), so that the vibrational component in single-particle motion appears.

According to our analytical treatment of oscillating modes in single-particle motion (see (15) and (11)) one can expect the oscillating contributions not only to the shape of velocity autocorrelation function $\psi(t)$, but to the function $F_s(k,t)$ as well.

3.2. Generalized modes in single-particle dynamics

Let us now analyze the spectral properties of MD-derived self-intermediate scattering functions $F_s(k,t)$ using the five-variable GM approach. In figure 4 one can see the real and imaginary parts of dynamic eigenvalues, obtained for a single-particle dynamics of the low-density LJ fluid. Complex eigenvalues $z_i(k) = \sigma_i(k) \pm \omega_i(k)$ correspond to oscillating modes in single-particle motion with the frequency $\omega_i(k)$ and damping coefficient $\sigma_i(k)$, while the purely real eigenvalues $d_i(k)$ describe the relaxing diffusive-like process. An interesting feature of low-density state is the different number of complex-conjugated eigenvalues $z_j^{\pm}(k)$ in the regions of small and intermediate wavenumbers. For $k > 1$ Å^{-1}, there exist two branches of oscillating modes (shown by closed and crossed boxes). For smaller wavenumbers, the oscillating mode $z_1(k)$ is not supported by the low-density LJ fluid, and two relaxing modes $d_2(k)$ and $d_3(k)$ appear in this region instead. Such a crossover from the kinetic relaxing modes to the kinetic propagating ones at finite wavenumbers was predicted in section 2 using a three-variable GM approach and can be described in this case analytically. Thus, we can conclude that due to the high value of self-diffusion ($\tau_{\rm dif} > 2\tau_{\rm vib}$), the long-wave oscillatory motion of particles, associated with the vibrational component of motion, is not supported in the low-density LJ fluid

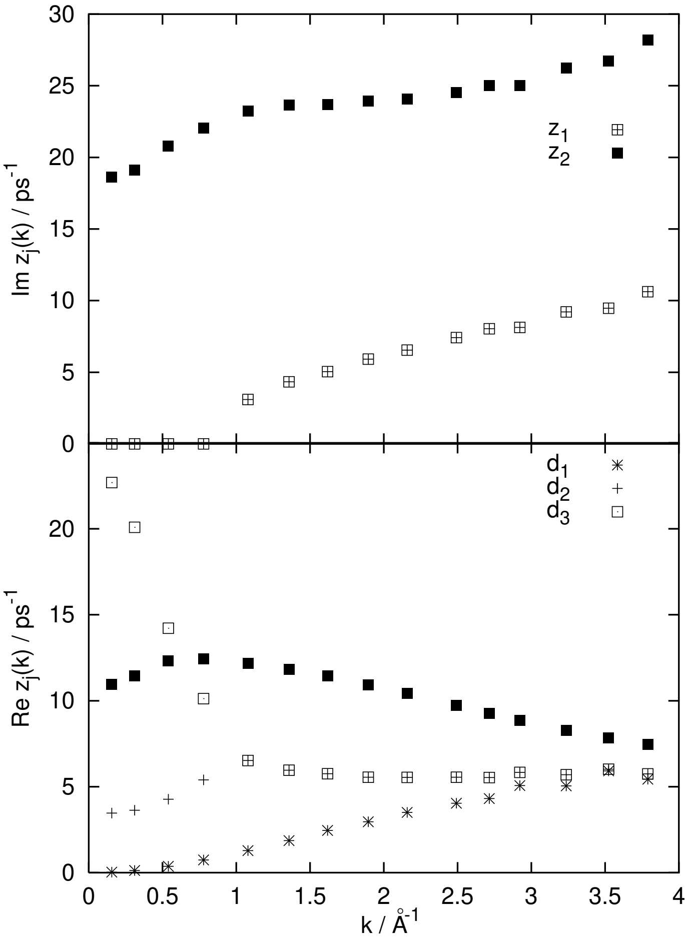

Figure 4. Frequency and damping coefficients of generalized oscillating modes in a LJ fluid, obtained for the five-variable basis set $\mathbf{A}^{(5)}(k,t)$ at low-density state.

at small wavenumbers range. For smaller spatial scales ($k > 1$ Å^{-1}), the vibrational component becomes more important and this results in the appearance of the lower branch of kinetic-like propagating modes.

