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Direct Computation of Dynamical Response by Molecular Dynamics: The Mobility of a Charged Lennard-Jones Particle

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A nonequilibrium molecular-dynamics method of computing the dynamical response is presented. It is applied to the mobility of a charged particle in a Lennard-Jones liquid and the results agree with those computed from the Green-Kubo formula and with experimental data on argon. A discussion is given of the linearity of the mechanical response. The linear-response term is evaluated explicitly by a perturbation formula and the character of the nonlinear terms is briefly considered.

In this Letter we present a method of computing directly by molecular dynamics (MD) the full dynamical response of a model system of interacting particles to an external disturbance. The method is simply an exploitation of Liouville's theorem and of the possibility offered by MD of computing the perturbed mechanical trajectory in phase space. Let us define in the $6N$-dimensional phase space Γ of our system the complete Hamiltonian, including the perturbation, as

$$H(p, q, t) = H_0(p, q) + H_{ext}(p, q, t), \qquad (1)$$

and let $\alpha(p, q)$ be a dynamical variable on Γ. If $H_{ext}(p, q, t) = 0$ for $t \leq 0$, $\rho_e = C \exp[-H_0/k_B T]$ is the equilibrium distribution function of the unperturbed system, and $\rho(p, q, t)$ is the one corresponding to the complete Hamiltonian (1), obtained by solving the Liouville equation with the initial condition $\rho(p, q, 0) = \rho_e$, then we can write that $\rho(p, q, t) = S^{\dagger}(t, 0)\rho_e$, where $S^{\dagger}(t, 0)$ is the adjoint of the complete time-evolution operator. In such conditions, as a consequence of the measure invariance of phase space under natural motion, the time-dependent average of the dynamical variable $\alpha(p, q)$ in the perturbed system can be expressed in terms of the equilibrium average of the quantity $\alpha(p(t), q(t)) = S(t, 0)\alpha(p, q)$. In fact we have in an obvious way

$$\langle \alpha, \rho(t) \rangle = \langle \alpha, S^{\dagger}(t, 0)\rho_e \rangle = \langle S(t, 0)\alpha, \rho_e \rangle. \qquad (2)$$

By the MD technique we can obtain the nonequilibrium average $\langle \alpha, \rho(t) \rangle$ by starting at $t = 0$ from various configurations of the equilibrium trajectory, given by the simple H_0 evolution, and computing the complete H evolution of the system between $t = 0$ and $t = t$:

$$\langle \alpha, \rho(t) \rangle = \langle S(t, 0)\alpha, \rho_e \rangle = \lim_{N \to \infty} N^{-1} \sum_{n=1}^{N} S_0(t_n, 0) S(t_n + t, t_n)\alpha, \qquad (3)$$

where $S_0(t_n, 0)$ is the H_0 time-evolution operator and the times t_n correspond to reasonably uncorrelated subsequent configurations of phase space that the system reaches along its equilibrium path.

The mobility of a charged particle in a Lennard-Jones (LJ) liquid has been determined in this way, taking into account ion-induced dipole interactions but neglecting dipole-dipole terms. We have followed closely the methods used in the MD "experiments" of Verlet and co-workers.[1] The sample used consisted of 256 particles. The pair potential between the neutral particles was taken as the LJ interaction $\Phi_{LJ}(r_{ij})$, with parameters appropriate to argon ($\sigma = 3.405$ Å, $\epsilon/k_B = 119.8$ K), and that between the single charged particle and the other 255 as the LJ interaction modified by the charge-induced dipole term:

$$V(r_{ij}) = \Phi_{LJ}(r_{ij}) - \tfrac{1}{2}\alpha e^2 r_{ij}^{-4}.$$

For the value of the atomic polarizability α we have assumed 1.6 Å^3. The LJ interaction was truncated at 2.5σ and the electrostatic interaction at 3.3σ.

