

COMMENTS

Comment on “Does lattice vibration drive diffusion in zeolites?” [J. Chem. Phys. 114, 3776 (2001)]

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In a recent paper,¹ Kopelevich and Chang propose a method to estimate the effect of lattice vibrations as a driving force for sorbate diffusion in zeolites—a class of microporous crystalline aluminosilicates. To achieve that, they use lattice dynamics (LD) (Ref. 2) to define a generalized Langevin equation for sorbate motion. The effects of lattice vibration are then estimated by two parameters, involving quantities present in the generalized Langevin equation and easily computed from LD results. Strangely enough, the LD formulation of the crystal, involving only the harmonic contribution from the lattice potential energy, is used by Kopelevich and Chang to discuss the relevance of the molecular dynamics³ (MD) simulations in the study of the diffusive process, forgetting that MD includes also anharmonic effects. Notwithstanding this extrapolation, although the general approach remains useful and interesting. However, the peculiar way in which they treat the low-frequency vibrational modes of the host crystal and in particular the “zero-frequency phonons,” which are always present in the dynamics of a crystal, is not convincing. The LD technique yields three zero frequency modes, which correspond to three uniform *time independent* solutions of the equation of motion and, actually, *they are not phonons*. It is important to stress that, as the zero-frequency modes leave the crystal unchanged, they cannot influence the diffusion of sorbates. Therefore, they do not contribute to the Langevin equation for the diffusive motion of the sorbate, since they do not represent vibrational modes. On the contrary, one has to include all the (properly weighted) other phonons present in the crystal. Among them, the numerically unstable low (but not zero) frequency phonons could require some care. However, their statistical weight, close to the one given by the Debye distribution,² is small, so that they contribute very little to the motion of the sorbate. Kopelevich and Chang, instead, consider the coupling of zero frequency modes with the sorbate molecule [Eqs. (75)–(79) of Ref. 1] and derive equations of motion, Eqs. (77) and (78), which lead to inconsistent results such as the fictitious “resonant blow up” of the crystal caused by the sorbed molecule. We will show that Eqs. (76)

and (77) contain errors and that the correct equations to be used do not contain any “blow up.” Let us rewrite the model Hamiltonian of Eq. (75) in Ref. 1,

$$H_T = \frac{1}{2} M \dot{X}^2 + \frac{1}{2} \sum_{j=1}^3 \dot{Q}_j^2 + \Phi_0(\mathbf{X}) + \sum_{j=1}^3 \hat{\phi}_j(\mathbf{X}) Q_j, \quad (1)$$

where \mathbf{X} is the vector representing the position of a point particle sorbate, Q_j ($j=1,2,3$) are the three zero frequency modes of the crystal, and the potential $\Phi(\mathbf{X}, \mathbf{Q})$ is approximated as the Taylor's development to the first order with $\Phi_0(\mathbf{X}) = \Phi(\mathbf{X}, \mathbf{Q}=0)$ and $\hat{\phi}_j(\mathbf{X}) = \partial\Phi/\partial Q_j|_{Q_j=0}$, $j=1,2,3$. Moreover, for the sake of simplicity, we assume the total mass of atoms in a zeolite cell m (associated with the Q_j 's) as mass unit. Since we have reduced the $3N$ normal modes to 3, we have

$$\hat{\phi}_j(\mathbf{X}) = \left. \frac{\partial\Phi}{\partial Q_j} \right|_{Q_j=0} = - \left. \frac{\partial\Phi}{\partial X_j} \right|_{X_j=0}, \quad j=1,2,3, \quad (2)$$

where the last equality results from the translational invariance of the potential energy Φ ,

$$\Phi(X_j + a_j, Q_j + a_j) = \Phi(X_j, Q_j), \quad j=1,2,3 \quad (3)$$

for any a_j . Taking a_j infinitesimal, translational invariance implies

$$\frac{\partial\Phi}{\partial X_j} + \frac{\partial\Phi}{\partial Q_j} = 0, \quad j=1,2,3 \quad (4)$$

from which the right-hand side of Eq. (2) follows. Translational invariance can be also imposed on the partial expansion of the potential energy assumed in Eq. (1). We can write

$$\Phi(X_j, Q_j) = \Phi(X_j, Q_j^0) + \sum_{j=1}^3 \frac{\partial\Phi(X_j, Q_j^0)}{\partial Q_j} Q_j, \quad j=1,2,3, \quad (5)$$

