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Generalized collective modes in liquid Cs near the melting point

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Abstract. The dynamical properties of liquid caesium near the melting point are investigated within the generalized collective-modes approach in a Markovian approximation. The generalized thermodynamic quantities and spectra of collective modes have been obtained for the five-variables description of longitudinal fluctuations. As the basis variables, three conserved and two nonconserved quantities have been used: the number density, longitudinal momentum, and energy density; and the first time derivatives of the longitudinal momentum and the energy density. All of the static and dynamic correlation functions were calculated directly from molecular dynamics simulations for 500 particles over 165 000 time steps, avoiding any fitting parameters. A comparison with the experimental data and results of previous molecular dynamics simulations is made.

1. Introduction

The approach of generalized collective modes [1–3] for the investigation of time correlation functions is a modern powerful method, which allows the self-consistent description of dynamical properties of liquids and gases in the hydrodynamic limit as well as beyond the region of small values of the wave-vector k and frequency ω . Within this approach the time correlation functions are obtained as the weighted sums of partial terms, each being associated with the relevant collective excitation as expressed via the eigenvector and eigenvalue of a generalized operator of evolution. Some generalized collective modes correspond in the hydrodynamic limit to the usual hydrodynamic ones. It was shown [3] that for longitudinal fluctuations the three generalized collective excitations with the lowest eigenvalues are equal in the hydrodynamic limit to the heat mode and two sound ones. The other collective modes with higher eigenvalues have finite damping coefficients in the hydrodynamic region and are called the kinetic modes. The number of generalized collective modes is determined by the number of independent dynamical variables; their time evolution may be obtained in computer experiments, and these variables form the basis for evaluation of the relevant time correlation functions. In [4] the seven-variables approximation has been suggested and in [5] the extension to a nine-variables description has been made. There has also been the first attempt to apply the approach of generalized collective modes to binary systems. For the investigation of the fast-sound phenomenon in a binary He–Ne mixture, Westerhuijs *et al* [6] proposed a kinetic model within the five-variables approximation. In

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[6] all elements of the kinetic matrix for finite k -values have been obtained using a procedure involving fitting to experimental data and then extrapolating to the hydrodynamic region.

Despite its attractiveness, the collective-modes approach demands very long molecular dynamics (MD) simulations or complicated fitting procedures [6]. Therefore, MD experiments for multivariable approaches [3–5] were performed for simple model Lennard-Jones systems. In our work we apply the approach described by Mryglod *et al* [4] to the investigation of collective modes in metallic Cs above the melting point. At this thermodynamic point the dynamic properties of liquid Cs have been widely investigated experimentally [7] and numerically using MD simulation [8–10]. Therefore, it seems to us to be a good subject on which to test the first calculations within the collective-modes approach applied to a dense metallic system.

This report is organized as follows. In section 2 we give a short description of the theoretical method, and the approximations which have to be made. Section 3 contains all of the details of the MD simulations, and section 4 is devoted to the discussion of our results in comparison with the experimental data and previous MD-simulation results [8].

2. The theoretical method

We consider a spatially homogeneous, isotropic system of N identical classical particles of mass m in volume V . We start from the definition of the square matrix of time correlation functions $\mathbf{F}^0(k, t)$. Each element of this matrix is the correlation function of two basis dynamical variables:

$$F_{ij}^0(k, t) = \langle A_i(\mathbf{k}, 0) A_j^*(\mathbf{k}, t) \rangle. \quad (1)$$

Here M microscopic dynamical variables $A_i(\mathbf{k}, t)$ form the basis set $\{A_i(\mathbf{k}, t)\}$ for the definition of the $M \times M$ square matrix $\mathbf{F}^0(k, t)$.

Within the Mori–Zwanzig formalism it is straightforward to write down the generalized Langevin equation for the matrix of time correlation functions $\mathbf{F}^0(k, t)$ [11, 3]:

$$\frac{\partial}{\partial t} \mathbf{F}^0(k, t) - i\Omega(k) \mathbf{F}^0(k, t) + \int_0^\infty \mathbf{M}(k, \tau) \mathbf{F}^0(k, t - \tau) d\tau = 0 \quad (2)$$

where $i\Omega(k)$ and $\mathbf{M}(k, \tau)$ are the frequency matrix and the matrix of the memory functions, respectively. This matrix equation can be rewritten in terms of the Laplace transform:

$$[z\mathbf{I} - i\Omega(k) + \tilde{\mathbf{M}}(k, z)] \tilde{\mathbf{F}}^0(k, z) = \mathbf{F}^0(k, 0) \quad (3)$$

and using the Markovian approximation for the memory functions $\tilde{\mathbf{M}}(k, z) \simeq \tilde{\mathbf{M}}(k, 0)$ we obtain the following equation:

$$[z\mathbf{I} + \mathbf{T}(k)] \tilde{\mathbf{F}}_M(k, z) = \mathbf{F}^0(k, t = 0) \quad (4)$$

where

$$\mathbf{T}(k) = -i\Omega(k) + \tilde{\mathbf{M}}(k, 0) = \mathbf{F}^0(k, 0) \tilde{\mathbf{F}}^0{}^{-1}(k, 0). \quad (5)$$