In the case of the high-density LJ fluid (see figure 5), the lower branch of propagating modes $z_1(k)$ exists in the whole k-region studied, that is the consequence of more elastic properties of high-density fluids in comparison with the low-density ones ($\tau_{\mathrm{dif}} < 2\tau_{\mathrm{vib}}$). However, taking into account the value of the damping coefficient, found for these modes, one can conclude that such excitations with the frequencies ~ 7 ps^{-1} are over-damped and may be observed only for the time scale up to 0.13 ps (which is seen, in fact, in figure 3).

For the both cases of LJ fluids considered, the high-frequency oscillatory modes $z_2(k)$ are found within the five-variable GCM scheme. However, the damping coefficients for these modes are large enough to significantly contribute to the single-particle dynamics in the k range considered. At both densities we found that the long-time processes are mainly connected with the extended hydrodynamic diffusive mode $d(k)$ which describes the self-diffusion properties in the hydrodynamic limit

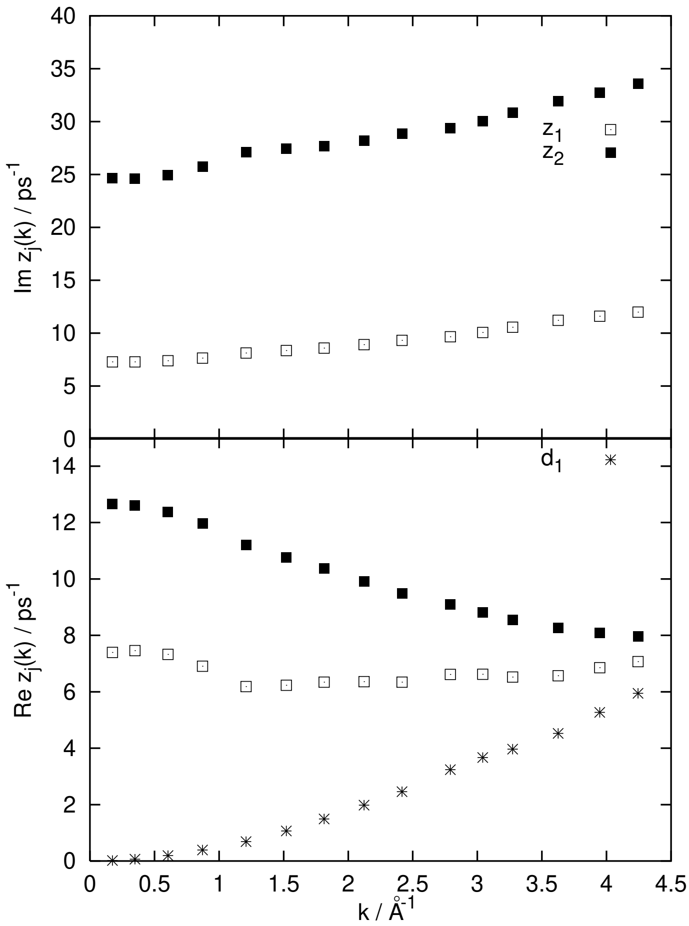

Figure 5. Frequency and damping coefficients of generalized oscillating modes in a LJ fluid, obtained for the five-variable basis set $\mathbf{A}^{(5)}(k,t)$ at high-density state.

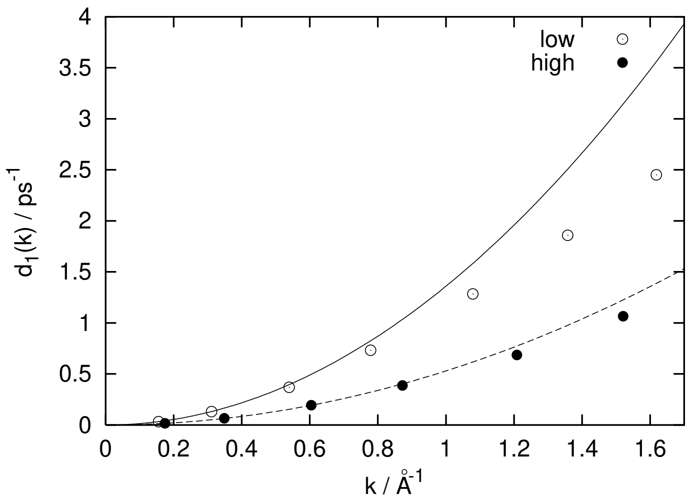

Figure 6. Generalized diffusive mode $d_1(k)$ of a LJ fluid obtained at low- (open circles) and high-density (closed circles). The hydrodynamic asymptotics $\sim\ k^2$ are shown by solid and dashed lines.

