Vacancy migration rates by molecular dynamics with constraints

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Abstract. Rate constants for vacancy migration in a Lennard-Jones crystal are evaluated within the frame of the reactive flux correlation function formalism by molecular dynamics simulation. In our calculation a key role is played by a holonomic constraint acting on the reaction coordinate. The definition of a suitable reaction coordinate is a subtle matter as becomes evident when using our techniques. We show how the ambiguities in the definition of the reaction coordinate can be circumvented. Our results are two orders of magnitude more precise than previous 'exact' calculations.

1. Introduction

Diffusion in solids is due essentially to rare hopping events; usually these events are made possible by the presence of defects. In this article we will deal essentially with methodological aspects of these phenomena and will focus our attention particularly on the vacancy–atom interchange in a simple model consisting of a perfect Lennard-Jones crystal and one missing atom or vacancy. The reactive flux correlation function formalism represents an adequate framework to study by computer simulation the dynamics of activated processes taking place in condensed matter. This formalism has been introduced by Yamamoto [1] and comes out from a direct application of the fluctuation–dissipation theorem. Chandler [2] showed clearly how to use that formalism in conjunction with molecular dynamics (MD) and also discussed the connection of this formalism with the transition state theory. It must be said that equivalent MD techniques to evaluate rate constants have been used previously by Bennett [3] for the study of defects migration in solids. The reaction coordinate, one of the essential ingredients of the reactive flux correlation function formalism, is in general a function of the full configuration space of the system. Its instantaneous value gives a microscopic description of the phenomenon or 'reaction' under study (the jump process in our case). Bennett [3] discussed the general properties that a reaction coordinate must satisfy. He also defined a suitable reaction coordinate for the vacancy–atom interchange process description: by choosing a diffusing atom among the neighbours of the vacancy, it measures the mutual 'distance' between the atom and the vacancy.

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In performing our calculations we have found that such a definition of the reaction coordinate is a rather poor one. In fact the values that this reaction coordinate can assume do not identify uniquely the position of the system within one of the two regions of configuration space between which the transition process that we are studying takes place. This ambiguity is eliminated if each atom (except the diffusing one) is localized around its equilibrium site in some way. The aim of this paper is to re-analyse the problem of the evaluation of rate constants by molecular dynamics of a particular hopping process in a model crystal viewed as an application of Chandler's theory of activated processes. We use computational techniques for the free energy part of the rate constant that are different from those usually applied to activated processes calculations (see, for example, Bennett [3], Rebertus *et al* [4] and Gillan *et al* [5]). More precisely we use a method previously introduced by Carter *et al* [6] and another one [7, 8] that in general should be computationally equivalent.

The application of these methods allows us to determine the rate constants with a high numerical precision (we used the same system as Bennett [3] to compare our results) and without the ambiguity involved in the definition of the reaction coordinate. This ambiguity disappears if there is an external field that keeps each atom (except the jumping one) localized. The easiest choice for this field is an harmonic spring that keeps each atom around its equilibrium site. The final results must be extrapolated to a field value of zero.

The outline of this paper is as follows: section 2 discusses the definition of the reaction coordinate and the reactive flux correlation formalism. In section 3 we describe the techniques in which an holonomic constraint on the reaction coordinate plays a central role. In section 4 we discuss the results for vacancy jump rate constant in a face-centred cubic (FCC) Lennard-Jones (LJ) system representing Argon at 60 K and 80 K and we make some concluding remarks.

2. Theoretical ideas

2.1. The reaction coordinate

We are considering the transition of a superimposed vacancy in a perfect crystal between two nearby sites. More precisely, the 'reaction' we are considering is the position interchange of a vacancy with a well-defined atom occupying a nearest-neighbour vacant site. A reaction coordinate is a parameter that allows one to locate the instantaneous state of the reaction. Each state corresponds to a well-defined region of the configuration space. A reaction coordinate is satisfactory if it has well-separated values when the system is in one of the stable states (two in our case) and assumes intermediate values when the system jumps between the stable states. In order to obtain a suitable identification of the two stable regions in configuration space (say A and B) and the transition state between them, a reaction coordinate must be a continuous function of the atomic coordinates, $\xi = \xi(r)$ [3]. We will consider that ξ takes a value near ξ_A if the system is in region A and a value $\xi_B > \xi_A$ if the system is in the region B. If we define $W(\xi_2) - W(\xi_1)$ as the reversible work done by external forces to bring the reaction coordinate from ξ_1 to ξ_2, $W(\xi)$ will have a shape with two minima located at $\xi = \xi_A, \xi_B$ (stable states), separated by a relative maximum at the transition state $\xi^\dagger$. If the height of the free energy barrier separating the stable and transition states is larger than few $k_B T$, then the reaction will be a rare event.