$\tilde{\mathbf{F}}_M$ denotes Laplace-transformed matrix of time correlation functions in the Markovian approximation and \mathbf{I} is the identity matrix. The following properties of time correlation functions in the Markovian approximation are very important from the point of view of sum rules:

$$\int_0^\infty \mathbf{F}_M(k, t) dt = \int_0^\infty \mathbf{F}^0(k, t) dt \quad (6)$$

$$\mathbf{F}_M(k, t = 0) = \mathbf{F}^0(k, t = 0). \quad (7)$$

We may diagonalize the $\mathbf{T}(k)$ -matrix (5):

$$\sum_{i=1}^M T_{ij}(k) X_{j,\alpha} = z^\alpha(k) X_{i,\alpha} \quad (8)$$

where $X_{j,\alpha}$ are the components of the α -eigenvector, and z^α is the relevant eigenvalue. Then equation (4) has the following solution in terms of eigenvectors and eigenvalues of the matrix $\mathbf{T}(k)$:

$$\tilde{F}_{ij}^M(k, z) = \sum_{i=1}^M \frac{G_{ij}^\alpha(k)}{z + z^\alpha(k)} \quad (9)$$

where

$$G_{ij}^\alpha(k) = \sum_{l=1}^M X_{i\alpha} X_{\alpha l}^{-1} F_{lj}^0(k, 0) \quad (10)$$

and in the time representation the solution has the form

$$F_{ij}^M(k, t) = \sum_{\alpha=1}^M G_{ij}^\alpha(k) \exp\{-z^\alpha(k)t\}. \quad (11)$$

This means that each correlation function $F_{ij}^M(k, t)$ can be expressed as a weighted sum of M terms with the time evolution, which is connected with the effective collective mode with eigenvalue $z^\alpha(k)$.

Thus, the entire problem of the time correlation function calculation is divided into three steps: (i) choice of the basis set of dynamical variables; (ii) MD simulations and direct calculations of the static averages $F_{ij}^0(k, t = 0)$; and (iii) solution of equation (4) in terms of eigenvectors of the matrix $\mathbf{T}(k)$ and calculation of all dynamic and thermodynamic properties of the system investigated.

3. Generalized collective modes within the five-variables approach

3.1. The basis set of dynamical variables

We introduce the operators for the number density \hat{n} , momentum \hat{j} and energy \hat{e} in the Fourier representation:

$$\hat{n}(k, t) = \frac{1}{\sqrt{N}} \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_i(t)) \quad (12)$$

$$\hat{j}(k, t) = \frac{1}{\sqrt{N}} \sum_{i=1}^N m \mathbf{v}_i(t) \exp(i\mathbf{k} \cdot \mathbf{r}_i(t)) \quad (13)$$

$$\hat{e}(k, t) = \frac{1}{\sqrt{N}} \sum_{i=1}^N e_i(t) \exp(i\mathbf{k} \cdot \mathbf{r}_i(t)) \quad (14)$$

where

$$e_i(t) = m(\mathbf{v}_i)^2/2 + \frac{1}{2} \sum_{i,j=1}^N (j \neq i) \Phi_{ij}. \quad (15)$$

\mathbf{r}_i , \mathbf{v}_i denote the positions and velocities of particles, and $\Phi_{ij}(\mathbf{r})$ is the two-body potential. The operators (12)–(14) form the set of hydrodynamic microscopic variables

$$\{A_i(\mathbf{k}, t)\}^{\text{hyd}} = \{\hat{n}(k, t), \hat{j}(k, t), \hat{e}(k, t)\}. \quad (16)$$

In [3, 4] the first time derivatives of (13) and (14) have been added to the basis set of hydrodynamic variables:

$$\dot{\hat{j}}(k, t) = \frac{1}{\sqrt{N}} \sum_{i=1}^N m(\mathbf{a}_i(t) + i\mathbf{k} \cdot \mathbf{v}_i(t)\mathbf{v}_i(t)) \exp(i\mathbf{k} \cdot \mathbf{r}_i(t)) \quad (17)$$

$$\dot{\hat{e}}(k, t) = \frac{1}{\sqrt{N}} \sum_{i=1}^N (\dot{e}_i(t) + i\mathbf{k} \cdot \mathbf{v}_i(t)e_i(t)) \exp(i\mathbf{k} \cdot \mathbf{r}_i(t)). \quad (18)$$

In (17) $\mathbf{a}_i(t)$ denotes the acceleration of the i th particle. Further extension of the basis set with higher time derivatives of (13) and (14) has been suggested in [4, 5].