In implementing the method, the MD runs are

broken into "segments" lasting typically for 70 time steps of 2×10^{-14} sec. The trajectories of the particles are computed twice in each segment, starting from the same initial configuration. In one case the calculation proceeds in the normal way, and is continuous throughout all segments; in the other one a constant force of order 1 eV cm^{-1} is applied to the ion. The drift velocity of the ion induced by the applied field is computed as a function of time simply by calculating the difference of the ion velocity in the perturbed and unperturbed trajectories, averaged over all segments making up the run. In fact, remembering that at equilibrium $\langle\vec{v}^{(1)}, \rho_e\rangle = 0$, we have

$$\langle S(t)\vec{v}^{(1)} - \vec{v}^{(1)}, \rho_e\rangle = \langle S(t)\vec{v}^{(1)}, \rho_e\rangle = \langle\vec{v}^{(1)}, \rho(t)\rangle = \vec{u}_D(t). \quad (4)$$

The mobility constant is given by $\vec{u}_D(\infty) = \mu\vec{F}$ at vanishingly small $\vec{F}$.

The force we applied is about 10^{-7} of the mean LJ force. It is only the subtraction operation which appears explicitly in the first term in (4) which makes possible the calculation of the drift velocity induced by such a small external field in a MD run of realistic length. The mobility constant is then obtained from the value which the drift velocity approaches after the relevant system relaxation time.

The method was tested first by computing the mobility constant of a neutral particle in an ordinary LJ system, applying to the particle an external force as in the calculations described above. The calculated mobility was in very good agreement with the diffusion constant obtained previously by integration of the velocity autocorrelation function (VAF).

The numerical success of the method is due to the correlation between the two mechanical trajectories in each segment, the perturbed and unperturbed one. On the other hand it is known[2] that if the system is ergodic the two trajectories will depart exponentially from each other as time increases and the respective values taken on them by the observables of the system become essentially uncorrelated. For this reason the method is inappropriate for the investigation of rather long-time phenomena. The growth with time of the distance between the corresponding phase-space points on the two trajectories has been found to be very accurately exponential in our system of 256 particles, following a short initial period in which the component containing the systematic response dominates. The coordinate-space and velocity-space terms are found to have an identical characteristic time, which is of the order of the mean time between collisions.

TABLE I. Mobility of positive ions in liquid argon.

T (K)	ρ (g cm^{-3})	μ (10^{-4} cm^2 V^{-1} sec^{-1}) MD	expt
85	1.46	5.2	...
90	a	...	6.5
112	a	...	13
113	1.22	13.4	...

[a]At vapor pressure.

In Table I the results for the ionic mobilities are compared with the experimental results of Davis, Rice, and Meyer[3] for the mobility of positive ions in liquid argon. The agreement is satisfactory, suggesting that the potential model used is adequate and that the interaction between the induced dipoles plays a minor role. The outstanding feature we observe is a very large reduction of the ionic mobility with respect to that of the neutral atom, by a factor of 4 at the triple point. Experimentally a factor of 5 is reported at 90 K.[3] This decrease of the mobility of the charge carriers is commonly attributed to the solidlike structure induced around the ion by the electrostriction forces. We have actually observed the formation of this structure. The process takes a rather long time ($\sim10^{-10}$ sec) after turn-on of the electric interaction and only when the radial distribution function around the ion has reached its stable solidlike shape can one begin the computation of the dynamic properties. The structure is very regular and stable in the dense liquid and the time spent by the ion neighbors in the respective shells is remarkably long. They are precisely located in a regular icosahedral pattern centered at the ion. The increased rigidity of the environment of the ion is reflected in its short-time dynamics as a rather rapid oscillation, giving rise to a characteristic double-peaked structure in the velocity power spectrum, i.e. in the Fourier transform of the VAF $C_v(t)$. For small values of the applied force the formalism of linear-response theory is applicable. In our method the VAF is obtained from the transient time-dependent behavior of the response in the ionic velocity as it approaches its asymptotic value. It is easy to show in fact that, within the framework of linear-response theory,[4] the mean

