Response to "Comment on a critique of the instantaneous normal mode (INM) approach to diffusion" [J. Chem. Phys. 109, 4693 (1998)]

J. Daniel Gezelter, Eran Rabani, and B. J. Berne
Department of Chemistry and Center for Biomolecular Simulation, Columbia University, New York, New York 10027

In our critique[1] of the instantaneous normal mode (INM) theory for self-diffusion,[2] we pointed out two flaws with the theory that are problematic if one wishes to study crystalline or glassy materials.

The first flaw is that the INM theory (in its most simple form) attempts to predict barrier hopping times using imaginary frequency INMs that have nothing to do with barrier crossings. In our critique, we showed that none of the current methods[3,4] are sufficient to remove nonbarrier anharmonicities from the imaginary frequency INMs in Lennard-Jones systems. To show this, we followed steepest descent paths from either side of a zero-force (ZF) INM and compared the structure of the liquids in the nearest local minima. If a ZF-INM is an indicator of a real barrier, one expects that quenching from either side of the barrier will lead to local minima with different structures. Instead, we found that a substantial fraction of the ZF, and double-well (DW) modes converged to the same local minimum on the potential energy surface, i.e., they were false-barrier (FB) modes.

The second flaw of the INM theory is that even if one could restrict the INMs to those that are truly associated with barrier crossings, not all barrier crossings lead to diffusive motion. Consider a rough potential energy surface (see Fig. 1 in Ref. 5), where the barriers that are sampled by the INM theory are primarily the small barriers between adjacent local minima, and are *not* the barriers which separate two basins.

In their Comment, Keyes *et al.* raise three substantive objections to our analysis: (1) They disagree with our conclusions because they are based on an analysis of an atomic liquid.[6] (2) They argue that the presence of false-barrier modes is insufficient to reject the INM theory. (3) They cite agreement with predictions of the soft-potential model as evidence in favor of the INM theory for diffusion. We now answer these points.

Keyes *et al.* argue that the INM theory is better for molecular liquids, and that our investigation of the theory in the atomic Lennard-Jones system was an unfair test. Their evidence for this position comes from observations made on water[7] and on CS_2.[4,8] In particular, they have calculated the number of pure translation modes and have observed that these modes vanish below T_g and have a very small contribution to the density of states in the α-fcc crystalline solid.

We have pointed out to Keyes *et al.* that the equilibrium crystalline structure of CS_2 is the face-centered *orthorhombic* lattice,[9] and while they acknowledge that there are some differences between the two structures, we feel that it must be emphasized that in the correct crystalline structure for CS_2, the problems with the INM theory for diffusion are the same as those we observed in Lennard-Jones argon system.

In order to compare the INM theory for diffusion in a molecular system with our results in the Lennard-Jones system, we have calculated the pure translation INM density of states and compare the fraction of unstable modes with the diffusion constant near the melting transition of the face-centered orthorhombic crystal (i.e., the correct crystalline structure).[10] The results for two different densities are shown in Fig. 1. Note that the results for the melting of the orthorhombic crystal of CS_2 do not show any appreciable differences from the simulations done on atomic systems (see Fig. 2 in Ref. 1). The nonequilibrium α-fcc crystal structure used by Keyes *et al.* obscures the extent of the problem with the INM theory at the melting transition.

Recently, Ribeiro and Madden have investigated the INM theory in ionic melts.[11] In their work, they found that no particular significance should be attached to classifications of the INMs into double-well or shouldered modes in these systems, and their findings did not support a special role for double-well modes in diffusion.[11] This implies that the observation by Keyes *et al.* that DW modes disappear at T_g,[4] and similar observations made by Sciortino and Tartaglia,[7] are not *general* across molecular systems.

Given that our results for the CS_2 melting transition are very similar to those we obtained for the atomic Lennard-Jones system,[1] and that the observations Keyes *et al.* make of the behavior of the DW modes in molecular systems is not general, the argument they make against our test of the INM theory does not appear to be correct.

The presence of the false-barrier modes in the crystalline solid and in supercooled liquids makes it impossible to use the INM theory as a black box to obtain diffusion constants without prior knowledge of the state of the material. Given only the fraction of unstable modes (pure translation, DW, or ZF), Keyes *et al.* will be unable to give a correct estimate of the hopping rate for a number of materials. Although they have found compelling evidence that the fraction of unstable modes scales with the diffusion constant in some liquids, and over some temperature ranges,[12–14] we do not believe that their *explanation* of this agreement[2,15] can be correct in light of the problems at the melting transition. Consequently, we do not believe it is correct to interpret imaginary frequencies as signatures of diffusive barrier crossings.

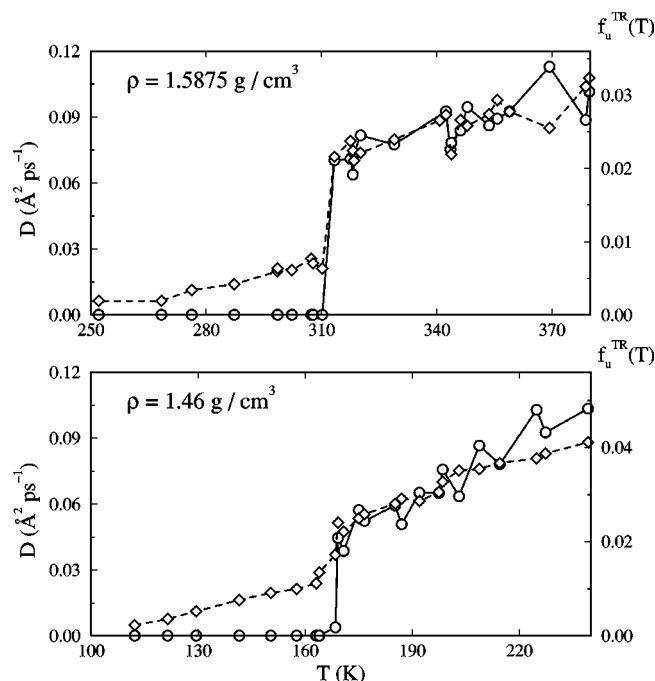It should be clear by now that no one knows the true