In our work we choose for investigation of the longitudinal fluctuations a basis set of five variables:

$$\{A_i(\mathbf{k}, t)\} = \{\hat{n}(k, t), \hat{j}^L(k, t), \hat{e}(k, t), \hat{j}^L(k, t), \hat{e}(k, t)\} \quad (19)$$

where $\hat{j}^L(k, t)$ denotes the longitudinal component of the current operator. Taking into account the relation

$$\frac{\partial \hat{n}(k, t)}{\partial t} = \frac{i\mathbf{k}}{m} \hat{j}(k, t) \quad (20)$$

and properties of time correlation functions [3, 4] we can see that the 25 correlation functions $F_{ij}^0(k, t)$ of interest are just purely real or purely imaginary. For simplicity we denote the absolute value of $F_{ij}^0(k, t = 0)$ in reduced units as f_{ij} . In the static limit the number of different nonzero correlation functions is reduced to seven averages. In our case the 5×5 Hermitian matrix of static correlation functions $\mathbf{F}^0(k, t = 0)$ has the form

$$\mathbf{F}^0(k) = \begin{pmatrix} f_{nn} & 0 & f_{ne} & -ikf_{jj}^L & 0 \\ 0 & f_{jj}^L & 0 & 0 & -if_{je}^L \\ f_{ne} & 0 & f_{ee} & -if_{je}^L & 0 \\ ikf_{jj}^L & 0 & if_{je}^L & f_{jj}^L & 0 \\ 0 & if_{je}^L & 0 & 0 & f_{ee} \end{pmatrix}. \quad (21)$$

Similarly, taking into account the properties of time correlation functions (see [3, 4]), $\tilde{\mathbf{F}}^0(k, z = 0)$ may be written as

$$\tilde{\mathbf{F}}^0(k) = \begin{pmatrix} \tau_{nn}f_{nn} & (i/k)f_{nn} & \tau_{ne}f_{ne} & 0 & f_{ne} \\ (i/k)f_{nn} & 0 & (i/k)f_{ne} & f_{jj}^L & 0 \\ \tau_{nn}f_{ne} & (i/k)f_{ne} & \tau_{ee}f_{ee} & 0 & f_{ee} \\ 0 & -f_{jj}^L & 0 & 0 & if_{je}^L \\ -f_{ne} & 0 & -f_{ee} & if_{je}^L & 0 \end{pmatrix} \quad (22)$$

where

$$\tau_{ij}(k) = \frac{1}{F_{ij}^0(k, 0)} \int_0^\infty F_{ij}^0(k, t) dt \quad (23)$$

are the hydrodynamic correlation times.

We have to emphasize that the theoretical approach described above does not contain any fitting parameter. Just the Markovian approximation is made to obtain equation (4). The applications of this method [4, 5] showed very reasonable results for the dynamical properties of the model Lennard-Jones system.

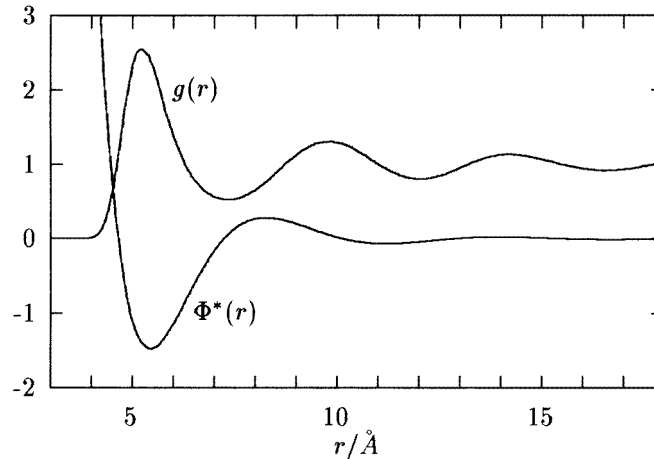


Figure 1. The pair distribution function $g(r)$ and the reduced potential $\Phi^* = \Phi_{ij}/k_B T$.

3.2. Molecular dynamics simulations

We performed MD simulations for liquid Cs with the mass density $n = 1832.1 \text{ kg m}^{-3}$ at the temperature 308 K using a system of 500 particles interacting through the oscillating potential $\Phi_{ij}(\mathbf{r})$ at the constant volume $V = L^3$. The effective two-body potential was obtained from pseudopotential theory using a simple Ashcroft empty-core pseudopotential [12] with the parameter $r_c = 2.72 \text{ au}$, and for the local-field correction the parametrization of Ichimaru and Utsumi [13] was used. The potential was calculated in tabular form on a grid with a mesh size of 0.04 \AA . In order to take into account the Friedel oscillations, the cut-off radius r_{cut} was chosen to be 18.12 \AA , in the vicinity of the sixth node. This kind of interatomic potential gives for the static and dynamic properties of liquid Cs a good agreement with experimental data [8]. The reduced interatomic potential is shown in figure 1.

The equations of motion were integrated by means of a fourth-order predictor–corrector Gear algorithm with a time increment of $\Delta t = 8 \times 10^{-15} \text{ s}$. The initial configuration of particles was the face-centred cubic lattice, and their initial velocities were randomly put into a Maxwellian distribution. The melting of the initial configuration and the subsequent thermalizing were performed in 13 500 time steps. The observation time in the equilibrium state of the system was 1320 ps (165 000 time steps) except for the smallest k -value, where it was enlarged to 4320 ps (540 000 time steps). The energy conservation for the whole MD run was to within less than 0.02%, due to the small value of Δt , the small grid size of the tabulated potential, and the sophisticated integration method. Every sixth configuration was taken into account in the computation of the static equilibrium averages. The time correlation functions were calculated by shifting the time origins ($\Delta t_0 = 6 \Delta t$) on the grid of 512 points in steps of $3 \Delta t$. Additional averaging of the correlation functions was performed over all N_k possible vectors \mathbf{k} (with $|\mathbf{k}| = k$) which are commensurate with the reciprocal lattice of the MD box due to periodic boundary condition. We restricted the k -region by imposing the upper bound $10k_{\text{min}}$, where $k_{\text{min}} = 2\pi/L$ was the smallest possible k -value of 0.16029 \AA^{-1} .