value of the ionic velocity $\langle \vec{v}^{(1)}, \rho(t)\rangle$ is proportional to the time convolution integral of the VAF and the time-dependent external force. If, as in our case, $\vec{F}(t)=\vec{F}_0\theta(t)$, where $\theta(t)$ is the step function,

$$\langle \vec{v}^{(1)}, \rho(t)\rangle = \vec{F}_0 \int_0^t C_v(\tau)\, d\tau \qquad (5)$$

and the time derivative of the drift velocity yields the VAF. It is obvious from (5) that if $\vec{F}(t)=\vec{F}_0\delta(t)$, $\vec{u}_D(t)$ displays $C_v(t)$ itself rather than its integral.

The result for $\langle \vec{v}^{(1)}, \rho(t)\rangle$ obtained in a typical run consisting of 200 segments is shown in Fig. 1, where its three spatial components are plotted. Only the component parallel to the applied force displays a systematic time behavior. The other two components are a measure of the residual statistical noise, which clearly grows with time.

For comparison we have also computed the drift velocity as the integral of the equilibrium VAF of the ion. The results of the two methods agree well, but the advantage in computing the actual response is that the statistical noise on a run of given length is very much smaller than in the standard calculation.

For this reason it is clearly desirable to apply the method to the computation of the collective response of model systems to the imposition of spatially varying force fields, for which the noise problem is always severe. Useful information has in this way been obtained on the collective dynamical properties of molten alkali halides.[5] In particular it was found that the computation of small cross-correlation functions becomes feasible because the spurious contributions to the cross correlation arising from spontaneous fluctuations are eliminated.

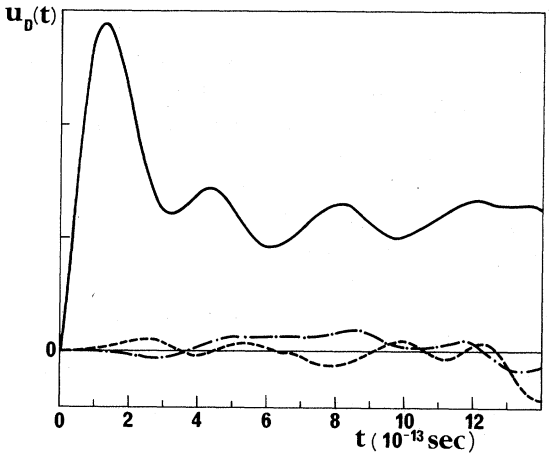

FIG. 1. Computed velocity response, $\vec{U}_D(t)$, in arbitrary units, in the linear region for positive ions at the triple point of argon. The amplitude of the force, applied in the x direction, is of the order of 1 eV/cm; that of the response is about 10^{-7} of the rms velocity. The components of $\vec{U}_D(t)$ are identified as follows: $U_{Dx}(t)$, −; $U_{Dy}(t)$, −·−; $U_{Dz}(t)$, − − −.

We now discuss the relation between microscopic motion and statistical linearity.[6] The calculated response is found to be linear with F_0 for all times during a segment. Deviations from mechanical linearity of the order of a percent are detected at the last steps of the segment only when F_0 reaches values of order 10^5 eV cm^{-1}. What is surprising about this result is that the response continues to be mechanically linear after the particles have undergone a few collisions and have fully reacted to the perturbation. Nonlinearity is introduced in the case of continuous potentials through higher-order terms in the Taylor expansion of the potential energy in the perturbed trajectory. These terms become important at long times as the distance between the paths in field F and in zero field increases.