FIG. 1. The temperature dependence of the diffusion constant (solid lines) superimposed with the fraction of unstable translational modes, f_u^{TR} (dashed lines) for carbon disulphide at two densities. The scale for the fraction of unstable modes is indicated along the right-hand side of the plots.

distribution of barrier heights in real liquids, and that the temperature dependence of this distribution does not necessarily need to follow the temperature dependence of the INM density of states. None of the filters that have been proposed thus far are capable of eliminating the false-barrier modes,[1] and even if one were able to remove the FB modes, the remaining modes could be primarily barrier modes that separate two adjacent local minima on a rough potential energy surface. Therefore, any phenomenological agreement between the INM densities of states of the real liquid and the soft-potential model may not say anything about the underlying barrier height distribution in real liquids.

The INM approach to diffusion has at its heart the empirical observation that, in some liquids, and at some temperatures, the fraction of modes which are unstable modes, f_u, is proportional to the diffusion constant, D,

$$D(T) \propto f_u(T) = \int_{-\infty}^{0} d\omega \, \rho_u(\omega;T). \qquad (1)$$

We grant that there are some imaginary frequency INMs that are indeed due to the system being present at or near the top of barriers to diffusion, but given the relative rarity of barrier crossings, one would expect to observe imaginary frequency modes that are associated with barrier crossings only around the same times that the system was actually involved in barrier crossing events. Since we can observe imaginary frequencies continuously throughout a simulation of relatively small size, the set of "diffusive barrier" modes is a small *subset* of the total number of unstable modes. One can argue that the diffusion constant should be directly proportional to

the number of open channels [or diffusive barrier modes, $f_D(T)$], so Eq. (1) is more correctly expressed as

$$D(T) \propto f_D(T). \qquad (2)$$

If one assumes (for the sake of argument) that the temperature dependence of the fraction of unstable modes and the fraction of diffusive barrier modes is similar,

$$f_D(T) = c f_u(T), \qquad (3)$$

then one can use the various forms of the INM theories presented in the literature and obtain quite good agreement with the correct diffusion constants. This agreement is due in large measure to the free parameters in the INM theory.

If, however, the constant c in Eq. (3) depends on the temperature, then the fraction of unstable modes will not be correlated with the true barriers to diffusion, and a theory which attempts to predict the diffusion constant using $f_u(T)$ will fail. This is exactly the case at the melting transition, and may also be true in some parts of the liquid regime. Before one can believe the INM theory even in the liquids, the proponents of the theory must show that Eq. (3) holds in general. This has not yet been done.

While we do not dispute the empirical observations of a linear relationship between the diffusion constant and the fraction of unstable modes in some liquids, we are very wary of any theoretical treatment that equates the existence of an unstable mode (regular, DW, or ZF) with a diffusive barrier crossing. How then should one understand the linear relation between $D(T)$ and $f_u(T)$ in liquids? One possibility is that when the system is at a temperature with many accessible barriers, there is a high degree of anharmonicity that is sampled by the system. This anharmonicity is measured by f_u even when the system is nowhere near the actual barrier to diffusion. Barrier crossings seem to imply anharmonicity, even though anharmonicities *do not* imply barrier crossings. This is the crux of our argument against the INM theory for diffusion.

We believe that before the predictions of an INM theory for diffusion can be trusted, it will be important to understand at a much deeper level the relationship between $D(T)$ and $f_u(T)$.

[1] J. D. Gezelter, E. Rabani, and B. J. Berne, J. Chem. Phys. **107**, 4618 (1997).
[2] T. Keyes, J. Chem. Phys. **101**, 5081 (1994).
[3] G. V. Vijayadamodar and A. Nitzan, J. Chem. Phys. **103**, 2169 (1995).
[4] W.-X. Li, T. Keyes, and F. Sciortino, J. Chem. Phys. **108**, 252 (1998).
[5] E. Rabani, J. D. Gezelter, and B. J. Berne, J. Chem. Phys. **107**, 6867 (1997).
[6] Note that our original paper was a critique of a body of work which championed the INM theory in precisely the same system. See Refs. 12–14 for examples.
[7] F. Sciortino and P. Tartaglia, Phys. Rev. Lett. **78**, 2385 (1997).
[8] W.-X. Li and T. Keyes, J. Chem. Phys. **107**, 7275 (1997).
[9] O. Steinhauser and M. Neumann, Mol. Phys. **37**, 1921 (1979).
[10] J. D. Gezelter, E. Rabani, and B. J. Berne (in preparation).
[11] M. C. C. Riberio and P. A. Madden, J. Chem. Phys. **108**, 3256 (1998).
[12] G. Seeley and T. Keyes, J. Chem. Phys. **91**, 5581 (1989).
[13] B. Madan, T. Keyes, and G. Seeley, J. Chem. Phys. **92**, 7565 (1990).
[14] G. Seeley, T. Keyes, and B. Madan, J. Chem. Phys. **95**, 3847 (1991).
[15] B. Madan and T. Keyes, J. Chem. Phys. **98**, 3342 (1993).