$k \to 0$. To show the right hydrodynamic behaviour of the relaxing mode $d(k)$, this mode is plotted in figure 6 together with the function Dk^2 (shown by solid and dashed lines for the low- and high-density fluids, respectively), where D is the self-diffusion coefficient. The values for D, obtained from hydrodynamic behaviour of the relaxing mode $d(k)$, are $5.3 \cdot 10^{-5}$ cm^2/s and $13.6 \cdot 10^{-5}$ cm^2/s at high and low density, respectively. Note that for the low density LJ fluid, the self-diffusion coefficient is almost three times larger than for the high density state. We can also compare these values of the coefficient D, found from the asymptotic behaviour of the relaxing mode $d(k)$, with the results obtained for D from the long-time properties of mean squared displacements. In the later case we found the following values for the self-diffusion coefficient D: $5.39 \cdot 10^{-5}$ cm^2/s at the low density and $14.06 \cdot 10^{-5}$ cm^2/s for the high density state, which is in very good agreement with the results of GCM treatment.

In general, from figures 4–6, one can conclude that the numerical results for the spectra of self-motion modes, obtained for the five-variable basis set $\mathbf{A}^{(5)}$, strongly support the conclusions of an analytical three-variable treatment made in the section 2.

3.3. Single-particle dynamics: Mode contributions

In the previous subsection, the spectra of generalized excitations for single-particle dynamics of a LJ fluid were calculated at two densities and the obtained results were analyzed in comparison with the predictions of the analytical three-variable treatment. In order to find the answer to the question about the contributions of each mode in different ranges of wavenumbers k, we also calculate the corresponding mode amplitudes as the functions of k. This allows us to study in more appropriate way the processes responsible for single-particle motions in different spatial scales.

As it was shown in section 2, the amplitudes of contributions from non-hydrodynamic kinetic-like modes to the single-particle time correlation function $F_s(k,t)$ should be proportional to k^2 [see (12) and (14)] in the range of small wavenumbers k. Figures 7a and 7b plot our results obtained for the amplitudes of mode contributions from the diffusive mode $d(k)$ (figure 7a) and from the oscillating ones (figure 7b). These amplitudes were calculated within the five-variable GCM scheme for the basis set $\mathbf{A}^{(5)}$ using the MD-derived functions needed. It is seen in figure 7 that, as it was expected, the main contribution to the shape of self-intermediate scattering function goes from the extended hydrodynamic mode $d(k)$. The contribution of the high-frequency pair of propagating modes $z_2(k)$ is very small even in comparison with the amplitude of $z_1(k)$. One can also see that, in complete agreement with our predictions, the amplitudes $B(k)$ have the asymptote $\sim\ k^2$ in $k \to 0$ limit, while the amplitude of diffusive mode $d(k)$ tends to unity in that limit. Note that in the range $k < 2.3$ Å^{-1}, the diffusive mode amplitude $d(k)$ is larger than unity, while the symmetric contribution from the oscillating mode $z_1(k)$ is negative. The possibility for such a behaviour of an amplitude $B(k)$, associated with the kinetic-like modes, was predicted within the analytical treatment in section 2.