In fact it is possible to compute the mechanical response by first-order perturbation theory without leaving the equilibrium run. This we have by adapting to MD the formal development presented by Hubbard and Beeby.[7] Let us define by $\vec{u}^{(i)}=\vec{X}^{(i)}-\vec{x}^{(i)}$, $i=1,\ldots,N$, the differences between the coordinates in the perturbed and unperturbed cases, with $\vec{u}^{(i)}(0)=0$ and $\dot{\vec{u}}^{(i)}(0)=0$, and let $U(\{x\})$ and $\vec{K}^{(i)}(t)$ be the potential energy of the system in the $\{x\}$ configuration and the external force, respectively. The equations for the evolution of the u's are

$$m\ddot{\vec{u}}^{(i)} = \Delta\left\{-\frac{\partial U}{\partial \vec{x}^{(i)}}\right\} + \vec{K}^{(i)}(t), \quad i=1,\ldots,N. \qquad (6)$$

In the linear approximation Δ indicates the first term in the Taylor expansion of the difference between the forces in the perturbed and equilibrium configurations. Note that this linear term contains second derivatives of the potential energy. It is now easy to integrate (6) during the computation of the equilibrium trajectory so that the linear response can be obtained without having to compute the trajectory twice. With a small enough applied force we have obtained complete numerical agreement between the directly computed response and the perturbation result.

Finally, an interesting application of the meth-

od is the study of nonlinear effects: Nonlinear terms can actually be isolated and averaged separately. We have not yet systematically exploited this possibility. We have verified only that in the expansion of the drift velocity in terms of the applied force, only the odd-power terms contain systematic contributions to the statistical average, as is obvious on the grounds of symmetry. The even-power terms are present only in the mechanical response. As a consequence, since the first nonvanishing term beyond linearity is quadratic for the mechanical response and cubic for the statistical one, the latter must have a wider linearity range.

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Observation of Akhiezer and Landau-Rumer Regimes in the Frequency Dependence of Shear-Wave Lattice Attenuation in CdS

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Brillouin-scattering measurements on acoustoelectrically amplified flux are used to determine the room-temperature frequency dependence of the lattice attenuation of ultrasonic shear waves in CdS up to a frequency of 7 GHz. The results show clearly a transition from the Akhiezer f^2 regime to the Landau-Rumer f^1 regime. The transition frequency provides an estimate of about 35 psec for the average lifetime of the thermal phonons involved in the ultrasonic attenuation process.

In this communication we report on Brillouin-scattering measurements of room-temperature lattice attenuation of slow shear waves propagating perpendicularly to the c axis in CdS. By extending the measurements up to 7 GHz, we were able to observe a clear transition from a quadratic frequency dependence (f^2) of the lattice attenuation α_l at low frequencies to a linear dependence at higher frequencies. We belive that this corresponds to a transition from the Akhiezer regime[1] to the Landau-Rumer regime,[2] and as far as we know this is the first time that the two regimes have been observed (at a single temperature) in one and the same material. The transition frequency is of considerable interest since it provides an estimate for the average lifetime τ of the thermal phonons involved in the ultrasonic attenuation process.[3] The Akhiezer f^2 law is expected to hold when $f \ll 1/2\pi\tau$. For $f \gg 1/2\pi\tau$, on the other hand, the energy hf of the ultrasonic phonons becomes large compared to the uncertainty $(h/2\pi\tau)$ in the energy of the thermal phonons with which the ultrasonic phonons interact. Selection rules resulting from energy and momentum conservation are then imposed on the phonon-phonon interaction, changing its nature and its frequency dependence. This is the range in which the lattice attenuation is expected[3] to increase linearly with frequency (the Landau-Rumer regime).

The frequency dependence of α_l has been measured in many materials[4,5] and an f^2 dependence, as well as other powers of f ranging between 1 and 2, have been reported. As to shear waves in CdS, extensive data[6-10] are available below about 4 GHz, the latest and most accurate results[9,10] exhibiting clearly an Akhiezer f^2-law dependence. No measurements were reported so far at higher frequencies.

The measurements to be presented here were carried out on acoustoelectrically amplified