With the help of directly calculated static correlation functions we can obtain the k -

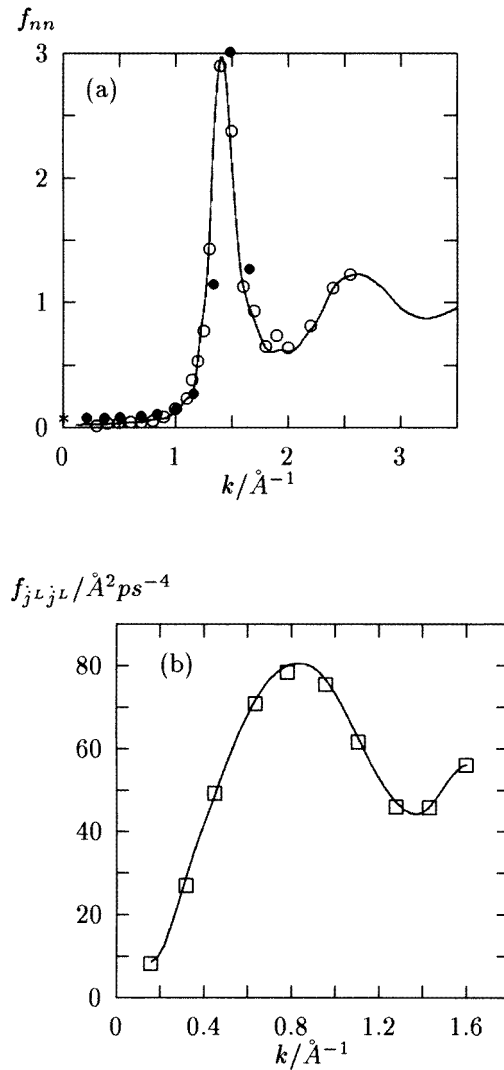


Figure 2. Static correlation functions. (a) Density–density. Full line—the Fourier transform of the pair correlation function; open circles—experimental data [7]; full circles—directly MD-calculated values; asterisk at $k = 0$ —the value from the isothermal compressibility [14]. (b) The static correlator between complex conjugate basis variables (17). Boxes—directly MD-calculated values; full line—the fourth moment of the dynamical structure factor divided by k^2 .

dependence of the generalized thermodynamic quantities using the expressions [3, 16]