[where $Q_j^0=0$ are the initial values of Q_j 's ($j=1,2,3$)] and impose the invariance to the left-hand side of Eq. (5),

$$\begin{aligned}
\Phi(X_j+a_j, Q_j+a_j) &= \Phi(X_j+a_j, Q_j^0) + \sum_{j=1}^3 \frac{\partial\Phi(X_j+a_j, Q_j^0)}{\partial Q_j} (Q_j+a_j) \\
&= \Phi(X_j, Q_j^0) + \sum_{j=1}^3 \frac{\partial\Phi(X_j, Q_j^0)}{\partial X_j} a_j + \sum_{j=1}^3 \frac{\partial\Phi(X_j, Q_j^0)}{\partial Q_j} (Q_j+a_j) + \sum_{j,k=1}^3 \frac{\partial^2\Phi(X_j, Q_j^0)}{\partial Q_j \partial X_k} (Q_j+a_j) a_k \\
&= \left[\Phi(X_j, Q_j^0) + \sum_{j=1}^3 \frac{\partial\Phi(X_j, Q_j^0)}{\partial Q_j} Q_j \right] + \sum_{j=1}^3 \left(\frac{\partial\Phi(X_j, Q_j^0)}{\partial X_j} + \frac{\partial\Phi(X_j, Q_j^0)}{\partial Q_j} \right) a_j \\
&\quad + \sum_{j,k=1}^3 \frac{\partial^2\Phi(X_j, Q_j^0)}{\partial Q_j \partial X_k} (Q_j+a_j) a_k = \Phi(X_j, Q_j). \tag{6}
\end{aligned}$$

Taking into account the condition given by Eq. (4), expressing translational invariance, we get

$$\sum_{j=1}^3 \frac{\partial^2\Phi(X_j, Q_j^0)}{\partial Q_j \partial X_k} Q_j = 0, \quad k=1,2,3. \tag{7}$$

Equation (7) can be rewritten, in sight of Eq. (2),

$$\sum_{j=1}^3 \frac{\partial^2\Phi(X_j, Q_j^0)}{\partial X_j \partial X_k} Q_j = 0, \quad k=1,2,3, \tag{8}$$

which is then a direct consequence of translational invariance. The equations of motion derived from the Hamiltonian, Eq. (1), read [see Eqs. (77) and (78) of Ref. 1]

$$M\ddot{X}_i = -\frac{\partial\Phi_0}{\partial X_i} + \sum_{j=1}^3 \frac{\partial^2\Phi}{\partial X_i \partial X_j} Q_j = -\frac{\partial\Phi_0}{\partial X_i}, \quad i=1,2,3, \tag{9}$$

$$\ddot{Q}_i = \frac{\partial\Phi_0}{\partial X_i}, \quad i=1,2,3, \tag{10}$$

which then trivially simplify to a pair of equations conserving linear momentum. No “blow up” is implied. There is another unfortunate choice taken in the numerical solution of Eqs. (77) and (78) of Ref. 1. Since it is assumed that the Q_j 's are initially at rest, one cannot assign an initial kinetic energy (then, for a point particle, initial finite velocity) to the sorbate molecule (as reported on p. 3784 of Ref. 1), because the system would have a nonzero initial linear momentum and would indefinitely translate. In any event we have verified that, dropping the last term of the right-hand side of Eq. (77) of Ref. 1 and assuming initially both the sorbate and the crystal at rest, an oscillating behavior for the Q_j 's and a strict conservation of total energy were observed for Xe in silicalite for hundreds of picoseconds. Once amended from the misleading considerations discussed above, the method proposed by Kopelevich and Chang can be useful and even applied to MD simulations, instead of LD, to evaluate the stochastic random force acting on the sorbate molecule, without any approximation for the potential function. In this form it could permit to estimate the effect of lattice vibration as a driving force for sorbate diffusion using simulation runs much shorter than those required to evaluate directly the diffusion coefficients. Finally, we are reminded that previous studies on this effect, based on a wealth of MD simulations,⁴⁻⁸ have permitted us to draw the following conclusions:

- (i) Lattice vibrations provide an efficient heat bath in any case.⁴
- (ii) At infinite dilution (one sorbate per simulation box) when the energy barrier to diffusion is low, the influence of the lattice vibration is relatively small.⁴⁻⁶ Otherwise, if the transition state involves the crossing of a window whose diameter is smaller than the sorbate diameter, the lattice vibration effect can be large (see, e.g., Ref. 7). However, when the barrier is high, but in the transition state the sorbate is not close to a channel wall, like for example benzene in NaY zeolite,⁸ the influence of lattice vibration is again small.
- (iii) At finite loading, when the diffusion is controlled by the collisions between sorbed molecules, neglecting lattice vibration has a strong effect on the diffusion dynamics, as it favors unphysical clustering and high-energy collisions, due to the lack of linear momentum conservation in sorbate motion.^{4,5}

In conclusion, with the provisos given in this comment, the results of Ref. 1 are important since, even if in some cases the choice of a rigid crystal does not alter dramatically the sorbate motion, the inclusion of lattice vibrations (resulting from LD, or, even better from MD simulations) is essential to provide in general a correct representation of the sorbate dynamics.

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