Structural dynamics of clusters near melting

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Unlike their bulk counterparts, clusters show a *smooth* transition from a low-temperature solidlike to a high-temperature liquidlike phase. Previous studies have established the variation of maximum Lyapunov exponent and the presence of $1/f$ noise in the power spectra of potential energy fluctuation as "dynamical indicators" of this transition. Here we propose that the coexistence can be efficiently studied using the self-part of the dynamic structure factor (DSF). To support our claim, we present molecular dynamics simulation results for the Ar_{13} cluster. We find that the spectral features of the DSF are strongly wavelength dependent and its long time behavior is anomalous, a result of the dynamic excursion between the two coexisting phases.

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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 [1]. 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 from its ground state through the temperature region where it changes from a rigid solidlike to a soft liquidlike phase [2].

The dynamics of a small cluster as it makes an excursion through different pathways in phase space can be seen through molecular dynamics simulation experiments. Such studies go back to the earlier work of Brian and Burton [3] which has been extended very thoroughly in a series of recent papers by Berry and his co-workers [2]. The major outcome of these simulation studies is that the short time averages of the kinetic energy of such systems, e.g., Ar_{13}, show a *bimodal* distribution. This corresponds to the coexistence of a "hot" solidlike phase and a "cold" liquidlike phase. More recently it has been shown by Nayak, Ramaswami, and Chakravarty [4] that the signature of the coexistence is clearly seen in the dramatic increase of the maximum Lyapunov exponent. In a subsequent paper Nayak *et al.* also established the presence of $1/f$ noise in the power spectra of the potential energy fluctuation of a "tagged" particle [5]. The cluster makes dynamic excursions between two regions of phase space with two distinct types of features, solidlike and liquidlike.

Since classical dynamics of clusters is chaotic, it has been rightly studied previously by looking at it as a "chaotic dynamical system." The presence of $1/f$ noise in the power spectra in potential energy fluctuation reflects a temporal scale invariance. But solid-liquid transitions are usually associated with a structural rearrangement, therefore one expects the frequency (ω) and wave-vector (k) dependent dynamic structure factor (DSF), $S(k,\omega)$, of the cluster to reflect the characteristic features associated with solidlike and liquidlike phases. In addition, by changing k, or equiva-

lently the length scale over which the dynamics is probed, one can expect to see the inhomogeneous nature of the cluster. These studies, although very demanding, have not been addressed properly in the past. In this Rapid Communication, we show that the DSF can be used as a very efficient tool to probe cluster melting. This is the main theme of this paper. One also notices that in a real experiment with neutrons the inelastic scattering cross section is directly proportional to the self-part of the dynamic structure factor giving further motivation to carry out a computer calculation of this quantity.

To strengthen our argument we also note that a similar situation arises in molecular dynamics (MD) simulation of two-dimensional fluids in the presence of strong substrate potential [6]. In these systems when the temperature is high the atoms spend most of their time undergoing diffusive motion as in a homogeneous liquid. As the temperature is lowered, the atoms get trapped for some time near the potential minima of the substrate potential undergoing a solidlike oscillatory dynamics. The net result is an interesting coexistence of two different types of dynamics which shows up as two central-peak structures (one narrow and the other broad) in the self-part of the DSF, $S_s(k,\omega)$, for certain values of k. Here we discuss in detail the frequency and wave-vector dependence of $S_s(k,\omega)$ for Ar_{13} near the melting region to see whether similar effects can be observed in their dynamics.

We have used the Lennard-Jones potential to describe the interaction between rare gas atoms. The potential energy is given by

$$V = \sum_{i<j} V_2(r_{ij}) = \sum_{i<j} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (1)$$

where r_{ij} is the distance between two atoms, and ϵ and σ are the two standard Lennard-Jones parameters. For Ar $\epsilon = 120$ K, and $\sigma = 3.4$ Å.

We have performed molecular dynamics [7,8] simulation for both constant E and constant T (Nosé dynamics) [9] ensembles for zero linear and angular momentum for the whole system. The equation of motion was integrated up to 1 ns in steps of 0.5 and 0.25 fs for constant E and constant T ensembles, respectively.

To explore the transition region, we start from an icosahedral configuration of Ar_{13} and heat it up slowly using a constant energy scheme. To identify the melting transition we have monitored the average kinetic energy $\langle \mathscr{E}_{KE} \rangle$ as a function of E in constant E simulation, and the average bond length fluctuation (either as a function of T or E) [2].

To probe the dynamics we have calculated the self-part of the DSF, $F_s(k,t)$, defined as

$$F_s(\vec{k},t) = \frac{1}{N} \sum_i \exp\{i\vec{k} \cdot [\vec{r}_i(0) - \vec{r}_i(t)]\}, \qquad (2)$$

and its Fourier transform $F_s(\vec{k},\omega)$.

