

1/f Spectra in Finite Atomic Clusters

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We study small clusters of atomic argon, Ar₇, Ar₁₃, and Ar₅₅, in the temperature range when they undergo a transition from a solidlike phase to a liquidlike phase. The power spectra of potential energy fluctuations of tagged atoms in the liquid state show 1/*f* behavior over a wide range of frequency *f*, unlike either the solid phase or bulk liquid, and suggest a new experimental means of detecting cluster melting. The origin of this temporal scale invariance is explored by studying the individual potential energy distributions, which are observed to become multimodal when the clusters melt.

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Molecular dynamics (MD) simulations of small Lennard-Jones clusters have given evidence for a transition from a solidlike phase to a liquidlike phase as the internal energy is increased [1,2]. It has been seen in a variety of studies that clusters of different sizes exhibit dynamical coexistence [3] of these phases over a well-defined energy range, in contrast to phase transitions in bulk matter.

One striking aspect of cluster dynamics is that correlations are long lived, and in this Letter we examine the persistence of correlations by studying fluctuations of the potential energy of tagged atoms. Such fluctuations, which are related to the internal temperature of the cluster, have a characteristic “1/*f*” power spectrum, indicating temporal scale invariance, which is seen over a considerable range of frequency *f*.

The classical dynamics of clusters is chaotic [4], arising from the nonlinear nature of the underlying potential energy surface [5]. This is reflected in large positive Lyapunov exponents, particularly in the liquidlike state [6]. The cluster moves from one configuration to another along an extremely jagged path on the potential energy surface (the local minima are the so-called inherent structures [7]). However, the intrinsic spatial anisotropy of clusters—the sharp difference between surface atoms and those in the interior—gives rise to memory effects, and the system retains some long-range temporal correlations.

Attention to the existence of such long-lived correlations was first drawn by Ohmine and co-workers [8] who observed large scale potential energy fluctuations in MD simulations of liquid water. Analysis in the frequency domain as well as in the time domain showed that the power spectrum of such energy fluctuations has a 1/*f* (more accurately, 1/*f*^α, 1 < α < 2) dependence [9]. 1/*f* noise is often seen as a temporal signature of complex dynamics, where there is no characteristic length or time scale. Correlations in such (usually nonequilibrium) systems decay with power laws resulting from the absence of an intrinsic

scale. One framework within which power-law correlations may arise in such systems (particularly if there are widely separated rates of relaxation) is the concept of a self-organized criticality [10,11]. The application of such ideas to the behavior of small systems—and the clusters considered here are indeed small—must be made with care. Systems consisting of a few atoms do not undergo true phase transitions in the same way as bulk matter does, and thus the critical state cannot be truly scale invariant. Nevertheless, the motion of atoms from surface to core [12,13] and vice versa in the cluster gives rise to temporal correlations which are long lived in the liquidlike phase.

In the present work, we study small clusters of rare gas atoms, Ar_{*n*} clusters of sizes *n* = 7, 13, and 55. Simulations are carried out using standard MD techniques [14]. The interatomic potential between neutral rare-gas atoms is taken to be the usual Lennard-Jones potential of the form

$$V(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6], \quad (1)$$

where *r_{ij}* is the distance between the atoms *i* and *j* and $-\epsilon$ is the minimum of the potential at distance $2^{1/6}\sigma$, σ being the unit of length. The classical equations of motion are integrated by the velocity Verlet algorithm; all the quantities are expressed in scaled form, time and distances by $(m\sigma^2/48\epsilon)^{1/2}$ and σ , respectively. We choose ϵ and σ appropriate to argon [15]: $m = 6.63382 \times 10^{-26}$ kg is the Ar mass, $\sigma = 0.3405$ nm, and $\epsilon = 119.8$ K. The time step used is 0.01 in reduced units (3.125 fs), and the total energy is conserved to within 0.01%.

The sizes studied, *n* = 7, 13, and 55, are “magic” numbers for rare-gas clusters [16]. Simulations are carried out for zero total linear and angular momentum [3], and the clusters were equilibrated for 3×10^5 MD steps. The average temperature *T* of the system is given by

$$T = \frac{2E}{(3N - 6)k_b}, \quad (2)$$

where N is the number of atoms, $k_b = 1.381 \times 10^{-23}$ erg/K is the Boltzmann constant, and E is the kinetic energy, suitably averaged over the entire trajectory.