$$h(k) = \frac{1}{k_B T k} f_{je}^L(k) \quad (24)$$

$$C_V(k) = \frac{1}{k_B T^2} [f_{ee}(k) - f_{ne}^2(k)/f_{nn}(k)] \quad (25)$$

$$\alpha(k)T = \frac{1}{k_B T} [h(k) f_{nn}(k) - f_{ne}(k)] \quad (26)$$

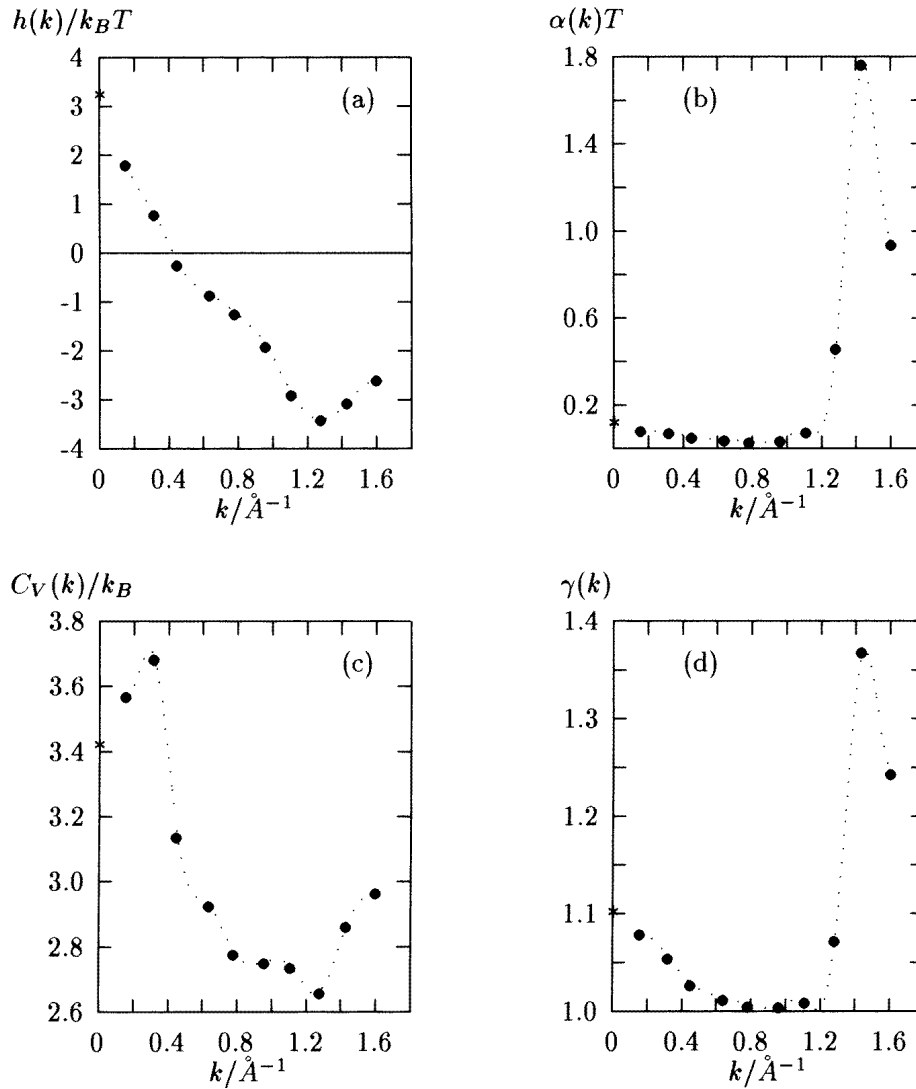


Figure 3. Generalized thermodynamic quantities for liquid Cs at $T = 308$ K: (a) the generalized enthalpy per particle; (b) the generalized linear-expansion coefficient; (c) the generalized specific heat at constant volume per particle; (d) the generalized ratio of specific heats. Asterisk at $k = 0$ in (b)–(d)—experimental values; that in (a)—the calculated value (28). Dotted lines—the spline interpolation.

$$\gamma(k) = \frac{C_P(k)}{C_V(k)} \quad C_P(k) = C_V(k) + k_B T^2 \alpha^2(k) / f_{nn}(k) \quad (27)$$

where k_B denotes the Boltzmann constant, $h(k)$ is the generalized enthalpy per particle, $\alpha(k)$ is the generalized thermal linear-expansion coefficient, and C_V and C_P are generalized specific heats at constant volume and constant pressure per particle, respectively.

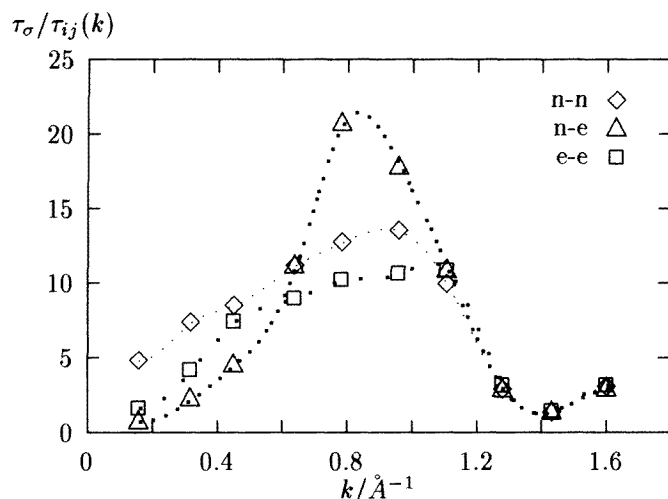


Figure 4. Inverse hydrodynamic correlation times as functions of the wave-vector: diamonds—density–density; triangles—density–energy; boxes—energy–energy. Dotted lines—the spline interpolation.

4. Results and discussion

We calculated the static structure factor (figure 2(a)) in two ways: (i) directly from the definition as the equilibrium average f_{nn} ; and (ii) via Fourier transformation of the pair correlation function (figure 1). In both cases the values obtained give a good agreement with the experimental data [7] and previous MD simulations [8, 9]. The value $S(k=0) = 0.02323$, obtained from the isothermal compressibility [14], is also in good agreement with the extrapolated theoretical values $S(k)$. To check the reliability of the calculated static averages we compared the relevant $f_{ii}, i = j^L, j^L$ with the second ($\langle \omega^2 \rangle(k)$) and fourth moments ($\langle \omega^4 \rangle(k)$) of the coherent dynamical structure factor [15]. The values $f_{jj}^L(k)$ within the numerical accuracy of 1% were equal to the square of the thermal velocity $k_B T/m = \langle \omega^2 \rangle/k^2$. The comparison of the directly calculated $f_{jj}^L(k)$ and $\langle \omega^4 \rangle/k^2$, which are shown in figure 2(b), seems to be very satisfactory. We would like to emphasize that all matrix elements in (21) and (22) were calculated directly from MD simulation avoiding any fitting parameters and numerical derivatives for time correlation functions.

In figures 3(a)–3(d) the generalized thermodynamic quantities (24)–(27) are shown. All curves display nonmonotonic behaviour in the region ~ 1.35 – 1.45 \AA^{-1} which corresponds to the position of the main peak of the static structure factor. The asterisk at $k=0$ for the generalized enthalpy per particle (figure 3(a)) denotes the calculated value [16]:

$$h(k=0) = \bar{e} + p/n$$

$$p = k_B T n - \frac{2\pi n^2}{3} \int_0^{r_{\text{cut}}} g(r) \frac{\partial \Phi_{ij}(r)}{\partial r} r^3 dr \quad (28)$$

where \bar{e} is the average energy per particle, calculated during the MD run ($\bar{e}/k_B T = -3.46727$), and $p, g(r)$, and n are the pressure, the pair distribution function, and the numerical density, respectively. The integral in (28) has been calculated without long-range corrections. The upper limit r_{cut} has been taken because the potential $\Phi_{ij}(r)$ beyond the cut-off radius was assumed to be equal to zero. In figures 3(b) and 3(c) asterisks at $k=0$ denote