From Eq. (2), one obtains

$$\left(\frac{\partial^2 F_s(k,t)}{\partial k^2} \right)_{k=0} = -\frac{1}{3} \langle |r(t) - r(0)|^2 \rangle. \qquad (3)$$

Therefore for a purely diffusive motion

$$\left(\frac{\partial^2 F_s(k,t)}{\partial k^2} \right)_{k=0} = -2Dt, \qquad (4)$$

i.e., $F_s(k,t) \sim \exp(-k^2 Dt)$. The corresponding $F_s(k,\omega)$ is a Lorentzian. On the other hand, for a ballistic propagation, the right hand side of Eq. (3) $\langle v^2 \rangle \sim t^2$, leading to a Gaussian $F_s(\vec{k},\omega)$.

Also, in order to compare our results with previous MD simulations [10] we have calculated the normalized velocity autocorrelation function (VACF) $A(t)$ given by

$$A(t) = \frac{\langle \vec{v}(t) \cdot \vec{v}(0) \rangle}{\langle \vec{v}(0) \cdot \vec{v}(0) \rangle}, \qquad (5)$$

and its Fourier transform, $V(\omega)$.

Earlier studies by Jellinek, Beck, and Berry [11] have shown that the general features of the cluster dynamics can be characterized by three different temperature or equivalently three different energy regimes: the low-temperature regime exhibiting solidlike properties, the coexistence regime which has the characteristic of both solid and liquid, and the high-temperature liquid regime. In the constant E simulation, the transition region is bounded between two energies E_f and E_m. For $E < E_m$, the diffusion constant D, obtained from the zero frequency limit of $V(\omega)$, was found to be practically zero. In addition, $V(\omega)$ showed sharp finite frequency structures associated with the nearly harmonic dynamics. For $E > E_m$, the diffusion constant was large as expected for a liquid and the finite frequency structures were washed out. In the coexistence region $V(\omega)$ showed the characteristic feature of a "cold liquid," namely, a finite but small $V(0)$, and that of a "hot" solid: broadened finite frequency peaks. In fact, a careful analysis of the energy dependence of $V(0)$ or the diffusion constant D reveals [10] that in the range $E_f < E < E_m$, the energy dependence of D changes rapidly near the midpoint of the interval $[E_f, E_m]$. For Ar_{13}, $E_f = -4.40$ (we will express the cluster energy in units of 10^{-14} erg/atom) and $E_m = -3.75$. We have chosen several values of E spanning the solid and the coexistence region. We have also taken two energy values which correspond to
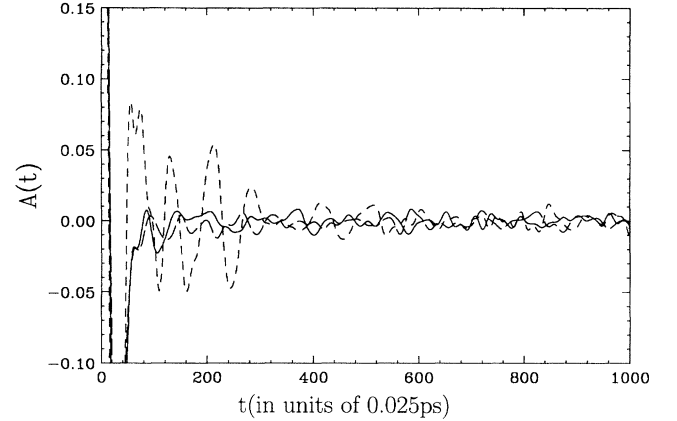

FIG. 1. Velocity autocorrelation for three different values of energies at the solid (dashed), transition (solid), and liquid (wide dashed) regime in the constant energy ensemble. The energies and the average temperatures are -4.78, -4.06, and -3.85 (in units of 10^{-14} ergs/atom), and 23.3, 33.8, and 35.9 K, respectively.

the fluid phase. It should be noted however that physical quantities vary smoothly as a function of E. Only when plotted as a function T (obtained from the mean kinetic energy per particle), these quantities show rapid changes near the transition temperature. The simulations for constant E and constant T give practically identical results. Here we present the results for constant energy simulations only.