We are considering the atom–vacancy interchange in a FCC lattice. Our model is made by N points of mass m and with coordinates $\{r\} = (r_1, \ldots, r_N)$. The reaction coordinate we need to define must depend on the distance between the instantaneous positions of the atom and the vacancy. The latter is determined by the instantaneous position of its nearest-neighbour atoms. A reasonable reaction coordinate used in previous works [3, 5] is

$$\xi(r) = \left[r_1 - \tfrac{1}{4}(r_2 + r_3 + r_4 + r_5)\right] \cdot \hat{j} \tag{1}$$

where $\hat{j}$ is the unit vector in the jump direction (110) of the crystal at $T = 0$ (see figure 1). Atom 1 is the jumper and atoms 2, 3, 4 and 5 define a 'gate' through which atom 1 must pass to reach the vacant site. In a perfect FCC crystal these atoms lie on a plane orthogonal to the vector joining atom 1 and the vacancy. If atoms $2, \ldots, 5$ oscillate around their perfect crystal positions, values of ξ near zero identify the transition region.
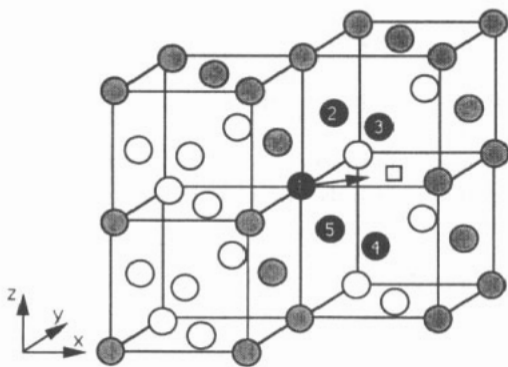

Figure 1. Geometry of the system around the vacant site (square). The jumping atom is atom 1. Its distance to the centre of mass of atoms 2, 3, 4 and 5 defines the reaction coordinate. The last can be seen as a way to measure the position of the jumping atom with respect to the two sites accessible to it.

In principle every nearest-neighbour atom of the vacant site (12 in a FCC crystal) is equally likely to jump in it. But we are focusing our attention on atom 1. Let us suppose that we can prevent in some 'artificial' way the other 11 rare events possible in our system. If we observe the behaviour in time of the reaction coordinate, it will be oscillating around one of the two possible symmetrical equilibrium values $\xi_A = -a/2$ or $\xi_B = a/2$ (where a is the nearest-neighbours' distance in the perfect crystal). On a timescale much longer than that characterizing the vibrational motion of the atoms, $\xi(t)$ will show a few fast transitions from state A to state B. We remark now, and we will discuss this particular issue later, that a reaction coordinate like (1) is meaningful only if it is based on the assumption that each atom except atom 1 is around its initial site. (We are not speaking of Wigner–Seitz cells because the equilibrium positions of the defective crystal are slightly different from those of the perfect crystal, and when the system is near the transition state a serious deformation of the lattice may occur.)

2.2. The reactive-flux correlation function formalism

If the timescale inherent to the activated process is well separated from all the others characterizing the microscopic dynamics, the rate constants for our reaction A $\rightleftharpoons$ B

(the two rate constant are equal for symmetry reasons) is given by the apparent plateau value of the reactive flux correlation function defined as

$$k(t) = \frac{1}{\langle \Theta_A \rangle} \left\langle \dot{\xi}(0) \, \delta(\xi(0) - \xi^\dagger) \, \theta(\xi(t) - \xi^\dagger) \right\rangle . \tag{2}$$

Here $\dot{\xi}(t)$ is the velocity of the reaction coordinate, $\theta(\xi(t) - \xi^\dagger)$ is the characteristic function for stable state B and $\langle \Theta_A \rangle = \langle \theta(\xi^\dagger - \xi) \rangle$ is the fraction of time that the system spends in the stable state A. $k(t)$ is, within constant factors, the flux of the reaction coordinate through the transition state for trajectories that are on the transition state at the beginning and for which, at later time t, $\xi(t) > \xi^\dagger$. This correlation function is characterized by two relaxation times. The shorter, τ_{vib}, is connected with the fast relaxation of the system from the initial transition state to one of the two stable states. The other, τ_{rxn}, is the decorrelation time of the two observable $\dot{\xi}(0)\delta(\xi(0) - \xi^\dagger)$ and $\theta(\xi(t) - \xi^\dagger)$ or equivalently is that during which the system loses memory of the initial state.

