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COMMENTS

Comment on a critique of the instantaneous normal mode (INM) approach to diffusion [J. Chem. Phys. 107, 4618 (1997)]

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Gezelter, Rabani, and Berne¹ (GRB) ask, "Can imaginary instantaneous normal mode frequencies predict barriers to self-diffusion?" Their answer is unreasonably negative. INM theory of the self-diffusion constant, D , employs the idea² that Im- ω modes are manifestations of barrier crossing. The first papers³ demonstrated proportionality between D and the fraction of Im- ω modes, f_{Im} , in Lennard-Jones (LJ) liquids, with a single constant of proportionality describing a wide range of T and P . A more complete theory,⁴ with no adjustable parameters, led to good agreement with simulated D at $\rho=1.00$ from supercooled $T=0.68$ to $T=20$ (all LJ units), and is also in accord with simulated barrier crossing rates obtained⁵ by RGB for $2.0>T>0.68$. Ribeiro and Madden⁶ (RM) find $D\sim f_{\text{Im}}$ to be "quantitative" in molten salts. However, in crystals or in supercooled liquids near the glass transition, T_g , $D\sim 0$ but "nondiffusive" (ND) modes persist. Several methods have been proposed to remove the ND-INM.

Exponential T -dependence of D in LJ, $\rho=1.00$, $0.68>T>0.33$ was obtained⁴ by treating modes with $|\text{Im}-\omega|$ less than a cutoff ω_c as ND. In CS_2 , $P=1$ atm, simply subtracting⁷ the modes remaining at T_g as ND, $f_{\text{Im}}(T)\rightarrow f_{\text{Im}}(T)-f_{\text{Im}}(T_g)$, leads to excellent $D(T)$ in the supercooled liquid. Dividing⁸ the Im- ω into double-well (DW) and shoulder (SH, shoulder in a global single well) modes via their potential energy profiles $U(q)$ yields obvious candidates for diffusive and ND modes. Delocalized DW vanish⁸ at T_g in atomic systems and the DW exhibit⁸ the postulated⁴ cutoff ω_c . RM observe diffusion in AgI in the absence of DW, but both D/f_{Im} and dD/df_{Im} are much smaller (RM, Fig. 3) than for NaCl which does have DW. A subset of the DW, "zero force" (ZF, force along a mode less than a cutoff value) modes accurately gave⁹ D in a normal LJ liquid.

GRB show that all the crystal ZF and most ZF in the coldest supercooled liquid are "false-barriers" (FB); quenches from both minima in $U(q)$ drain to the same local minimum of the N -body potential. Thus, GRB argue that D cannot be reliably calculated from ZF modes nor from any other proposed diffusive modes. We disagree:

(1) GRB consider LJ only. While they acknowledge that "...the situation may be more complex for molecular liquids," we assert that the situation is *clearly more favorable to INM* in molecular liquids. Consider¹⁰ LJ at $\rho=0.85$, and CS_2 and water at $P=1$ atm; the double-well/shoulder ratio $f_{\text{dw}}/f_{\text{sh}}$ at the freezing point has the values 3.8, 1.1, and 0.45.

Reference 6 for LJ, $\rho=1.00$ shows $f_{\text{Im}}\sim f_{\text{DW}}$ at T_g with neither vanishing; subtracting the small number of SH as ND has a negligible effect. In sharp contrast¹¹ water has $f_{\text{Im}}\sim f_{\text{sh}}$, and $f_{\text{DW}}=f_{\text{Im}}-f_{\text{sh}}\sim 0$ at the kinetic glass transition,¹⁰ T_c , while f_{Im} is substantial; subtracting the SH leads to a quantity which mirrors the diffusion constant. LJ with short ranged, radial interactions has¹⁰ a large fraction of Im- ω , DW, and ND DW modes while network-forming water has a low fractions of all three; CS_2 is intermediate.

We suggested¹² that coupling to rotation was causing spurious translational ND in CS_2 and calculated "pure translation" (TR) INM from the Hessian of derivatives with respect to center-of-mass coordinates. Figures 1 and 2 show that the TR Im- ω densities of states (DOS) vanish at $T_g\sim 100$ K and also in the α -fcc crystal; $f_{\text{Im}}^{\text{TR}}(T)$ mirrors (Fig. 2) $D(T)$ in the liquid. The behavior of the DW modes of water and of the TR Im- ω modes of CS_2 is exactly what one would hope to see in a bona fide indicator of barrier crossing. For the three substances considered "diffusive" modes are more easily selected as the complexity of the potential increases. The α -fcc crystal is slightly higher in energy than the orthorhombic structure but the latter has (see the accompanying Comment) more Im- ω modes. A better understand-

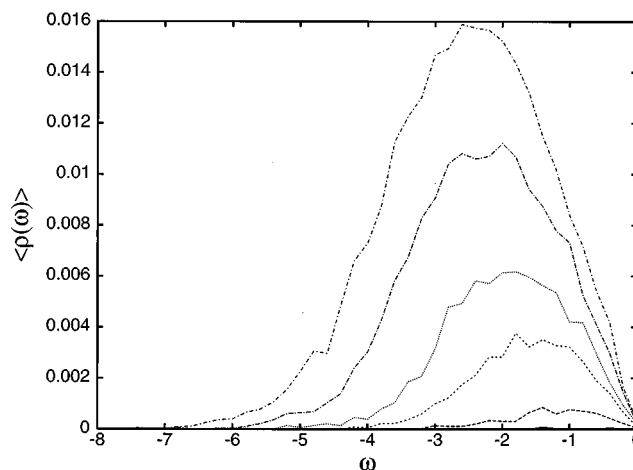


FIG. 1. Im- ω pure translation densities of states vs frequency (Im- ω shown as $-\omega$, ps^{-1}) in normal and supercooled liquid CS_2 , $P=1$ atm, at $T=298$ K (largest peak), 244 K, 193 K, 135 K, and 100 K $\sim T_g$ (no Im- ω modes).

