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Conjugate gradient filtering of instantaneous normal modes, saddles on the energy landscape, and diffusion in liquids

J. Chowdhary and T. Keyes
Department of Chemistry, Boston University, Boston, Massachusetts 02215

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Instantaneous normal modes (INM's) are calculated during a conjugate-gradient (CG) descent of the potential energy *landscape*, starting from an equilibrium configuration of a liquid or crystal. A small number (~ 4) of CG steps removes all the Im$-\omega$ modes in the crystal and leaves the liquid with *diffusive* Im$-\omega$ which accurately represent the self-diffusion constant *D*. *Conjugate gradient filtering* appears to be a promising method, applicable to any system, of obtaining diffusive modes and facilitating INM theory of *D*. The relation of the CG-step dependent INM quantities to the landscape and its saddles is discussed.

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I. INTRODUCTION

For some time [1,2] we have been pursuing the idea that the self-diffusion constant *D* can be expressed in terms of the imaginary-frequency instantaneous normal modes (INMs); we are particularly interested in supercooled liquids. The INMs are the eigenvectors of the Hessian matrix of second derivatives of the potential energy *U* with respect to the mass weighted coordinates for a typical equilibrium configuration. The frequencies ω_α are the square roots of the eigenvalues. Because a liquid configuration is not a minimum of *U*, eigendirections exist with downward curvature, yielding negative eigenvalues and imaginary frequencies. Im$-\omega$ modes are also called unstable (*u*) and the fraction (out of all $3N$ modes) of unstable modes is f_u.

Our approach is best discussed in terms of the topology of the potential energy surface in the configuration space, the [3,4] *landscape*. Stillinger and Weber showed [5] how to partition the landscape into the basins of the local minima, or *inherent structures* (ISs); a configuration is mapped to the basin to which it will drain via steepest descent minimization. For the (low) *T* of interest here the same results are obtained with the more efficient conjugate-gradient (CG) algorithm. Diffusion requires [3] that the system move among the basins via saddle barriers, which exhibit [6] Im$-\omega$. At high *T* such motion is unconstrained. Below a crossover temperature, often identified with the [7] mode-coupling temperature T_c, *inherent structure transitions* become more difficult. The reasons for the crossover are still being debated; activation and the distribution of barrier heights play a key role but nonactivated dynamics along low-barrier pathways is also possible (entropic transport) at low *T*. A landscape approach based on saddles [8–10] instead of minima naturally includes nonactivated saddle-to-saddle pathways above T_c. In any case, paths with downward curvature of *U* are followed and it is plausible that f_u reflects the extent of IS transitions, or of saddle transitions, and thence *D*. We have given [1,6] landscape-based derivations of this relation, albeit with many approximations; the most recent arguments invoke [2] a random energy model. The upshot is that the *dynamical* quantity *D* is expressed in terms of a *static*, *equilibrium* average quantity f_u, meeting one of the fundamental goals of nonequilibrium statistical mechanics and opening the door to new theories and algorithms based upon, e.g., intelligent sampling.

In 1993 we found [6] that Im$-\omega$ persist in the crystal where $D\approx 0$. This has led to several attempts to isolate *diffusive* modes, discarding the effects of anharmonicities and two-level systems which produce Im$-\omega$ but do not contribute to *D*. One approach is [11] to classify the modes according to their one dimensional potential energy profiles $U(q)$, obtained by moving the system along the eigenfunction. There are two types of Im$-\omega$ profiles, double wells (DWs) and those with anharmonic shoulders (SHs) in a global single well. DWs and SHs are obvious candidates for diffusive modes and nondiffusive anharmonicities, respectively. The method is somewhat uncertain because the eigenfunction is only calculated once and loses its physical significance after a small displacement. In water $D\sim f_{dw}$ is [12,13] obeyed very well. Ordinarily T_c is estimated by fitting $D(T)$ to the mode-coupling [7] form $D=c(T-T_c)^\beta$; it is the temperature at which *D* extrapolates to zero from above, using a carefully chosen *T* range. Sciortino and Tartaglia [12] showed that INM could be used to obtain T_c, i.e., $f_{dw}(T)$ also extrapolates to zero at T_c. More evidence for the relation between $f_{dw}(T)$ and T_c was provided by La Nave *et al.* [13]. It is significant that the static average $f_{dw}(T)$ yields the dynamical T_c.