We examine the typical variation of the total potential energy of an individual Ar atom (labeled k)

$$V_k(t) = \sum_{j \neq k} V(r_{kj}(t)). \quad (3)$$

The power spectrum of the potential energy of the tagged atom k is calculated for a trajectory of length τ by a fast-Fourier-transform method

$$S(f) = \lim_{\tau \rightarrow \infty} \left| \frac{1}{\tau} \int_0^\tau dt V_k(t) \exp(-ift) \right|^2, \quad (4)$$

where f is the frequency. These spectra are then averaged over different realizations of the MD trajectory at the same temperature.

The power spectrum of individual atomic potential energy fluctuations in an Ar₅₅ cluster at $T = 37.5$ K is shown in Fig. 1. Shown in the inset is the power spectrum of a tag atom in Ar₇ at $T = 20.2$ K, when these systems have just gone into the liquidlike state. Similar power spectra are also seen in the liquid state of Ar₁₃, which are not shown here. The spectra have a distinct $1/f^\alpha$ dependence over a wide frequency range. The exponents α for these power spectra are 1.28 and 1.5 for $n = 7$ and 55, respectively. The spectra are flat below a frequency f_c , indicating that on short time scales the individual motions are strongly correlated while motions separated by a time scale of the order 300 ps are not. A similar loss of correlation occurs with the increase of internal temperature of the clusters. At high temperature in the liquid state the power spectrum tends to flatten, i.e., becomes more white-noise-like. In the extreme limit, say, in the gas phase, one would expect that correlations will die out rapidly, and a flat spectrum will result. Consequently, the exponent α decreases with an increase in the internal temperature, as shown in Fig. 2 for the case of Ar₁₃. This happens because at lower

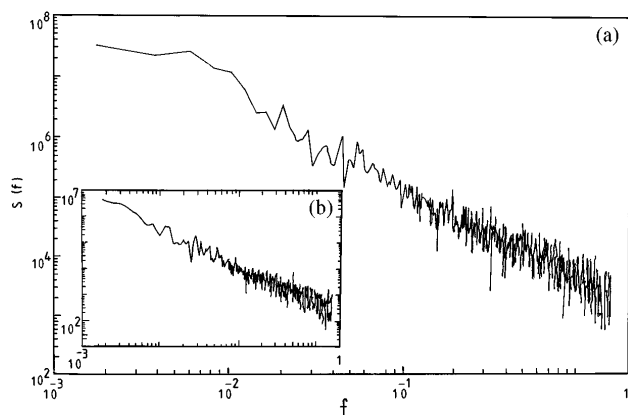


FIG. 1. Power spectrum of individual atomic potential energy fluctuations in the liquid state of Ar₅₅ at $T = 37.5$ K. Also shown is the power spectrum of a tag particle in the liquid state of Ar₇ at 20.2 K.

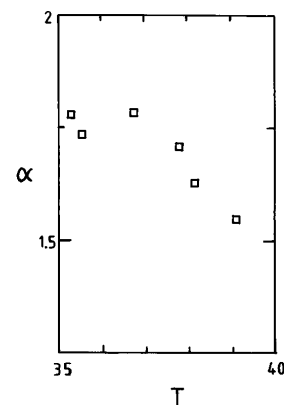


FIG. 2. The dependence of the scaling exponent α on the temperature in Ar₁₃ liquid clusters.

temperatures the dynamics of the cluster is less diffusional and hence the motions are strongly correlated for longer times. (Note that determination of the scaling exponent is not very precise since the cutoff frequency also shifts with temperature.) The exponent varies with cluster size and at a given temperature is smaller for larger clusters; in the limit of bulk liquid Ar, the spectrum is flat [9].

During the dynamical evolution of the cluster, the atoms constituting the cluster move from one configuration (or one instantaneous structure) to another. In order to understand the origin of potential energy fluctuations we have determined the actual minima on the potential energy surface by quenching from the instantaneous to the inherent structures: The molecular dynamics is interrupted at equal intervals of times and the kinetic energy of each particle is set to zero. The equations of the motions are damped, and then followed until a potential minimum is found [7]. The resulting inherent structures give a picture of the path taken by the cluster as it explores successive minima in the multidimensional energy surface. The potential energy of these inherent structures is very similar to that of instantaneous structures indicating the observed fluctuation and the long-range correlation is an intrinsic property of the underlying potential energy surface (see also Ref. [9]).

