

Interaction-induced light scattering in Lennard-Jones argon clusters: Computer simulations

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Molecular-dynamics simulations have been used to calculate the time-correlation functions and spectra of the depolarized light scattering from a Lennard-Jones argon cluster Ar_{13} . Three thermodynamic phases of Ar_{13} have been studied (solid, solid-liquid coexistence region, liquid) and striking differences between the depolarized Rayleigh spectra of these phases were found. [S1050-2947(97)06509-8]

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I. INTRODUCTION

During the last decade, there has been a great deal of interest in studying very small, nanometer to subnanometer scale, aggregates of particles because their properties are significantly modified from those of bulk materials. Examples are atomic and molecular clusters containing a small number of particles. A distinct feature of clusters as compared to the bulk, particularly of the small ones, is that the local environment can vary dramatically from one atom to the other. This leads to large inhomogeneities in their physical properties. One expects to see the effects of this inhomogeneity in their dynamical properties as one heats a cluster through the temperature region where it changes from a rigid solid to a liquidlike phase. The dynamics of a small cluster as it makes an excursion through different pathways in phase space can be seen through molecular dynamics (MD) or Monte Carlo (MC) simulation experiments. Many studies over the past few decades, based on either MD or MC simulations, have revealed several characteristics of clusters. Clusters undergo the phase transition from solidlike to liquidlike phases as the total energy is increased [1]. The single sharp melting-freezing point of a bulk solid bifurcates in a cluster to give distinct and separate freezing T_f and melting T_m points. The temperature range between T_f and T_m is the cluster coexistence region in which potential energy distributions are found to be bimodal, indicating that the cluster exists in dynamical equilibrium and fluctuates back and forth between the solidlike and liquidlike form [2].

Closely connected with the many-body dynamics of the particles in a system is the phenomenon of depolarized (Rayleigh) light scattering, for the bulk atomic liquids already investigated by the MD method [3]. Naturally, one would like to know whether and how the above-mentioned peculiarities of particles' dynamics in a very small system influence the depolarized Rayleigh spectra of clusters. This is the subject of our computer experiments.

II. SIMULATION DETAILS

The interatomic potential between argon atoms is taken to be the usual Lennard-Jones potential of the form $V(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$, where r_{ij} is the distance between the atoms i and j , and $-\epsilon$ is the minimum of the potential at a distance $2^{1/6}\sigma$. For Ar $\epsilon/k_B = 119.8$ K, $\sigma = 0.345$ nm, k_B is the Boltzmann constant, and the mass of

the argon atom is $m = 6.63382 \times 10^{-26}$ kg. More sophisticated potentials exist for the argon-argon interaction [4]. However, at the present stage we do not make a comparison with some experimental data so the detailed form of the potential is not crucial in this context. The classical equations of motion are integrated up to 10 ns by the velocity Verlet algorithm. The integration time step used is 0.25 fs, which ensures that the total energy is conserved to within 0.01%. The appropriate correlation functions were averaged over 10^3 time origins. The origins were separated by a time interval equal to 20 integration time steps. Our calculations were carried out for a constant energy ensemble for zero total linear and angular momentum of the whole system and the clusters were equilibrated for 2×10^5 MD steps. The average energy can be adjusted as desired by a process of adiabatic heating (or cooling), wherein the velocities are scaled by a factor slightly exceeding (or less than) 1, for a limited time interval at a sufficiently slow rate. This is particularly useful in probing the coexistence region, when the cluster wanders erratically between solid and liquid configurations.

III. RESULTS

The depolarized light scattered by bulk monatomic fluids has been studied for many years. The spectral line shape reflects the time dependence of the polarizability anisotropy of colliding pairs of atoms. The major contribution to the anisotropy is described by the dipole-induced-dipole mechanism (DID) [5]. The DID interactions result from the fact that the incident light beam induces an oscillating dipole on the i th particle and this dipole generates an oscillating local field at the j th particle. The DID mechanism is a two-body interaction that gives rise to two-, three- and four-body correlations contributing to the intensity of scattered light. The depolarized Rayleigh spectrum is the Fourier transform of the polarizability anisotropy autocorrelation function $G(t)$, which for a monatomic sample of N atoms is [5]