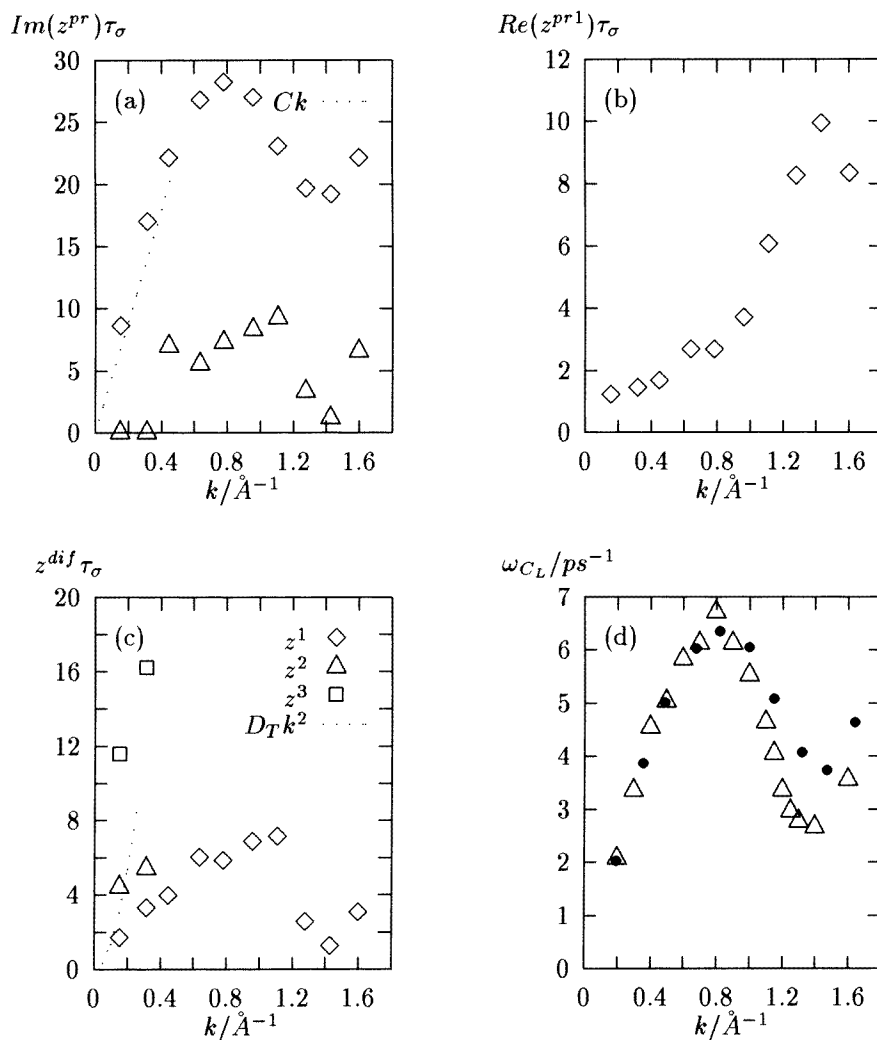


Figure 5. The dispersion of the generalized collective modes. (a) The imaginary part of the eigenvalues for propagating modes. Dotted line—linear dispersion with the experimental value of the speed of sound [14]. (b) The real part of the eigenvalue of the sound-like mode. (c) Purely real eigenvalues. Dotted line—the heat mode (30) with the experimental value of D_T [14]. (d) The peak position of $C_L(k, \omega)$. Triangles—experimental data [17]; full circles—calculated values.

experimental values. For these generalized thermodynamic quantities we may extrapolate theoretical curves well to the points that show experimental values: $\alpha = 28.92 \times 10^{-5} \text{ K}^{-1}$, $\gamma = 1.102$, $C_V = 0.214 \text{ J g K}^{-1}$ [14]. The specific heat C_V has been determined also via the temperature fluctuations [11] during the MD run. The value $C_V = 0.225 \text{ J g K}^{-1}$ obtained is in a reasonable agreement with the experimental data and the extrapolated value of $C_V(k \rightarrow 0)$.

The k -dependences of the inverse hydrodynamic correlation times (23) in terms of the time-scale $\tau_\sigma = (m/k_B T)^{1/2}/k_{\min}$ are presented in figure 4. The curves display behaviour