Equation (2) is the average ($\langle \cdots \rangle$) of the product of observables at different times $\dot{\xi}(0) \, \delta(\xi(0) - \xi^\dagger)$ and $\theta(\xi(t) - \xi^\dagger)$, over the canonical probability density $\mathrm{e}^{-\beta H}$, where $H(r,p)$ is the Hamiltonian of the system. It can also be seen as the average of $\dot{\xi}(0) \, \theta(\xi(t) - \xi^\dagger)$ over the *joint* probability density $\mathrm{e}^{-\beta H} \, \delta(\xi(0) - \xi^\dagger)$. The average in the numerator of equation (2) divided by the probability density of ξ at $\xi^\dagger$ gives the average, *conditioned* at $\xi^\dagger$, of $\dot{\xi}(0) \, \theta(\xi(t) - \xi^\dagger)$.

In reference [6] it is shown that the average conditioned at $\xi^\dagger$ of an observable $A(r)$ can be obtained as a weighted average of A over a dynamics with the constraint $\xi = \xi^\dagger$ imposed, i.e.

$$\frac{\langle A(r)\delta(\xi(r) - \xi^\dagger) \rangle}{\langle \delta(\xi(r) - \xi^\dagger) \rangle} = \frac{\langle |Z|^{-1/2} A(r) \rangle_{\xi^\dagger}}{\langle |Z|^{-1/2} \rangle_{\xi^\dagger}} . \tag{3}$$

Here $\langle \cdots \rangle_{\xi^\dagger}$ represent averages taken over the canonical probability density for a system *constrained* at the hypersurface $\xi(r) = \xi^\dagger$. The weight $|Z|^{-1/2}$ (where $|Z| = \sum |\partial \xi / \partial r_i|^2 / m$) removes the bias generated by the constraint on the dynamics of the system. The quantity $\langle \delta(\xi - \xi^\dagger) \rangle = P(\xi = \xi^\dagger)$ is the probability density to observe the reaction coordinate at the transition state. In dynamical terms the left hand side term of (3) can be viewed as an average over a trajectory in the configuration space in which only points with $\xi(r) = \xi_2$ contribute, while the right hand term side is a ratio of averages over trajectories in which the *holonomic constraint* $\xi = \xi^\dagger$ is imposed (configurational 'blue moon ensemble' of Carter *et al* [6]).

An analogous relation [6] can be used to evaluate conditional time correlation functions between an observable A at $t = 0$ and another B at a later time t using initial conditions taken from a trajectory constrained at $\xi(r) = \xi^\dagger$:

$$\frac{\langle A(0)B(t)\delta(\xi(0) - \xi^\dagger) \rangle}{\langle \delta(\xi(r) - \xi^\dagger) \rangle} = \frac{\langle |Z|^{-1/2} A(0)B(t) \rangle_{\xi^\dagger, \mathrm{M}}}{\langle |Z|^{-1/2} \rangle_{\xi^\dagger}} \tag{4}$$

where now $\langle \ldots \rangle_{\xi^\dagger, \mathrm{M}}$ means that in evaluating the correlation function, the constraint has been imposed only to sample the initial configuration, while the momenta are extracted from a maxwellian distribution and the dynamical evolution of the system is unconstrained.

Equation (2) can then be written as

$$k(t) = \frac{1}{\langle \Theta_A \rangle} \frac{\left\langle |Z|^{-1/2} \dot{\xi}(0) \theta(\xi(t) - \xi^\dagger) \right\rangle_{\xi^\dagger, M}}{\langle |Z|^{-1/2} \rangle_{\xi^\dagger}} P(\xi = \xi^\dagger). \tag{5}$$

Classically, for $t \to 0^+$, $k(t)$ becomes [6]

$$k(0^+) \equiv k^{\text{TST}} = \frac{1}{\langle \Theta_A \rangle} \left\langle \dot{\xi} \theta(\dot{\xi}) \delta(\xi - \xi^\dagger) \right\rangle = \frac{1}{\langle \Theta_A \rangle} \frac{1}{\sqrt{2\pi\beta}} \frac{1}{\langle |Z|^{-1/2} \rangle_{\xi^\dagger}} P(\xi = \xi^\dagger). \tag{6}$$

Here, k^{TST} is the transition state theory approximation to the rate constant. Within this theory it is assumed that all trajectories passing over the transition state with $\dot{\xi} > 0$ end up in the region B and remain there for a time much longer than τ_{vib}.