Figure 1 shows the normalized VACF for three different values of energy corresponding to the solid, the transition region, and the liquid phase and Fig. 2 gives the corresponding power spectra which was first calculated by Jellinek, Beck, and Berry [11]. Here we reproduce their results for slightly different values of energy and average temperature for the sake of completeness. The energies are -4.78, -4.06, and -3.85, respectively. The corresponding average temperatures are 23.3, 33.8, and 35.9 K. For a similar set of temperatures simulations performed with the Nosé dynamics give practically identical results. The power spectra in both the ensembles show similar behavior; a relatively large value
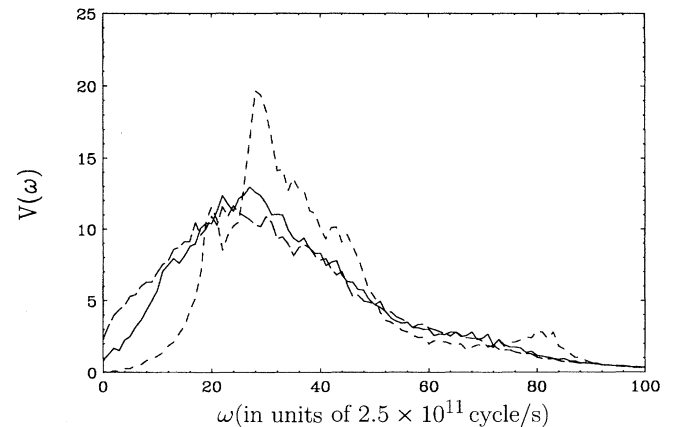

FIG. 2. The corresponding power spectra where the symbols have the same meaning as above (Fig. 1).
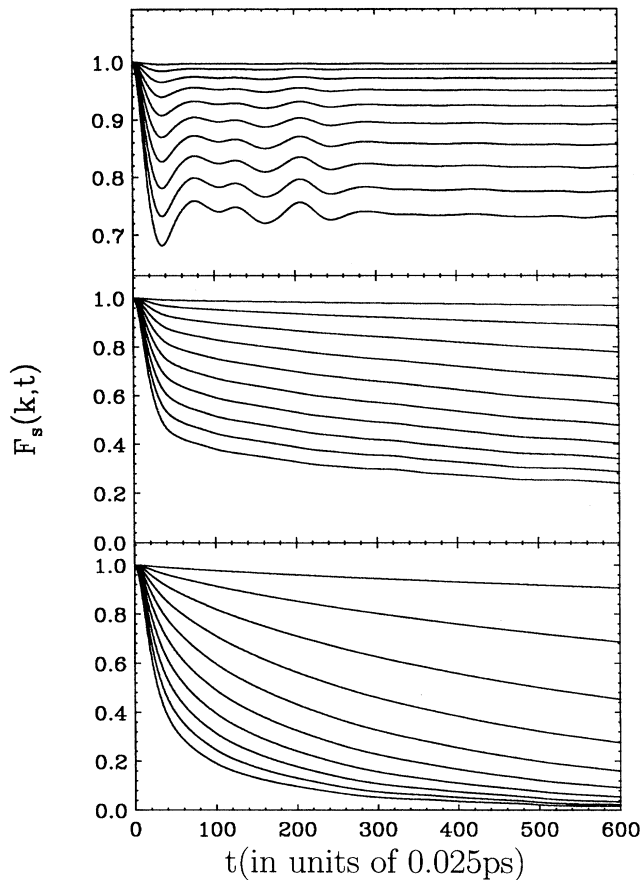
FIG. 3. $F_s(k,t)$ for solid (top), transition (middle), and liquid (bottom) for several values of k (from 1 to 10) in units of 3.4 Å^{-1}. In each figure the magnitude of the wave vector increases from top ($k=1$) to bottom ($k=10$).

FIG. 4. The corresponding Fourier tranforms. The magnitude of the wave vector increases from bottom ($k=1$) to top ($k=10$).

for $V(\omega=0)$ for the high-temperature phase, zero for the solid phase, and a very small but finite value for the coexisting phase. Similar simulation results were reported by Berry and co-workers as mentioned earlier.

Finally we discuss in detail the k dependence of $F_s(k,t)$ and its Fourier transform in the three different temperature regimes mentioned above. The small k values are determined by the average size of the cluster. Our simulations show that the average size varies from 3σ to 4σ. So values of k ranging from $k\sigma=1.0$ up to 10 would be reasonable to explore the structural dynamics. From Eq. (4), we see that for $k=0$, $F_s(k,t)$ is independent of t at all temperatures and therefore $F_s(k,\omega)$ is a δ function. As we increase k, we reach a characteristic length scale comparable to the size of the cluster. Near this k (k_c) one should be able to optimally probe the inhomogeneous aspects of the cluster dynamics. For larger values of k, one essentially probes the high-frequency quasiharmonic dynamics. For the Ar$_{13}$ cluster we estimate $k_c\sigma\cong2$.