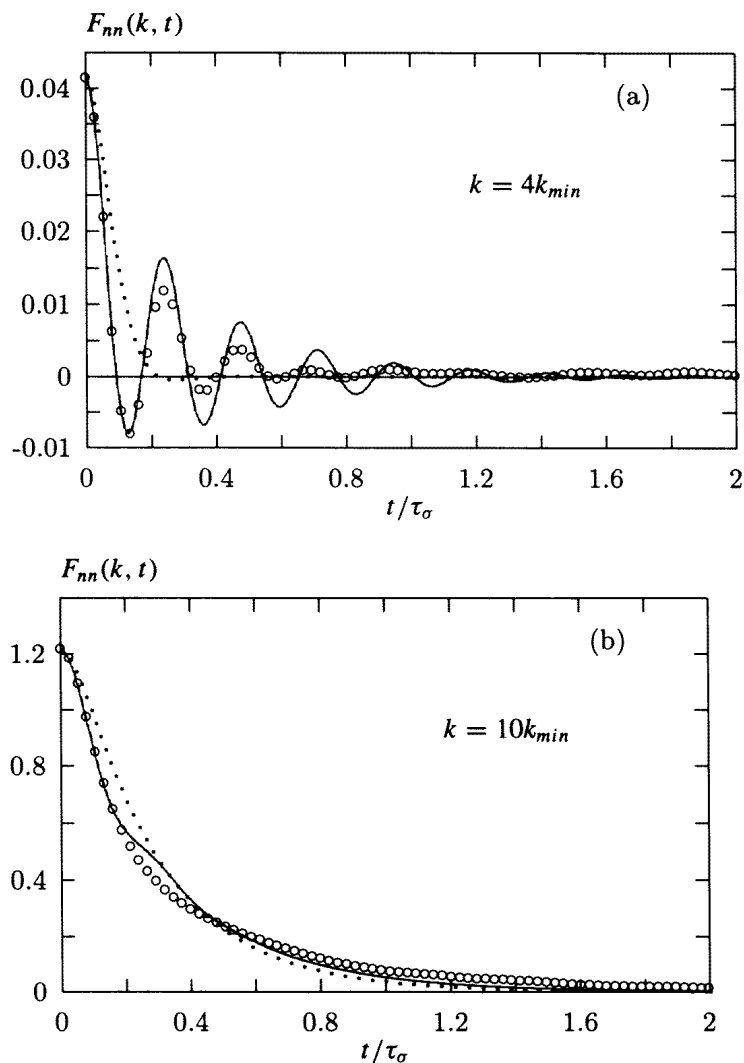


Figure 6. Time correlation functions: density–density ((a), (b)) and energy–energy ((c), (d)), for two values of k . Open circles—MD-calculated time correlation functions; dotted lines—Markovian approximations (11) within the three-variables basis (16); full lines—Markovian approximations within the five-variables basis (19).

with a minimum in the k -region of the main peak of the static structure factor that is similar to the results obtained in [4, 5] for a model Lennard-Jones liquid.

Within the five-variables approach we obtained five generalized collective modes. At small k -values up to $2k_{min}$ there exist two propagating modes with complex conjugate eigenvalues and three diffusive ones with purely real eigenvalues z^α . This is in agreement with the five-modes results for Lennard-Jones fluids [3, 4], where also just two propagating modes in the region of small wave-vectors have been obtained. These propagating modes display dispersion which is typical of the sound excitations, and in the hydrodynamic region the dependence on k of the imaginary part becomes a linear function with a coefficient that

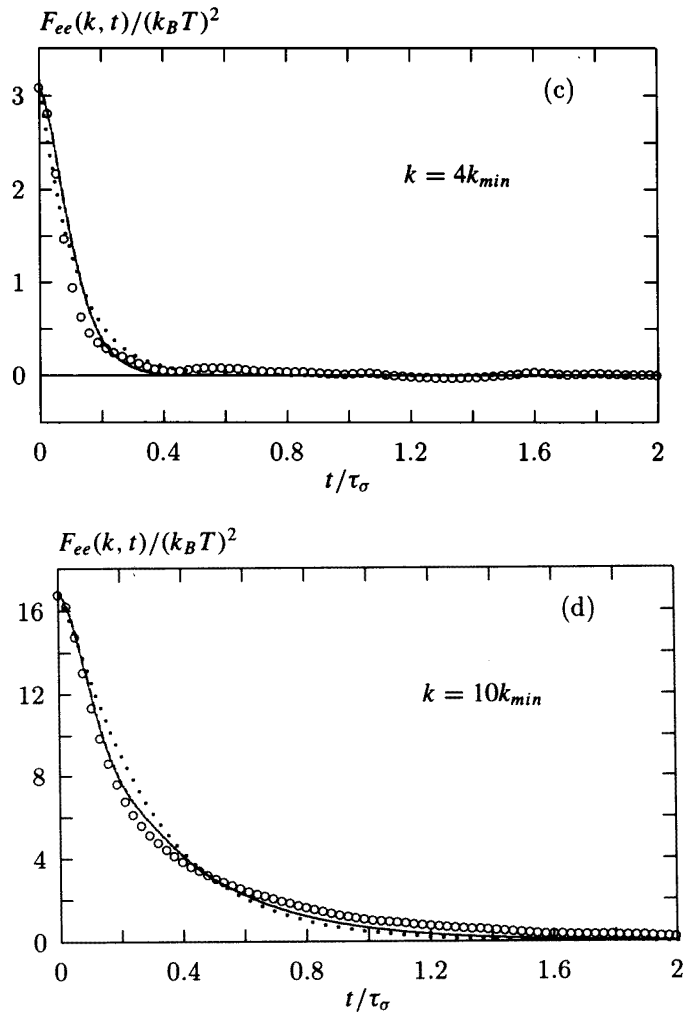


Figure 6. (Continued)

has the meaning of the adiabatic speed of sound:

$$z^\pm(k \rightarrow 0) = \Gamma k^2 \pm iCk. \quad (29)$$

In figure 5(a) the linear dispersion with the experimental value of the adiabatic speed of sound [14] is shown. Our results give the linear coefficient $C = 1180 \text{ m s}^{-1}$ —that is, $\sim 20\%$ larger than the experimental value. The dispersions of the imaginary parts of the propagating modes are shown in figure 5(a). The nonhydrodynamic propagating modes appear for $k > 2k_{min}$ and for them the strong damping $\text{Re}(z^{pr2})\tau_\sigma \simeq 13\text{--}16$ is typical. In figure 5(b) the real part of the eigenvalue for the sound-like propagating mode $z^{pr1}(k)$ is shown. For the smallest k -value we calculated the sound attenuation coefficient $\Gamma = 1.03 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, which is in a very good agreement with the value of $1.01 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ [8], obtained from the fit to the MD density–density time correlation function.

In figure 5(c) the dispersion of purely real eigenvalues is shown; in the hydrodynamic

region it has to behave in the manner predicted by linear hydrodynamics:

$$z^h(k \rightarrow 0) = D_T k^2 \quad (30)$$

and this mode is called the heat mode. For the smallest k -value we obtained the value $D_T = 1.39 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, which is approximately two times smaller than the experimental value of $3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. In figure 5(c) another two purely real eigenvalues z^{dif} are shown; these exist for $k < 3k_{\text{min}}$ and for $k \rightarrow 0$ remain finite and real, in contrast to those for the heat mode (30). We have obtained that within the five-variables description the second purely real mode at the smallest k -value has an eigenvalue comparable with the hydrodynamic one (figure 5(c)), and gives a small contribution to the dynamical structure factor. This leads to the calculated value of D_T being incorrect, and to ‘soft’ dispersion for the lowest real eigenvalue. We enlarged the MD run up to $540\,000 \Delta t$ to get for the smallest k -point well converged values of the static averages f_{ij} , but could not obtain a better agreement with the experimental data for the coefficient D_T . The results of [4, 5] display similar dispersion for a Lennard-Jones system within the five-variables approach, and only the seven- and nine-variables approaches show better agreement with the hydrodynamic dispersion (30).

Using (11) we calculated the Fourier transform of the longitudinal current–current time correlation function:

$$C_L(k, \omega) = \frac{1}{\pi} \text{Re} \sum_{\alpha=1}^M \frac{G_{j^L j^L}^\alpha(k)}{i\omega + z^\alpha(k)} \quad (31)$$

which allowed us to compare the peak positions of $C_L(k, \omega)$ with the experimental data [17] (figure 5(d)), and in the range of k -values up to 0.8 \AA^{-1} we obtained a very good agreement.

In comparison with those of Lennard-Jones systems [3, 5], the density–density time correlation functions of dense metallic systems display strong oscillations for small k -values. To display the role of the basis set choice we compare the MD-calculated time correlation functions $F_{nn}^0(k, t)$ and $F_{ee}^0(k, t)$ with their Markovian approximations (figures 6(a)–6(d)). As is seen from figure 6(a) within the three-variables approximation (with basis set (16)), it is not possible to reproduce the fast oscillations of $F_{nn}^0(k, t)$, while the five-variables approximation gives much better agreement with MD results. For all $k < 8k_{\text{min}}$ we obtained that the three-variables approximation described the MD-calculated $F_{nn}^0(k, t)$ poorly. For k_{min} the value of the speed of sound extracted from the eigenvalue of the propagating mode was 820.9 m s^{-1} , whereas the damping coefficient was nearly three times larger than the one obtained within the five-variables approximation. For $k \geq 8k_{\text{min}}$ the three-variables approximation reproduces $F_{nn}^0(k, t)$ better (figure 6(b)). The MD-calculated functions $F_{ee}^0(k, t)$ (figures 6(c), 6(d)) display over the whole range of k -values nonoscillating behaviour that allows one even within the three-variables approximation to obtain a relatively good approximation for them. From the point of view of short-time behaviour the three-variables approach retains the information about the second time derivative at $t = 0$ of the density–density time correlation function, whereas the five-variables approximation allows one to take effectively into account up to the fourth time derivative at $t = 0$ of $F_{nn}^0(k, t)$ (the static averages f_{jj}^L and f_{jj}^L in (21)) and the second time derivative of $F_{ee}^0(k, t)$ (f_{ee} in (21)). Figures 6(a)–6(d) show that the five-variables approximation gives a considerably better agreement for short-time behaviour of Markovian approximations with MD results than is obtained within the three-variables approximation. For the extended basis set with second and higher time derivatives of (13) and (14), it is possible to take into account the sixth and higher time derivatives at $t = 0$ of $F_{nn}^0(k, t)$, but this demands large computational effort.

We may conclude in this report that in applying the approach of generalized collective modes without any fitting parameters to dense metallic systems, even within just the five-variables approximation we can obtain a reasonable agreement with experiment for the peak position of $C_L(k, \omega)$ and the thermodynamic quantities in the hydrodynamic region. To achieve better agreement with experiment for the dispersion of generalized collective modes for liquid Cs, calculations with the extended basis set of seven dynamical variables are desirable.

Acknowledgments

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