The DW description is not so successful in other materials but an extension which accounts for the IS visited along the DW directions [14] looks promising. Recognizing that rotational anharmonicities dominate the Im$-\omega$ in CS_2 we [15] introduced *pure translation* (TR) modes of the center-of-mass Hessian, obtaining a superb description of diffusion. The relation $D=f_{tr}\langle\omega_u^{tr}\rangle$, is accurate to within the error in the simulation for 56 supercooled states with a range of 134*X* in D. The basic INM theory of diffusion is also further refined in the second article of Ref. [15].

II. CONJUGATE GRADIENT FILTERING

A unified route to diffusive modes is required. Here we present the method of *conjugate gradient filtering*, illustrated for the unit-density Lennard-Jones (LJ) liquid but easily ap-

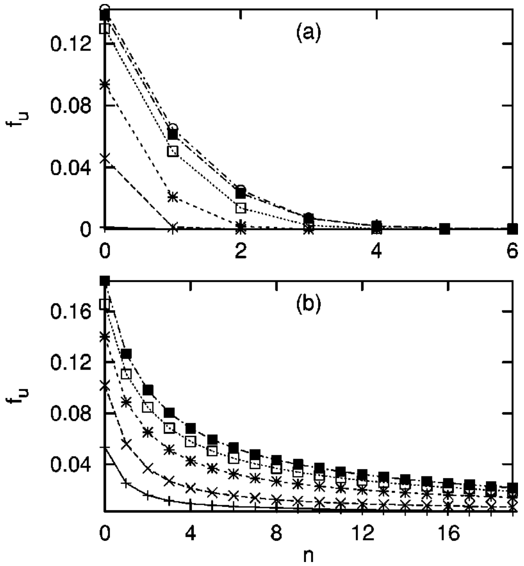

FIG. 1. The fraction of imaginary frequency modes vs the number n of CG steps for (a) the crystal (T = 0.4, 0.8, 1.2, 1.6, 1.7, and 1.75) and (b) the supercooled liquid (T = 0.4, 0.8, 1.2, 1.6, and 2.0), with T increasing from bottom to top. Some data are not shown to avoid congestion.

plicable to other systems. Simulations are performed with $N=108$ atoms for $0.4\leqslant T\leqslant 2.0$ (LJ units). The crystal melts at $T\approx 1.75$. Solidification of the supercooled liquid is frequent at the lower T with $N=108$ and when it occurs, we simply terminate the run.

Starting with a representative configuration, a CG minimization [16] is initiated and the INMs are calculated as a function of the number n of CG steps taken, giving rise to a family of unstable fractions $f_u(n,T)$. The significant observation is that, while (nondiffusive) Im$-\omega$ are present in the finite-T crystal, they vanish [Fig. 1(a)] very quickly with n, being almost completely eliminated after four CG steps. In contrast [Fig. 1(b)], in the supercooled state, following an initial sharp drop, Im$-\omega$ persist, even at the lowest T, for tens of steps. If nondiffusive Im$-\omega$ in the liquid are anything like those in the crystal it is clearly suggested that they are eliminated by the first few steps and one should seek a relation between D and $f_u(n)$, $n\approx 4$. The fractions $f_{dw}(n)$, $f_{sh}(n)$, and the potential $\langle U(n)\rangle$ and its gradient $\langle|\nabla U(n)|\rangle$ exhibit similar trends, the last two indicating that the first few steps bring the system down a steep landscape.

Figure 2 shows $f_u(n,T)$, $n=0-6$, for the supercooled liquid. The value of n employed to represent D must include the sharp drop in nondiffusive Im$-\omega$ but avoid larger n where diffusive modes are removed as well. Of course the method should not be based upon an arbitrary choice of n. A simple, systematic procedure is to fit the n dependence of $f_u(n)$ for the supercooled states to a double exponential, $f_u(n)=f_f*\exp(-k_f*n)+f_{dif}*\exp(-k_{dif}*n)$, to account for fast ($f$) nondiffusive and slow diffusive decay with n. The coefficient f_{dif} represents the fraction of diffusive Im$-\omega$. Figure 2 includes $f_{dif}(T)$ for comparision with $f_u(n,T)$, and it is seen to lie between $f_u(3)$ and $f_u(4)$, confirming that most of the nondiffusive, and few of the diffusive, Im$-\omega$ are eliminated by four CG steps. *We regard $f_{dif}(T)$ as the fundamental INM-derived indicator of diffusion*; it is obtained with the recipe that is applicable to any potential or stepwise minimization algorithm. In the following, $f_u(4,T)$ is discussed only because it is, for this system, an excellent approximation to $f_{dif}(T)$ which is not subject to the additional numerical uncertainties of a fit.