Following the dynamics of the individual particles gives additional insight into the long-lived correlations. The distance of the tagged atom from the center of mass of the cluster, $R_k(t)$, can be compared with the individual potential energy $V_k(t)$. When the atom stays on the surface of the cluster, $R_k(t)$ is large, and its individual energy is also high compared to when it is in the core. There is a high degree of correspondence between variations in $R_i(t)$ and $V_i(t)$ since major energy changes occur principally when a given atom travels from the surface of the cluster to the core (see Fig. 3). The correspondence is not exact though, since there are strong cooperative effects. In order for an atom to travel from the surface to the core, it must overcome several potential

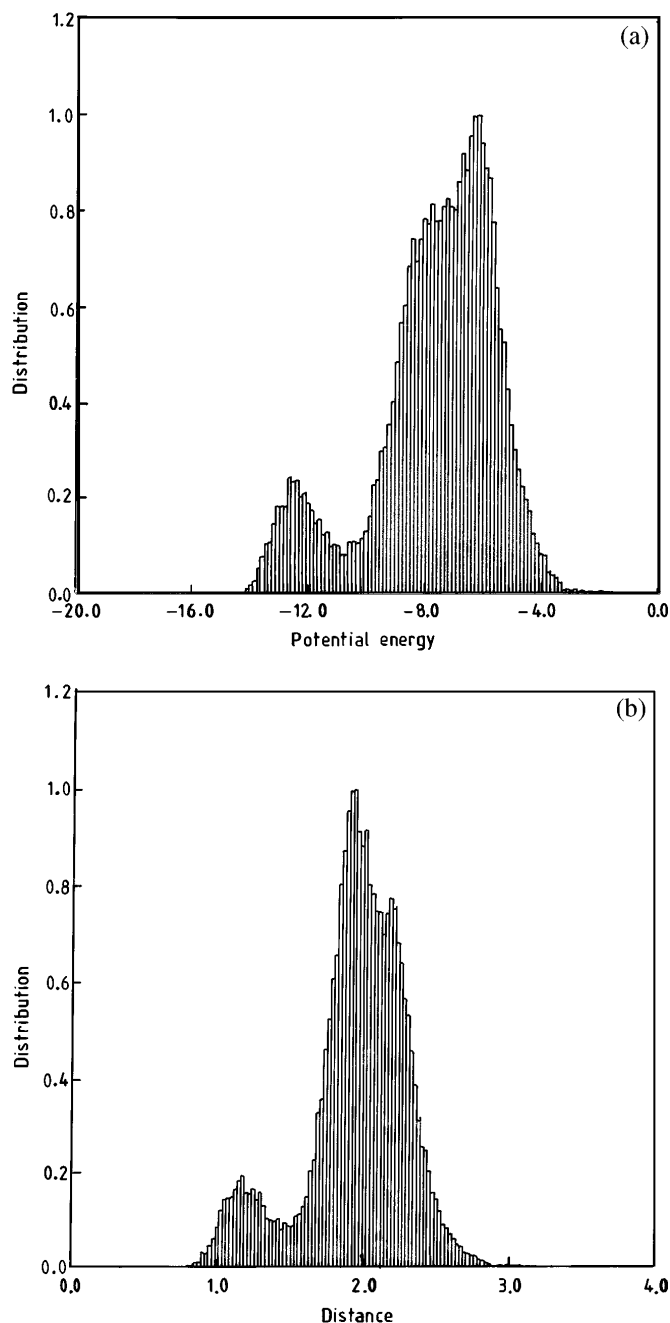


FIG. 3. (a) Potential energy distributions and (b) $R_i(t)$ distribution of the same tag atom in Ar_{55} cluster in the liquid state.

energy barriers. Thus the relaxation process here can be modeled as a *sequence* of activation processes. In fact, the distribution of individual atomic potential energies in the liquid state is seen to be a superposition of Gaussians, depending on the shell structure of the cluster [2]. The individual potential energy distribution $P(V)$ has the form

$$P(V) = \sum_{i=1}^n A_i \exp[-(V - V_i^0)^2 / 2\sigma_i^2], \quad (5)$$

where A_i is the amplitude, V_i^0 is the position, and σ_i is the variance of i th Gaussian. For Ar_{55} , for example, this

is a sum of three Gaussians [see Fig. 3(a)], indicating that there is a range of different barriers encountered by atoms as they move about in a cluster.