Equation (5) can be compared with the more familiar way of writing $k(t)$:

$$k(t) = k^{\text{TST}} \kappa(t) \tag{7}$$

where $\kappa(t)$ is the transmission coefficient. The plateau value of $\kappa(t)$, attained for $\tau_{\text{vib}} \ll t \ll \tau_{\text{rxn}}$, represents the dynamical correction to transition state theory due to the possibility of recrossings.

3. Techniques for the probability density of the transition state

We are studying rare processes. This means that a brute-force calculation of $P(\xi = \xi^\dagger)$ by MD requires very long time trajectories (much longer than τ_{rxn}). Special techniques have been developed to evaluate quantities like $P(\xi = \xi^\dagger)$. The common idea of all MD techniques is to force artificially the sampling of ξ in the regions of phase space that would rarely be visited by a normal trajectory. Of course at the end one must be able to remove from the results the bias introduced in the dynamics. This bias can be an external and continuous potential, like in the MD version of the umbrella sampling method [9]. In this work we calculated the probability density of the transition state in two ways, both involving the use of a ξ-constrained dynamics.

The probability density to find the system at any point of configuration space compatible with a prescribed value ξ_1 of $\xi(r)$ is

$$P(\xi = \xi_1) = \langle \delta(\xi(r) - \xi_1) \rangle \equiv C e^{-\beta W(\xi_1)} \tag{8}$$

where $\beta = 1/k_B T$, $\langle \cdots \rangle$, as usual, is the canonical ensemble average and $W(\xi)$ is the potential of mean force associated with the reaction coordinate. The constant C is determined by the normalization condition on $P(\xi)$.

The difference $W(\xi_2) - W(\xi_1)$ is the reversible work needed to bring the system from some reference value ξ_1 of ξ to ξ_2. The difference of the potential of mean force is given by (Tobias and Brooks [7], Paci *et al* [8])

$$W(\xi_2) - W(\xi_1) = -k_B T \ln \frac{\left\langle |J^{-1}| |J_{\xi_2}| e^{-\beta \Delta V} \delta(\xi(r) - \xi_1) \right\rangle}{\langle \delta(\xi(r) - \xi_1) \rangle}$$

$$= -k_B T \ln \frac{\left\langle |J^{-1}| |J_{\xi_2}| |Z|^{-1/2} e^{-\beta \Delta V} \right\rangle_{\xi_1}}{\langle |Z|^{-1/2} \rangle_{\xi_1}}. \tag{9}$$

In deriving equation (9) we must define a set of generalized coordinates $u = (\xi, q)$ with $q = (q_1, q_2, \ldots, q_{3N-1})$ and $|J| = |\partial r / \partial u|$ the Jacobian of the canonical transformation $\{r\} \Leftrightarrow \{u\}$. In passing from the first to the second equality in equation (9) we have used equation (3). Then, instead of evaluating a conditional average over a free trajectory, we evaluate an average over a constrained trajectory. For each point of these trajectories $\Delta V = V'(\xi_2, q(r)) - V'(\xi_1, q(r)) \equiv V_{\xi_2}(r) - V_{\xi_1}(r)$. The quantity $V'(u)$ is the potential energy of the system expressed in terms of generalized coordinates $\{u\}$ and $V_{\xi_2}(r)$ and $|J_{\xi_2}|$ are the values of V and $|J|$ at a point that is the projection on the hypersurface $\xi(r) = \xi_2$ of a given point on the trajectory. The quantity $V_{\xi_1}(r)$ is the value of V corresponding to the the hypersurface $\xi(r) = \xi_1$. To evaluate the expression on the right hand side of equation (9) a constant-temperature constrained molecular dynamics can be carried out using standard methods [10–12]. At each time step the quantities $V_{\xi_1}(r)$ and $|J_{\xi_1}|$ must be calculated as described above.

From the definition (8) of the potential of mean force, one can also define the mean force as

$$
F(\xi_1) \equiv -\frac{d}{d\xi_1} W(\xi_1) = \frac{\left\langle \left[-\frac{\partial V}{\partial \xi} + \beta^{-1} \frac{\partial \ln |J|}{\partial \xi} \right] \delta(\xi(r) - \xi_1) \right\rangle}{\langle \delta(\xi(r) - \xi_1) \rangle}
$$

$$
= \frac{\left\langle |Z|^{-1/2} \left[-\frac{\partial V}{\partial \xi} + \beta^{-1} \frac{\partial \ln |J|}{\partial \xi} \right] \right\rangle_{\xi_1}}{\left\langle |Z|^{-1/2} \right\rangle_{\xi_1}} \tag{10}
$$