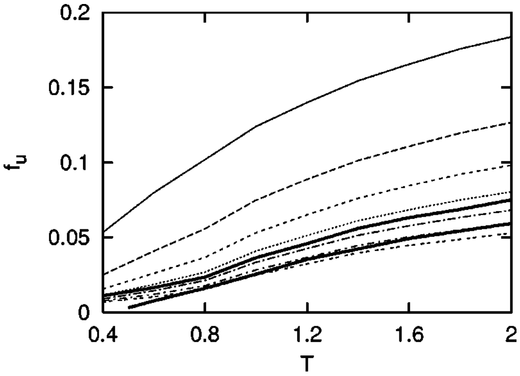

FIG. 2. T dependence of $f_u(n)$ for n = 0–6 (top to bottom), of the fraction f_{dif} of Im$-\omega$ left after the fast drop in the double exponential fit (upper bold line), and of the average fraction of unstable directions at the critical point, $\langle k\rangle$ (lower bold line).

One way to test the proposed relation between D and filtered INMs is [12,13] by calculation of T_c. Fitting $D(T)$ in the range $0.6\leqslant T\leqslant 2.0$ gives $T_c=0.48$. The estimated T_c is sensitive to the range of T employed, which must be chosen so T_c is the temperature at which D would vanish via extrapolation of the higher-T mechanism. If $f_u(n)$ represents diffusion, it too should yield T_c. Fitting $f_u(n)=c[T-T_c^{inm}(n)]^{\beta(n)}$ for the same T range, we find that $T_c^{inm}(n)$ increases with n (Fig. 3, inset) as nondiffusive modes are eliminated. The n dependence is well fit to $T_c^{inm}(n)=0.41+0.06*[1-\exp(-0.52*n)]$, with $T_c^{inm}(n\to\infty)=0.47\approx T_c$. Results which are essentially identical are obtained from f_{dif}, $T_c^{dif}=0.46$, and from four steps, $T_c^{inm}(4)=0.47$. Of course enough CG steps will remove all the Im$-\omega$ and lead to nonsense.

For an INM expression of $D(T)$ over a wide T range the appropriate relation is between f_u and the velocity correla-

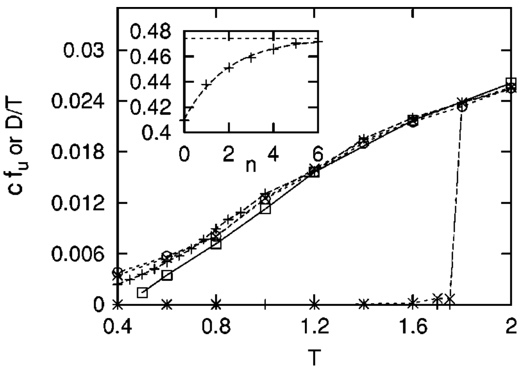

FIG. 3. Comparison of D/T (+), 0.34 f_{dif} (○), 0.375$f_u(4)$ (×) (liquid and crystal) and 0.44$\langle k\rangle$ (□). Inset is the CG step number dependence of $T_c^{inm}(n)$.

tion time D/T, since they both reach constant values at high T and constant density. Comparison of D/T with $f_{dif}(T)$ and $f_u(4,T)$ for $0.4 \leqslant T \leqslant 2.0$ is given in Fig. 3. Filtering the Im$-\omega$ with four CG steps and no "fine tuning" yields an excellent INM representation of diffusion for all T; $f_{dif}(T)$ and $f_u(4,T)$ are indistinguishable. This method is not very sensitive to the choice of n, and good proportionality of $f_u(n)$ to D exists for $n=3, 5,$ and 6 as well. Not only is D well described, the melting transition as indicated by the filtered INM is sharp unlike the usual [6] INM description.