The correlation function $C_k(t)$ for the tag atom is given by

$$C_k(t) = \langle V_k(\tau)V_k(t + \tau) \rangle, \quad (6)$$

with $\langle \dots \rangle$ denoting the average over τ . $C_k(t)$ for Ar_{55} is shown in Fig. 4. The dependence is exponential, $C(t) = \exp(-t/\tau)$, τ being the relaxation time. The power spectrum of such a process is [10,17]

$$S(f) = \frac{4\pi}{1 + (2\pi f\tau)^2}. \quad (7)$$

However, given that there is a distribution of relaxation times, it is known [17] that the power spectrum has the dependence $S(f) = 1/f^\alpha$, $1 < \alpha < 2$.

The existence of multiple time scales thus accounts for the observed $1/f^\alpha$ dependence. Below the freezing temperature, the power spectrum is peaked at the characteristic normal mode frequencies of the global minimum [9]. As the cluster melts, time scales corresponding to diffusional motion come into play. For large clusters, the time scale for motion from the surface to the core is very different from those motions on the surface or within the core. For smaller clusters, the distinctive time scales are more properly characterized as those corresponding to vibrational motions around the minima, and those that correspond to permutational isomerizations (i.e., motions over saddle points connecting different minima). The anisotropic nature of the cluster appears to play a crucial role—in liquid argon, owing to the isotropy of the

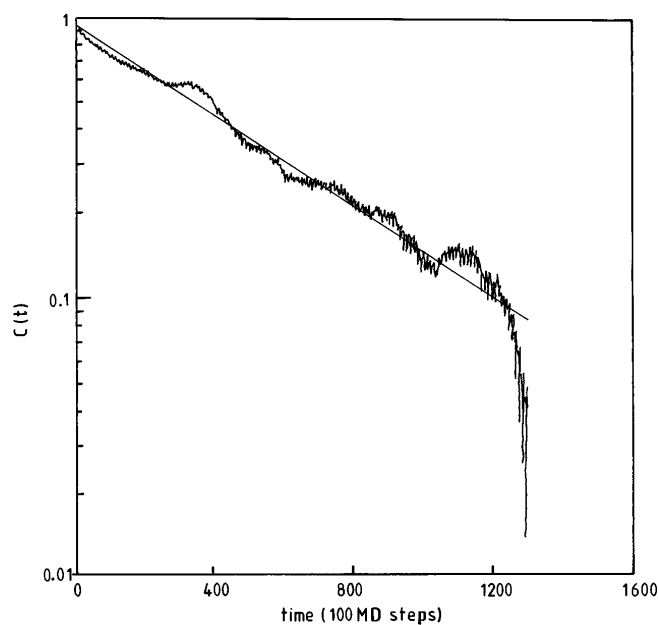


FIG. 4. Correlation function of potential energy fluctuation of the tag atom whose distribution is shown in Fig. 3.

system, the loss of memory is more rapid and $C_k(t)$ is δ correlated, giving rise to a flat spectrum [9].

At higher temperatures in the liquid state, the nonrigidity of the cluster increases and complex collective motions become increasingly more facile. Consequently, multiple time scales cease to exist, and the system loses the characteristic $1/f$ signature and becomes more like white noise. An alternate probe of this mechanism is the introduction of impurity atoms; we observe that in XeAr_{n-1} clusters, the more massive Xe atom, which is largely localized in the core, has a unimodal potential energy distribution and, consequently, a flat spectrum [13].

The persistence of correlations is a feature of complex systems, and, as such, clusters can be considered as another example of systems with complex or "emergent" dynamics [10,11,18]. This effect is amenable to experimental verification. In a related context, it has been observed that the depolarized Raman scattering spectrum of liquid water [19] has a marked $1/f$ falloff, which has been attributed to similar long-range correlations [9]. One possible route is through the spectroscopy of a rare-gas cluster doped with a chromophore [20], although studies on binary Xe-Ar clusters [13] indicate that qualitatively new features may result due to introduction of the dopant. A more attractive alternative is therefore to study a homogeneous cluster which is susceptible to spectroscopic interrogation. In this regard, and as an illustrative case, N_2 clusters seem apt: Bulk nitrogen forms an unassociated liquid, and $(\text{N}_2)_n$ clusters will consequently be dynamically similar to Ar_n , even though the geometries may be different. Further, Raman spectroscopic studies of $(\text{N}_2)_n$ [21] and $(\text{N}_2)_n$ benzene [22] have been recently carried out as well. Such techniques can, we hope, be adapted to probe the dynamical correlations associated with the melting transition in finite clusters.

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