$$G(t) \propto \left\langle \sum_{i,j,k,l=1}^N \beta_{ij}(t) \beta_{kl}(0) \right\rangle, \quad (1)$$

where i, j, k, l identify different atoms. The pair anisotropy β_{ij} in the DID limit is [6]

$$\beta_{ij}(t) = \sigma^3 [3x_{ij}(t)z_{ij}(t)/r_{ij}^5(t)], \quad (2)$$

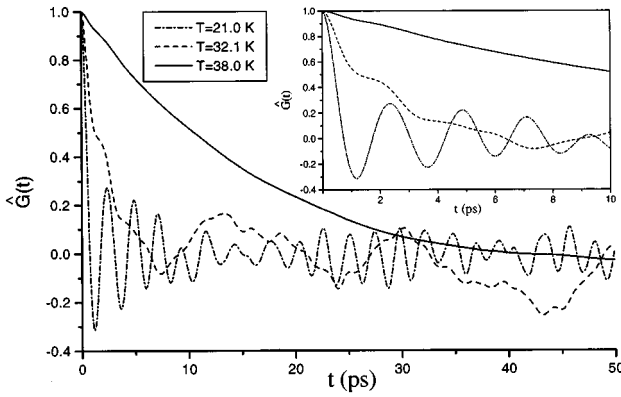


FIG. 1. The normalized total light scattering correlation functions $\hat{G}(t)$ of an Ar_{13} cluster at three thermodynamic phases: solid state at $T=21$ K, solid-liquid dynamical coexistence region at $T=32.1$ K, and liquid at $T=38$ K.

where x_{ij} and z_{ij} are components of the separation vector \mathbf{r}_{ij} between the i th and j th atoms. The correlation function $G(t)$ can be decomposed into pair, triplet, and quadruplet contributions

$$G(t) = G_2(t) + G_3(t) + G_4(t), \quad (3)$$

$$G_2(t) \propto \left\langle \sum_{i,j=1}^N \beta_{ij}(t) \beta_{ij}(0) \right\rangle, \quad (4)$$

$$G_3(t) \propto \left\langle \sum_{i,j,k=1}^N \beta_{ij}(t) \beta_{ik}(0) \right\rangle, \quad (5)$$

$$G_4(t) \propto \left\langle \sum_{i,j,k,l=1}^N \beta_{ij}(t) \beta_{kl}(0) \right\rangle. \quad (6)$$

The first term $G_2(t)$ in Eq. (3) is responsible for depolarized light scattering in the low-density limit [gas phase where $G(t) \cong G_2(t)$], while the other two can become important at high density. For the bulk samples at liquid densities, the positive two- and four-body contributions are almost exactly canceled by the negative three-body term, and the total intensity is much smaller than any of the components [3].

In this paper the n -body correlation functions $G_n(t)$ ($n=2,3,4$) and $G(t)$ of Ar_{13} cluster have been calculated *via* the MD method at several temperatures corresponding to the solid state phase ($T=21$ K), the solid-liquid coexistence region ($T=32.1$ K), and the liquid state phase ($T=38$ K).

The normalized total correlation functions $\hat{G}(t) = G(t)/G(0)$ are presented in Fig. 1. One observes the striking differences between $\hat{G}(t)$ plots representative of three temperature regimes (phases) mentioned above. For the solidlike domain at low temperature $T=21$ K each atom oscillates around its equilibrium position (no diffusion). As expected, the corresponding total correlation function $\hat{G}(t)$ pulsates too, reflecting the oscillatory motions of atoms. On the contrary, at higher temperature $T=38$ K (liquid state of Ar_{13}) the correlation function $\hat{G}(t)$ decays slowly, regularly, and without feature. A similar, very monotonic decay was also reported for $\hat{G}(t)$ of bulk liquid argon [6–9]. However, the function $\hat{G}(t)$ of a liquid Ar_{13} cluster decays much more