III. INM'S AND SADDLES

A few CG steps bring the system towards the lower energy part of the landscape and remove most of the nondiffusive modes. Further insight into the utility of CG filtering may be gained with a landscape-based understanding of the minimization algorithm. The minima are extrema or *critical points* (CPs) of zero order, but the higher-order CPs, the saddle barriers, are of interest also [2,8–10]. The minima are the lowest-lying CPs, and [2,6,8–10] the energy increases with the order K, the number of Im$-\omega$. For $T > T_c$ [8–10] the system is closer to a saddle than to a minimum. Then, in the method of steepest descent, $\langle U(n)\rangle$ exhibits [17] a rapid drop at small n, an intermediate plateau, and ultimately falls to the constant value U_{is}.

The rapid drop arises from degrees of freedom with large gradients. From the INM point of view these are the high Re$-\omega$ modes or Im$-\omega$ caused by bumps or other roughness on the landscape. We believe the latter are the nondiffusive modes eliminated by filtering. On the other hand, a *reaction coordinate* in the vicinity of a saddle barrier, the prime candidate for a diffusive mode, has a small gradient and an Im$-\omega$ that persists for many minimization steps. The plateau is found when the large-gradient degrees of freedom have been minimized but little motion has yet occurred along the reaction coordinates. The system should be closest to a saddle after the first several steps, the number of steps for maximum proximity being dependent on the initial gradient and curvature along the available degrees of freedom. Since the algorithm is searching for a minimum it will not visit the finite-order CP adjoining a high-T configuration, and after tens or hundreds of steps it finds the IS. For the CG algorithm, we expect the same trend although the choice of conjugate directions, as opposed to the direction of the gradient, will in general keep the system farther away from the CPs.

These ideas may be implemented explicitly by noting that the CPs [18] are minima of the squared gradient $W=|\nabla U|^2$. We have minimized W in liquid configurations from our MD runs, determining the associated CP, denoted $\mathbf{r}_c$. The *saddle mapping* [8–10] is an extension of the IS mapping which is appealing at $T > T_c$. Above T_c the system maps [8–10] to a finite-order CP, below $T > T_c$, to the IS. Thus T_c may be estimated [8–10] by extrapolation of $\langle K\rangle$ to zero from above. The potential energy of a supercooled liquid exceeds that of the associated CP—of any order—because most of the displacement away from the CP is along stable directions of upward curvature. During minimization of U at $T > T_c$ the configuration $\mathbf{r}(n)$ passes by the associated CP of nonzero order while falling towards the IS. The distance $\delta r_c(n) = \sqrt{(1/N)|\mathbf{r}(n)-\mathbf{r}_c|^2}$ then reaches a minimum at intermediate n. Below T_c, the IS and $\mathbf{r}_c$ are identical and $\delta r_c(n)$ decays to zero monatonically.

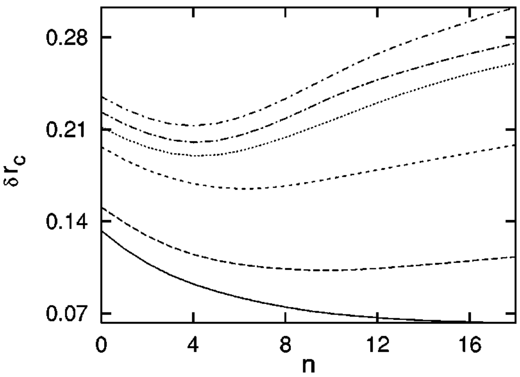

FIG. 4. Distance of the configuration after n CG steps from the critical point as a function of n, for T = 0.5, 0.6, 0.8, 1.2, 1.6, and 2.0 (T increasing bottom to top).

Figure 4 shows $\delta r_c(n)$ for $T=0.5$, 0.6, 0.8, 1.2, 1.6, and 2.0 averaged over 20 independent configurations. At high T ($T > 0.9$), the magnitudes of $|\nabla U|$, $\langle\omega_s\rangle$, and $\langle\omega_u\rangle$ are large, causing rapid approach to the reaction coordinate and associated CP. In this case four steps bring the system closest to the CP. With decreasing T, the gradient and curvature of the landscape decreases. As a result, even though a channel around the reaction coordinate is reached in about four steps, more are required for the closest approach to the CP, due to the slow quenching of small-gradient degrees of freedom. Similarly, the distance of the system from the CP decreases, as measured both from the instantaneous configuration and from the reaction coordinate during minimization.