where again we used equation (3). Equation (9) is valid for any pair of values ξ_1, ξ_2. However if ξ_1 is far from ξ_2, the factor $e^{-\beta \Delta V}$ can be vanishingly small and the sampling needed to estimate the expectation value will be difficult. Thus, equation (9) can only be used to compute the difference between the potential of mean force corresponding to two nearby values of the reaction coordinate ξ. Equation (10) gives for each value of ξ the absolute value of the mean force acting on ξ. The potential of mean force can be obtained by integrating the force function. To do this, the force must be known on a set of ξ closely spaced values. If we take $\xi_1 = \xi$ and $\xi_2 = \xi \pm \delta \xi$ in (9) and $\xi_1 = \xi$ in (10), for $\delta \xi \to 0$ it is straightforward that (9) and (10) yield the same information about $W(\xi)$.

4. Results and discussion

We have already pointed out that the reaction coordinate (1) is meaningful if only one atom is allowed to jump, while all the others oscillate around their equilibrium position. However it can happen that another atom may jump in the vacant site instead of the chosen one. In previous studies this feature has probably been underestimated. It can be easily understood that the reaction coordinate (1) can fail to visualize the path of our reaction. In fact its value changing from $-a/2$ to $a/2$ represents the motion of atom 1 between its initial site and the vacancy only if none of the other 11 nearest neighbours of the vacancy jumps on it. Otherwise the values taken by ξ will no longer represent the relative position of atom 1 and the vacancy. Near melting temperature it is not very unlikely that another atom will jump into the vacancy (or in one of the two half-vacancies) even during a 'short' ξ-constrained simulation.

Our idea here is to introduce an external field that localizes atoms around their equilibrium positions. Final results will be calculated by extrapolating to zero field. We have added to the true Hamiltonian

$$H(\boldsymbol{r}, \boldsymbol{p}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} \sum_{j>i}^{N} v(r_{ij})$$

where $v(r)$ is the pair LJ potential, an 'artificial' harmonic potential term given by

$$V'(\boldsymbol{r}_2, \dots, \boldsymbol{r}_N; \lambda) = \lambda \frac{K_{\max}}{2} \sum_{i=2}^{N} |\boldsymbol{r}_i - \boldsymbol{r}_i^0|^2 \tag{11}$$

where $K_{\max}$ is of the order of magnitude of the spring constant of an harmonic crystal with mean square displacement of atoms comparable to that of the crystal under study, and $\{r_i^0\}$ are the equilibrium positions of the atoms in the crystal. λ is a parameter such that for $\lambda = 0$ we recover the original system. For $\lambda > 0$ we have a system similar to the original one but in which fluctuations that can lead an atom other than atom 1 to jump are prevented.

Intuitively, the positions $\{r_i^0\}$ should be those of the crystal relaxed in presence of the vacancy. However by applying (9) and (10), we evaluate the mean value of certain observables while the reaction coordinate is constrained at some value. The relaxed configuration of the crystal is strongly dependent on the value of this constraint.

It is intuitive that if the $\{r_i^0\}$ are fixed and are not dependent on the constrained value of ξ at which the dynamics is evolved, then when we measure constrained averages for values of ξ near the transition state these will be strongly λ-dependent. The extrapolation for $\lambda = 0$ would then be hard. The transition state probability density evaluated in this way goes quickly to zero for $\lambda > 0$. This can be understood if we consider that although the springs have a weak influence on the 'typical' oscillatory dynamics of the crystal they hinder the rare fluctuations that can carry atom 1 far from both equilibrium sites accessible to it.

We therefore use positions $\{r_i^0\}$ that are obtained by relaxing the system with a constraint over ξ. The procedure to extrapolate correctly using ξ-dependent relaxed $\{r_i^0\}$ is not straightforward. In fact it is clear that using ξ-dependent relaxed values for $\{r_i^0\}$ we cannot compute $W(\xi; \lambda)$. The reason is that for different values of the constraint ξ we have systems with different Hamiltonians ($\{r_i^0\}$ are functions of ξ) and then incompatible differences in equation (9) and forces in equation (10). To achieve consistency we have first of all to evaluate (9) and (10) at each value of ξ_1, for few values of λ. Then we extrapolate those quantities for $\lambda = 0$. Only after that can we sum up the differences of potential of mean force or integrate the force to evaluate $W(\xi)$.