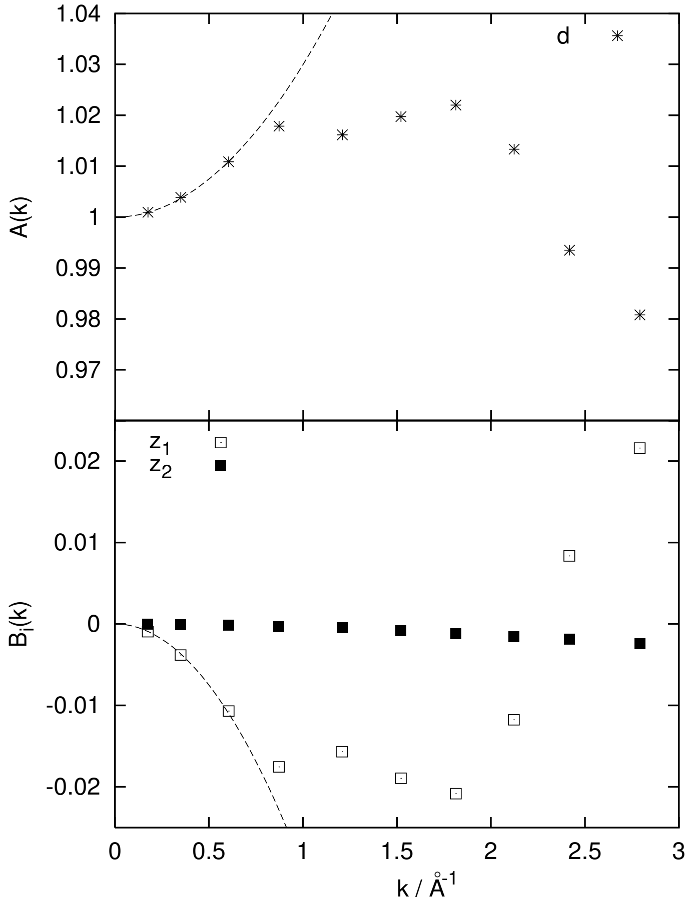

Figure 7. Amplitudes of mode contributions to $F_s(k,t)$ for the high-density LJ fluid: (a) contribution $A(k)$ of the diffusive mode and (b) symmetric oscillating contributions $B_1(k)$, $B_2(k)$ of propagating modes $z_1(k)$, $z_2(k)$. The long-wavelength asymptotes are shown by dashed lines.

3.4. Generalized self-diffusion coefficient

The generalized (k,ω)-dependent transport coefficients often allow one to consider the specific features of transport phenomena on different spatial and time scales. Let us introduce the generalized self-diffusion coefficient $D_s(k,\omega)$ in complete analogy as it was done previously with the generalized shear viscosity $\eta(k,\omega)$ [23]. The following general relation between the relevance memory function and the generalized diffusion coefficient $\tilde{D}_s(k,z)$,

$$\tilde{D}_s(k,z=\mathrm{i}\omega)=D_s^{'}(k,\omega)-\mathrm{i}D_s^{''}(k,\omega)=\frac{1}{k^2}\tilde{\varphi}_s(k,z=\mathrm{i}\omega), \tag{18}$$

can be used, where $\tilde{\varphi}_s(k,z)$ is the Laplace-transform of the lowest-order memory function for $F_s(k,t)$. The memory function can be evaluated from MD-derived self-intermediate scattering function $F_s(k,t)$, namely:

$$\tilde{\varphi}_s(k,z=\mathrm{i}\omega)=\frac{1}{\int_0^\infty \mathrm{e}^{-\mathrm{i}\omega t}F_s(k,t)\mathrm{d}t}-\mathrm{i}\omega. \tag{19}$$

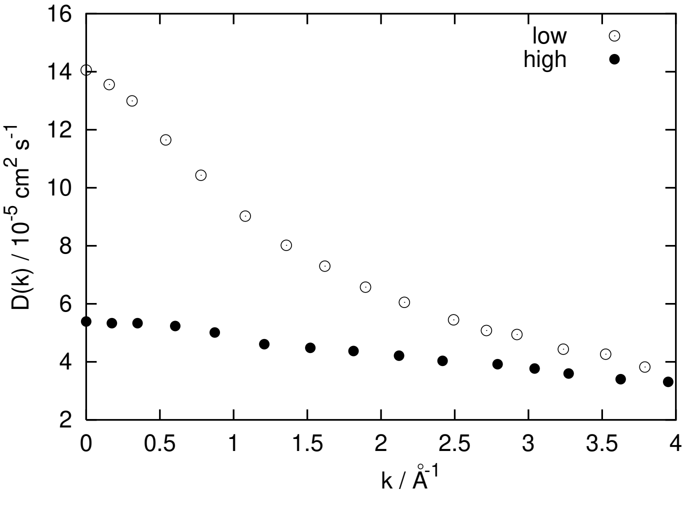

Figure 8. Generalized self-diffusion coefficient $D(k)$ of a LJ fluid, calculated at low- (open circles) and high-density (closed circles). Values at $k = 0$ correspond to estimates found from long-time asymptotics of mean-squared displacements.

In this study we report only the generalized static self-diffusion coefficient, which is obtained from (18) in static limit $\omega = 0$, so that, using (19) and (6), one gets:

$$D_s(k) = D_s^{'}(k, \omega = 0) = \frac{1}{k^2 \tau_s(k)} \tag{20}$$

with $\tau_s(k)$ being the generalized correlation time. Figure 8 plots the results, obtained for the generalized self-diffusion coefficient $D_s(k)$ of a pure LJ fluid at two considered densities. As it was mentioned before, the values at $k = 0$ were also estimated from the long-time behaviour of the mean squared displacements. The evaluated values are in a very good agreement with the small-k behaviour of the generalized coefficient $D_s(k)$ obtained from equation (20). Note that the function $D_s(k)$ has a visible tendency to go to a finite constant when $k \to 0$. This means that the generalized correlation time $\tau_s(k)$, calculated in our MD experiment, has the right asymptotics (proportional to $1/k^2$), predicted by the hydrodynamic theory. In the large wavenumbers limit (or, in other words, in the free-particle limit, where Gaussian-like approximation for $F_s(k,t)$ can be used) it is expected [3] that the generalized diffusion coefficient $D_s(k)$ behaves like $\sim 1/k$. Our results for $D_s(k)$ shown in figure 8 support this prediction for both states considered. This allows us to conclude that in a large k domain the collisional processes with short-time scale (less that τ_{col}) are strongly dominating.