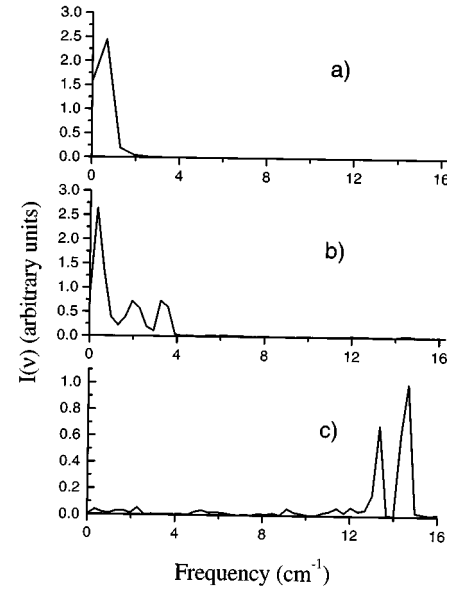


FIG. 2. Frequency transforms $I(\nu) = \int_0^\infty dt \hat{G}(t) \cos(2\pi\nu t)$ of the total correlation functions $\hat{G}(t)$ of an Ar_{13} cluster at three thermodynamic phases: (a) liquid at $T=38$ K, (b) solid-liquid coexistence region at $T=32.1$ K, (c) solid state at $T=21$ K.

slowly than its counterpart of bulk liquid. For example, for bulk liquid argon at $T=89$ K the correlation function $\hat{G}(t)$ decays to zero after ~ 3 ps [6], while for liquid Ar_{13} it persists for a period about ten times longer (see Fig. 1). The DID interaction varies as r_{ij}^{-3} and $\hat{G}(t)$ depends almost entirely upon interactions among atoms that are within the distance no longer than 3.5σ . This interaction dies down slowly enough to guarantee that in a bulk liquid many neighboring atoms (several tens) will contribute significantly to $\hat{G}(t)$. In an Ar_{13} cluster each atom has only 12 neighbors, and the resulting interaction is much weaker. An additional cause of the observed slow decay of $\hat{G}(t)$ may be that the liquid phase of the argon cluster Ar_{13} exists only in the low-temperature range 36–41 K (Ar_{13} vaporizes at ≈ 42 K). The diffusion of atoms in the low-temperature liquid is less effective and much slower, compared to the atoms' mobility in the liquid phase of a bulk system, which exists in substantially higher temperature.

The plot of $\hat{G}(t)$ for the liquid-solid coexistence region at $T=32.1$ K is again different from both cases discussed above. Its behavior interpolates between the decay of $\hat{G}(t)$ for the solid and the liquid state, which reflects the complicated dynamics of atomic motion in this unusual thermodynamic phase. The inset in Fig. 1 shows in detail the discussed correlation functions $\hat{G}(t)$ for the short-time region. In Fig. 2 we present the corresponding power spectra of the depolarized light scattering of Ar_{13} cluster, i.e., the Fourier transforms of the functions $\hat{G}(t)$. Significant differences between the light-scattering spectra of the various phases are observed.

For the bulk materials, the separate two-, three- and four-body correlation functions $G_n(t)$ are sometimes discussed, in addition to the total function $G(t)$. An example of the separately calculated $G_n(t)$ for Ar_{13} in the liquid phase at $T=38$ K is shown in Fig. 3. The cancellation effect of nega-

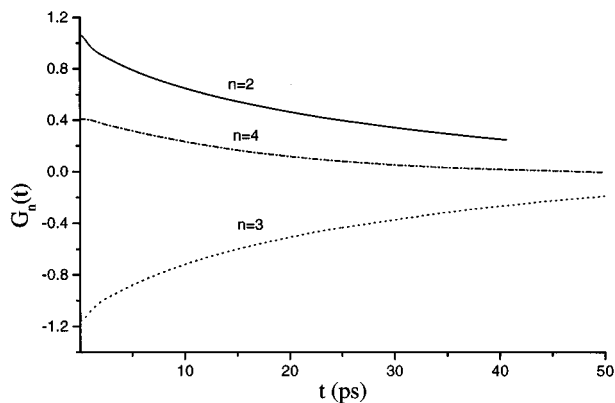


FIG. 3. The two-, three- and four-particle correlation functions $G_n(t)$ ($n=2,3,4$) of an Ar_{13} cluster in the liquid state at $T=38$ K.

tive $G_3(t)$ with positive $G_2(t)$ and $G_4(t)$, characteristic of the bulk systems, is clearly seen for the cluster case too.