4.1. The transition state theory rate constant

With the linear reaction coordinate of equation (1) the transformation of coordinates needed to evaluate (9) and (10) is simply linear, so that the Jacobian determinant $|J| = \sqrt{2}$ is a constant. For this reason the term depending on $|J|$ in the expression of the mean force (10) is zero. In fact the term $\partial \ln |J| / \partial \xi$ represents the apparent force that would arise from the non-inertial character of the ξ variable. In the same

way the ratio $|J_{\xi_2}|/|J_{\xi_1}| = 1$ simplifies (9). In this particular case $|Z|^{-1/2} = \sqrt{4m/5}$ is also a constant.

Taking $\xi_2 - \xi_1 = \pm\delta\xi$ in equation (9) and performing a number of ξ-constrained simulations, varying the value of ξ by 2δ at each simulation, the potential of mean force can be computed over the range of interest within an additive constant. From (10) the mean force on ξ can be directly computed and the potential is obtained by numerical integration.

Our simulations were carried out on a system of 255 LJ particles disposed on a FCC array, namely 4^3 unit cells with a missing atom. The array is initially relaxed in presence of the constraint on the reaction coordinate. The best LJ parameters that reproduce Argon are $\sigma = 3.405$ Å and $\epsilon/k_B = 119.8$ K, where k_B is the Boltzmann constant. All the numbers we report are in reduced units σ,ϵ and m where the latter is the mass of an Argon atom ($m = 66.9 \times 10^{-24}$ g).

The simulation was carried by MD at fixed volume, temperature and number of particles (Nosé–Hoover technique [10,11]). Periodic boundary conditions were used, along with a cut-off of the potential at $r = 2.5\sigma$. The constraint on the reaction coordinate were imposed using the SHAKE algorithm [12]. The equations of motion were integrated using the classical Verlet algorithm with a timestep $h = 0.005\sigma\sqrt{m/\epsilon} \simeq 10^{-14}$ s.

We have calculated $W(\xi)$ and $F(\xi)$ for $0 < \xi < 0.9a$. The first, along with $P(\xi)$, is symmetric with respect to $\xi = 0$ while $F(\xi)$ is antisymmetric. We pushed the calculation of $P(\xi)$ up to values of ξ beyond the equilibrium position because it needed to be normalized. The calculation was truncated at $\xi = 0.9a$ where $P(\xi)$ is equal to $10^{-10}\sigma^{-1}$ for $T = 0.505$ ϵ/k_B and $10^{-6}\sigma^{-1}$ for $T = 0.67$ ϵ/k_B respectively. The value for the spring constant appearing in equation (11) was taken as $K_{max} = 400$ ϵ/σ^2 for both temperatures. As described earlier in this section we calculated each average three times for three different values of λ. All relevant quantities were extrapolated for $\lambda = 0$. The values of λ used were 0.08, 0.24, 0.4 and 0.1, 0.4, 1 for the lower and the higher temperature respectively. Each average was computed over trajectories 40 000 timesteps long (plus 4000 of equilibration). Statistical errors on the measured quantities were estimated by evaluating the standard deviation on a set of 20 segments of trajectory each 2000 timesteps long. In figures 2 and 3 we report, respectively, the potential of mean force obtained from (9) and the mean force obtained from (10). In figure 4 we report the probability density of the reaction coordinate. Error bars on our entries are invisible within the scale of the figures reported. The results for $P(\xi = \xi^\dagger)$ are reported in table 2. The consistency of the two different methods used is evident. Also reported in table 2 are values of k^{TST} obtained from equation (6), where $P(\xi = \xi^\dagger)$ is the mean of the two values reported previously.

Table 1. Temperature, density, nearest-neighbours' distance, mean energy and pressure, in reduced units, for the two points of the phase diagram of the LJ crystal under investigation.

T	ρ	a	$< E >$	$< P >$
0.505	1.0026	1.1215	−6.914	−0.55
0.670	0.9688	1.1344	−6.288	−0.34

Table 2. Probability density (in units of σ^{-1}) of $\xi = \xi^\dagger = 0$ using the two methods (see text) for the two points of the phase diagram for the LJ model crystal under investigation; k^{TST} (in units of $\sigma\sqrt{m/\epsilon}$) is evaluated from equation (6) using the mean of the two results for $P(\xi = \xi^\dagger)$; $\kappa(t^*)$ (adimensional) is the the transmission coefficient.