4. Conclusions

The main results of this study are as follows:

(I) The GCM approach is developed for the study of single-particle dynamics in a pure liquid. We start from the simple three-variable scheme and within the analytical treatment testify our method by comparing with the results known previously from the memory function formalism. It is shown that two kinds of processes determine mainly one-particle dynamic properties in a dense fluid. One of them is connected with long-time diffusive motion, and another reflects the elastic properties of a fluid, caused by interactions with the nearest neighbours of the tagged particle – vibrational component of motion or the so-called “cage effect”, which reflects mainly collective properties of a fluid.

(II) Within the GCM approach, each dynamical process can be associated with the relevant excitation, and the spectrum of these excitations can be obtained by solving the eigenvalue-problem for the dynamic matrix, defined for some basis set of dynamic variables. In the three-variable scheme it is shown that in addition to the diffusive-like mode there are the so-called kinetic-like modes, which may describe the oscillating (*collective*) motions in single-particle dynamics. We found that the amplitudes of kinetic modes are proportional to k^2, so that it is difficult to observe their contribution to the self-intermediate scattering function $F_s(k,t)$, but, otherwise, this contribution is dominant in the velocity autocorrelation function $\psi(t)$.

(III) Within the three-variable GCM scheme, the crossover from the relaxing-like behaviour of $\psi(t)$, usually observed in gases and low-density fluids, to the oscillating solid-like behaviour of $\psi(t)$, typical of high-density liquids, is described. We also derived the condition which allows us to distinguish these two cases. It is shown that the existence of an oscillating component in $\psi(t)$ is determined by the value of self-diffusion coefficient D_s and the elastic properties of a fluid, connected mainly with the value of the so-called Einstein frequency. Our theoretical findings are supported by numerical calculations performed within the five-variable GCM scheme for a LJ liquid.

(IV) In order to verify our conclusions, made within the analytical treatment, we compare the results, obtained in the five-variable GCM scheme, with the MD simulations, performed for a LJ fluid at two densities. A very good agreement between the both groups of results is found in a wide range of wavenumbers k considered. It is shown, that the numerical analysis strongly supports our analytical results. In particular, the amplitudes, describing the contributions of kinetic modes to the function $F_s(k,t)$, display the k^2-dependence.

(V) The generalized k-dependent self-diffusion coefficient $D_s(k)$ of a LJ fluid is studied at both densities considered. We found that the values of $D_s(k)$ at $k \to 0$ are in good agreement with the data obtained for D from long-wavelength asymptotics of generalized hydrodynamic relaxing modes $d(k)$. For large wavenumbers k, the free-particle-like behaviour is observed.

An interesting issue, which has to be considered more in detail, is the relation between oscillating single-particle modes and propagating collective excitations, observed in the collective dynamics of fluids. This problem will be the subject of our next study.

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Колективна динаміка в одночастинковому русі для простих флюїдів

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У методі узагальнених колективних мод досліджується одно-частинкова часова кореляційна функція $F_s(k,t)$ простих флюїдів. Для тризмінного базового набору одно-частинкових динамічних змінних отримано аналітичний вираз для відповідної функції розсіяння, що містить осциляційні вклади. Обговорюється значення цих вкладів і показано, що вони зникають у випадку негустих флюїдів. Цей же підхід, розвинутий в п'яти-змінній схемі, використано для аналізу одночастинкових часових кореляційних функцій, розрахованих методом молекулярної динаміки для леннард-джонсівського флюїду при двох значеннях густини. Показано, що запропонований нами метод дозволяє дуже добре відтворити функцію $F_s(k,t)$ в усій області зміни значень хвильового вектора k, яка розглядалася. Вивчено також поведінку узагальненого коефіцієнта дифузії як функції k.

Ключові слова: *одночастинкова динаміка, леннард-джонсівський флюїд, автокореляційна функція швидкості, дифузія*

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