The configurations $r(n)$ arising in minimization of U map to an n-dependent CP, and after a few steps a CP different from that obtained from the original configuration is found. The order of the CP to which $r(n)$ maps decreases with n, a feature that should show up in processes that lead the system down the energy landscape, as in aging dynamics of glasses [19].

The energy of a snapshot configuration always lies above that of the CP. Thus during minimization of U the system energy crosses the energy of a nonzero-order CP at the n, denoted n_x, which minimizes $\delta r_c(n)$; $U(n_x) \sim U_{CP}$. Since the average number of Im$-\omega$ appears to be governed by U [6,8–10], there should be a relation between $f_u(n_x)$ and the averaged fraction of unstable directions at the CP, $\langle k\rangle$ ($k = K/3N$). Figure 2 includes $\langle k(T)\rangle$ along with the $f_u(n)$ for $n=0$–6 vs T. Indeed, at the T where $n_x \sim 4$, $f_u(4$–$5)$ and $\langle k\rangle$ are almost identical and $\langle k\rangle$ must represent D/T. A relation between $\langle k\rangle$ and D is of course implicit in the estimate [8–10] of T_c from $\langle k\rangle$. In Fig. 3, 0.44 times $\langle k(T)\rangle$ is plotted along with D/T, with excellent agreement at the higher T. Fitting $\langle k(T)\rangle$ gives $T_c^k = 0.47$, almost identical to the results obtained from $D(T)$ and filtered INM's.

As $T \to T_c$, $\langle k\rangle$ falls below $f_u(4)$, and thus [since $D/T \sim f_{dif} \approx f_u(4)$ at all T] fails to capture the T dependence of D/T. What then is the suitability of using $\langle k\rangle$ as an indicator of diffusion? We believe that, for this particular system, four CG steps bring the system near the reaction coordinate in the vicinity of, and higher in energy than, the CP. The additional Im$-\omega$ found at the higher energy represent legitimate diffusive directions which must be counted, and $\langle k \rangle$ is not a good indicator of diffusion for $T \leqslant T_c$. For the same reasons, it yields an excellent value for T_c itself.

IV. DISCUSSION

In a smoothly varying one-dimensional landscape of barriers and minima with a single lengthscale [e.g., sin(*x*)], f_u is simply the probability that the system is above the inflection points, and is obviously related to *D*. The connection is not straightforward, however, on the $3N$ dimensional, multiscale, rough landscape of a liquid. CG filtering works by bringing the system away from regions of nondiffusive Im$-\omega$ by ''riding'' the associated large gradients. At $T > T_c$ proximity to the physically relevant saddle barriers results. To a large extent the one-dimensional simplicity of interpretation is restored in the subsequent INM calculation.

Our proposal is that the fraction of ''diffusive'' Im$-\omega$ may be obtained as f_{dif}, the coefficient of the slow decay in a biexponential fit to $f_u(n)$. In unit-density LJ f_{dif} and $f_u(4)$ are almost indistinguishable. Excellent representations of $D(T)$ and T_c are obtained with either in the supercooled liquid, and $D \approx 0$ is recovered in the crystal. In general there is nothing special about $n=4$. If use of another algorithm with another liquid led to a fast decay lasting, e.g., seven steps, presumably f_{dif} would be close to $f_u(7)$.

Removing the large gradients and bringing the system through the region of fastest change in $\delta r_c(n)$ prior to the INM calculation is the essential operation in obtaining a good representation of *D*. This corresponds to introducing the average fraction $\langle k \rangle$ of Im$-\omega$ of the associated saddle at higher supercooled *T*, but $\langle k \rangle$ underestimates *D* at $T \leqslant T_c$. The method may be applied to any potential and we will test it for molecular and ionic liquids in future work, seeking an INM theory of *D* based upon a unified prescription for diffusive modes related to the reaction coordinates for diffusion.

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