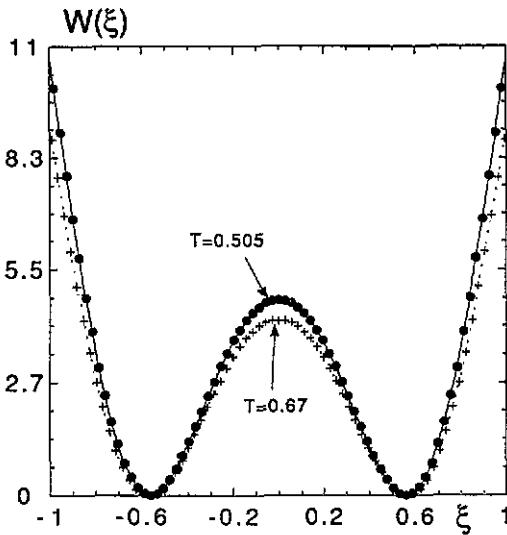| | $P(\xi = 0)$ | | | |
	differences method	mean-force method	k^{TST}	$\kappa(t^*)$
$T = 0.505$	$(2.48 \pm 0.17)10^{-4}$	$(2.72 \pm 0.11)10^{-4}$	$(1.63 \pm 0.15)10^{-4}$	0.905
$T = 0.670$	$(4.20 \pm 0.14)10^{-3}$	$(4.15 \pm 0.13)10^{-3}$	$(3.04 \pm 0.22)10^{-3}$	0.875

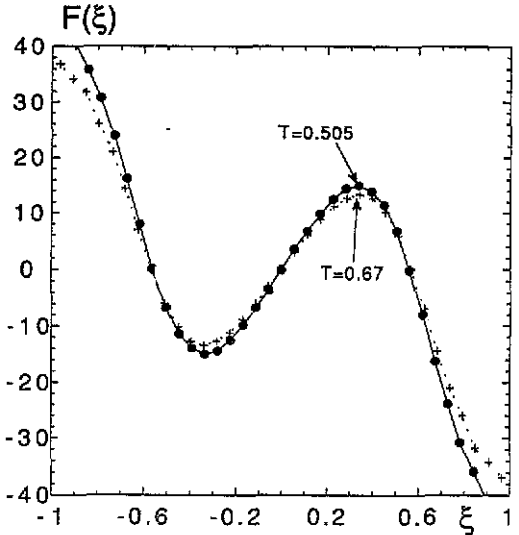**Figure 2.** Potential of mean force on ξ evaluated using equation (9).

Figure 3. Mean force on ξ evaluated using equation (10).

4.2. The transmission coefficient

From the definition (7), and using (2) and (6) the transmission coefficient is given by

$$\kappa(t) = \frac{\left\langle \dot{\xi}(0)\theta(\xi(t) - \xi^\dagger)\delta(\xi(0) - \xi^\dagger)\right\rangle}{\left\langle \dot{\xi}\theta(\dot{\xi})\delta(\xi - \xi^\dagger)\right\rangle} = \sqrt{2\pi\beta}\left\langle |Z|^{-1/2}\dot{\xi}(0)\theta(\xi(t) - \xi^\dagger)\right\rangle_{\xi^\dagger, \text{M}} \qquad (12)$$

the corresponding result with the simplification implied in the linearity of the reaction coordinate being

$$\kappa(t) = \sqrt{8\pi\beta/5}\left\langle \dot{\xi}(0)\theta(\xi(t) - \xi^\dagger)\right\rangle_{\xi^\dagger, \text{M}} . \qquad (13)$$

$\kappa(t)$ has been evaluated by MD as an average over a set of trajectories that, initially lying on the hypersurface $\xi(r) = \xi^\dagger$, are followed in their unconstrained dynamical evolution. The initial configurations for the trajectories have been collected by extracting a configuration every 500 timesteps from a trajectory constrained at $\xi = \xi^\dagger$
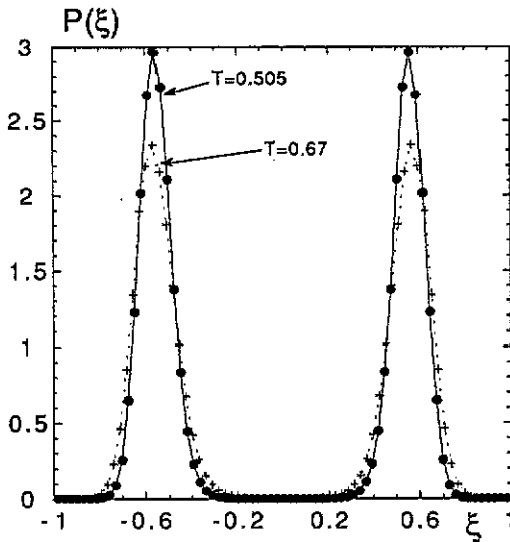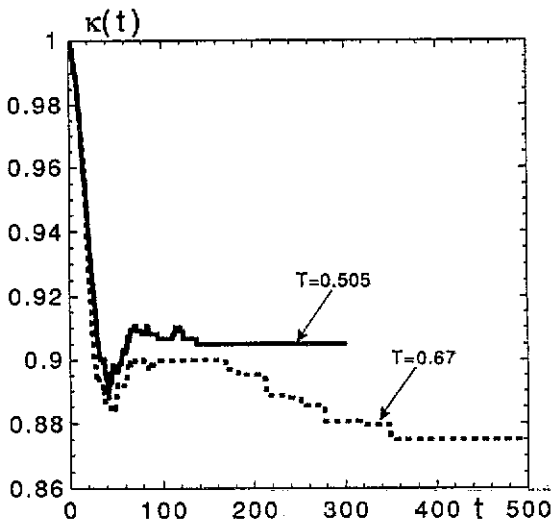
Figure 4. Probability density of ξ.