The relationship between the ratios of the component $G_n(t)$ correlation functions and the anisotropic fluctuations that cause depolarized light scattering can be explored by examining the self-correlation function. This describes the fluctuations in induced anisotropy of an individual atom [10], and is experimentally probed by dielectric relaxation and in the molecular case by depolarized Raman scattering:

$$G_s(t) \sim \left\langle \sum_i \beta_i(t) \beta_i(0) \right\rangle, \quad (7)$$

where β_i , the induced anisotropy of an atom i , is defined by $\beta_i = \sum_{j(j \neq i)} \beta_{ij}$. It follows from this definition that

$$G_s(t) = 2G_2(t) + G_3(t). \quad (8)$$

If the environment of an atom is isotropic for all times, as in a static face-centered cubic lattice, for example, then the induced anisotropy β_i is zero. In this case, the total correlation function, which can be written as $G(0) = \langle \sum_{i,j} \beta_i \beta_j \rangle$, is zero, as is the self-contribution. It follows from Eqs. (3)–(6) and (8) that the ratio of pair-triplet-quadruplet terms is 1:–2:1, the total of course being zero. Therefore, if at $t=0$ the ratio of $G_2:G_3:G_4$ is 1:–2:1, it means that the environment of the atoms is permanently isotropic. In fact, at $T=38$ K the $t=0$ ratios for Ar_{13} are 1:–1.09:0.38, which indicates that the fluctuations from isotropy in a liquid Ar_{13} are substantial (note that in dilute gas the ratio is 1:0:0, reflecting large

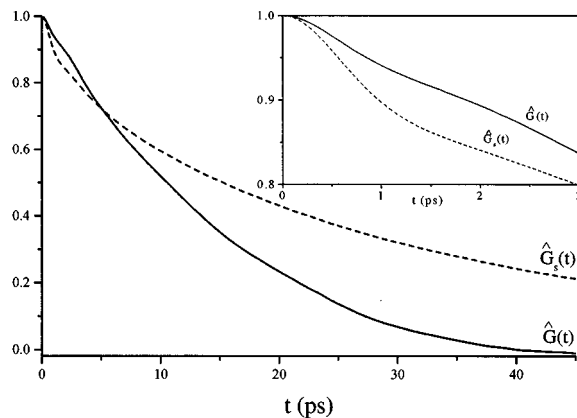


FIG. 4. Comparison of the normalized, self- $\hat{G}_s(t)$ and total $\hat{G}(t)$ correlation functions of Ar_{13} cluster in the liquid phase ($T=38$ K).

instantaneous anisotropies). In Fig. 4 we show the normalized total and self-correlation functions for liquid Ar_{13} . Compared to $\hat{G}(t)$, the self-correlation function $\hat{G}_s(t)$ decays faster for short time $t < 5$ ps. For times greater than 5 ps, the total correlation function $\hat{G}(t)$ decays more rapidly than the self-contribution $\hat{G}_s(t)$, which reflects the fact that the anisotropy of an atom β_i decouples more rapidly from that of its neighbors β_j than it does from itself. The inset in Fig. 4 shows the short-time region of $\hat{G}(t)$ and $\hat{G}_s(t)$.

Several issues may be addressed for future work, including the following: (i) sensitivity of the simulated spectra to the detailed form of interatomic potential, i.e., other than a simple LJ potential, (ii) inclusion of overlap and hyperpolarization effects in the pair polarizability of argon atoms [5], which become more important for small r_{ij} , when the electron clouds of the two atoms overlap, (iii) simulations on clusters of different compositions and sizes. The present work is mainly of theoretical interest since the intensity of the depolarized light scattering of small clusters is much weaker than in the bulk material. The low-temperature environments where the small atomic or molecular clusters probably can exist are some areas of the interstellar space. These studies might be linked to the discussion on the spectrum of cosmic dust [11].

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