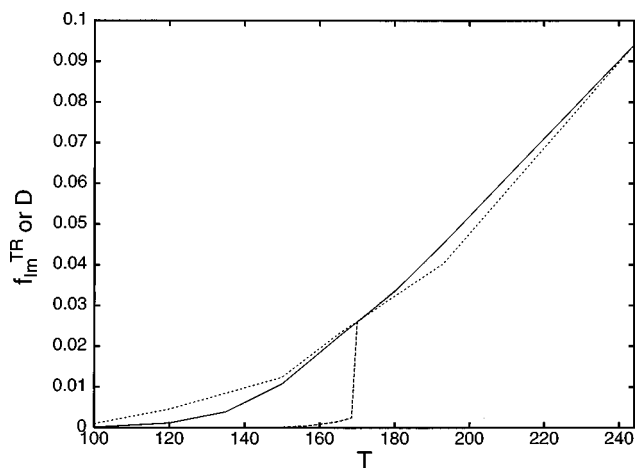


FIG. 2. Fraction $f_{\text{Im}}^{\text{TR}}$ of pure translation Im- ω modes in CS₂ vs T for normal and supercooled liquid (solid line), and for α -fcc crystal and normal liquid (large dash); small dashes are liquid-state $D(T)$ matched to $f_{\text{Im}}^{\text{TR}}$ at $T = 244$ K. Liquid at $P = 1$ atm, crystal at same density as liquid at each T .

ing of INM in crystals will be instructive, particularly of the relation to the stability of phonons in simulation models, but our focus is liquids.

(2) While ND are plentiful in LJ, that is insufficient cause to reject INM theory of D . GRB's attitude is that INM are unusable if they are tainted with *any* ND modes. However, all we require is that ND do not dominate $D(T)$. If the T -dependence of the ND is weak or similar to that of the diffusive modes, there is also little difficulty.

At $\rho = 1.00$, $T = 1.0$ GRB (Fig. 7) shows that the ZF DOS is considerably greater than the FB ZF (nondiffusive) DOS; diffusive modes probably dominate for $T > 1.0$, so the success of INM theories is no puzzle. As T falls from 1.0 to 0.89, the fraction of FB rises, but must fall again as $T \rightarrow 0$. The number of FB ZF is the ZF number, decreasing with increasing T , times the fraction. This is roughly consistent with a weakly T -dependent set of FB at low T . The T -dependence of FB is also seen in the low- T plateau in the prefactor $a(T)$, GRB, Fig. 3, which they ascribe to FB dominance. Conversely, we would say that as T is increased above the plateau region ($T > 0.75$) FB become unimportant. Atomic systems are the worst case for INM but, even so, the current theories of D remain useful.

(3) The functional form of the simulated Im- ω DOS in LJ liquid, $\rho = 1.00$, is¹³ $\sim \omega \exp(-\omega^2/T)$ at $T \sim 10$ and $\sim \omega \exp(-\omega^4/T^2)$ at $T \sim T_g$ with crossover occurring at $T \sim 3$, leading¹³ to a crossover of $D(T)$ from $\exp(-E/T)$ (Arrhenius) to $\exp(-E^2/T^2)$ in agreement with many experiments¹⁴ and which has been related^{13,15,16} to the poten-

tial energy "landscape." RM find that the dos for ions with freer motion exhibits the high- T form and vice versa. We have analytically reproduced¹⁵ this behavior, and found the cutoff ω_c for DW, by treating the INM as local excitations in the soft potential model.¹⁵ Fits to the limiting high- T and $T \sim T_g$ analytical forms¹⁶ yield the crossover T with nothing adjustable, and we obtain $T \sim 2.8$ in good agreement with simulation. The theory^{15,16} invokes barrier crossing in an ensemble of one-dimensional $U(q)$. The straightforward conclusion is that the Im- ω dos is understandable in terms of one-dimensional barrier crossing.

GRB write "We give evidence of the lack of validity of many of the key assumptions of the INM theory." The theory stands on its own, and we have not seen such evidence from GRB. Their Figs. 7 and 3 help explain why, for $T > (0.75 - 1.0)$, FB are not fatal in LJ. GRB Fig. 1 shows that the approach of Ref. 5, using ZF modes, reasonably represents $D(T)$ for the normal LJ liquid at $\rho = 0.84$ and 0.94 and yields half of the discontinuity in D upon melting at $\rho = 0.94$. It is likely, had GRB simulated $D(T)$ in the supercooled liquid, that the good agreement would continue. In any event we hope it is clear that LJ is a poor starting point for a general evaluation of the INM approach. Finally, we have accepted the FB analysis for the sake of argument, but it must be noted that the $U(q)$ are calculated¹⁰ without changing the INM eigenfunctions as the particles move, and the relevance of the fate of quenches from their two minima is yet to be established.

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