Figure 3 shows $F_s(k,t)$ for different values of k and for three different temperature regimes. In the solidlike phase (top), the nearly harmonic dynamics of the cluster shows up as well defined oscillations. The amplitudes of these oscillations increase with k. The structure factor remains quite
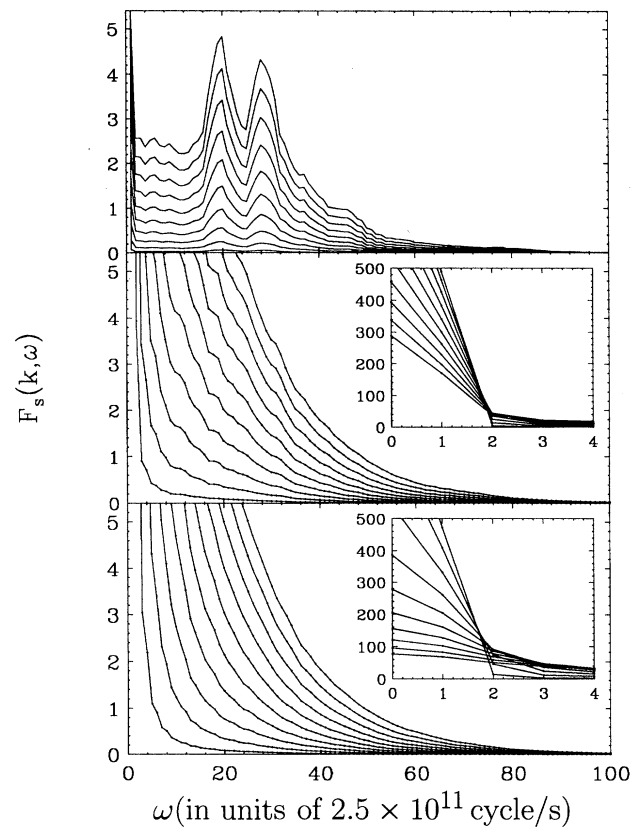
large for times up to 20 ps (several times larger than the oscillation period) even for large values of k. For example, for $k\sigma=10$, $F_s(k,t)$ is about 0.72 for $t=20$ ps. In fact, $F_s(k,t)$ appears to approach a constant value for large k. Our numerical data show that the k dependence of this asymptotic value of $F_s(k,t)$ is a Gaussian. This is nothing but the Debye-Waller factor for the cluster. In the liquidlike phase (bottom) the oscillations are completely washed out and for the same value of k, $F_s(k,t)$ decays to about 0.04 for the same time. Now let us concentrate on the coexistence regime (middle). In marked contrast to both the liquid and the solid regimes, the $F_s(k,t)$ in the coexistence regime shows roughly two distinct time scales; the initial decay is rather fast (1–2 ps) and then the correlation persists for long time with a very slow decay. This slow decay corresponds to a long lived correlation which, unlike the solid regime, eventually decays, but at an extremely slow rate. We emphasize that this difference is *qualitative* and can be used as an identification mark to infer if the system is in the coexistence regime.

In Fig. 4 we give $F_s(k,\omega)$ for several values of k for the same three values of E for which we computed the VACF, its power spectrum, and the self DSF [12]. In the solidlike phase, one sees well defined peaks whose spectral amplitude increases with k. This is characteristic of quasiharmonic dynamics where the peaks appear at the same frequencies where $V(\omega)$ shows peaks. In the liquidlike state, $E>E_m$, one sees a Lorentzian structure for small k which changes to

a Gaussian for large k, again a characteristic feature of liquid dynamics. In the coexistence region the overall features of the spectral function are closer to those of a liquid than to a solid, excepting at very low frequencies. For large frequencies the $F_s(\vec{k}, \omega)$ in the transition region is almost that of a liquid. But careful inspection shows that for all values of the wave vector if one approaches from the high-frequency side towards $\omega \to 0$, the two superimposed patterns start to deviate. For the coexistence regime the curve shifts towards the origin and the approach to $F_s(k, \omega = 0)$ is sharper than the corresponding curve for the liquid for the same value of k. The value of ω where this deviation starts to occur depends on the particular value of k.

In summary, we have pointed out that the dynamics of a cluster near melting can be probed at different length scales through $F_s(k, \omega)$. In particular, $F_s(k, \omega)$ shows a line shape

characteristic of a quasilocalized liquid, a narrow central peak sitting on top of a broad one. We have carried out similar analysis for an Ar_{19} cluster whose ground state structure is a double icosohedron [13]. Here also we find the same characteristics to identify the transition regime. However, it is worth noticing that both Ar_{13} and Ar_{19} belong to "magic clusters" and the surface atoms form closed shells. It would be worthwhile to see if clusters whose one or many surface atoms are loosely bound exhibit multimdodal distribution and a concomitant anomalous tail in $F_s(k, t)$. This study is currently under investigation, and we plan to report it in a separate publication.

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