Figure 5. Transmission coefficient.

and 200 000 timesteps long. Initial velocities for these trajectories have been extracted from a Maxwellian distribution. Such trajectories have been followed for a time long enough to observe the plateau for $\kappa(t)$ (figure 5). At the lowest temperature the plateau is reached after about 150 timesteps; The value of κ on the plateau is about 0.9. It means that almost every time that a trajectory coming from one stable region intersects the transition state with positive velocity, we have a successful transition. At the highest temperature (that is indeed near the melting temperature for Argon) the plateau value of κ is slightly lower than in the previous case. Anyway, although it is a well-established fact [3, 14], we remark that transition state theory is rather accurate in this particular case. The exact values found for the transmission coefficient

are reported in table 2.

We also have to say that this way of evaluating the transmission coefficient is completely equivalent to that previously used by Gillan *et al* [5] although the complete justification of the method in the general case was given by Carter *et al* [6].

4.3. Concluding remarks

In table 3 our values of the rate constant k are compared with those obtained by Bennett [3] and by De Lorenzi and Jacucci [13]. The results of Bennett were obtained with an equivalent method, namely MD simulation without any kind of approximation but using different techniques to accelerate the frequency of jumps. It can be noticed that the uncertainty of his results is much greater than that obtained by our method. The results of De Lorenzi and Jacucci were obtained by a quasiharmonic lattice-dynamics calculation. They compared their results with those of Bennett, concluding that lattice dynamics underestimates the jump rate in a systematic way. A comparison of our results with those obtained by De Lorenzi and Jacucci shows that their systematic underestimation is, in reality, much less relevant. Moreover it can be seen that lattice-dynamics results are very good even near the melting point, so that it is possible to state that the effects of anharmonicity on vacancy diffusion rate constant are not very relevant.

Table 3. Logarithm of the rate constant (in units of $\sigma\sqrt{m/\epsilon}$) compared with the results of Bennett [3] and De Lorenzi and Jacucci [13].

	$\ln k = \ln k^{\mathrm{TST}} \kappa(t^*)$		
		Bennett	De Lorenzi *et al*
$T = 0.505$	-8.822 ± 0.092	-7.5 ± 1.0	-9.2
$T = 0.670$	-5.929 ± 0.074	-5.0 ± 0.5	-6.1

If one assumes that the only mechanism that makes diffusion in crystals possible is the position interchange between an isolated vacancy and one of the nearest-neighbour atoms, the diffusion coefficient is simply $D = (n/N)(z/6)\, k\, a^2$. In this relation (n/N) is the concentration of vacancies, z is the coordination number (12 in a FCC crystal), a is the nearest neighbours' distance and k the rate constant that we calculated above.

For the two points of the phase diagram of Argon in our study, we have $D = 1.1 \times 10^{-9} \sigma\sqrt{\epsilon/m} = 5.9 \times 10^{-13}$ cm^2 s^{-1} at $T = 60$ K and $D = 1.44 \times 10^{-6} \sigma\sqrt{\epsilon/m} = 7.7 \times 10^{-10}$ cm^2 s^{-1} at $T = 80$ K. We used the values of Squire and Hoover [15] for the vacancy concentration. Experimental values of these quantities are affected by important errors. We can quote the result of Bernè *et al* [16] who, for a temperature around 80 K, found $D = 2^{+4}_{-1} \times 10^{-9}$ cm^2 s^{-1}. This value is in agreement with ours. Moreover our results are sure to be an underestimate of the real diffusion coefficient because only one mechanism contributing to diffusion is taken in account.

Also, other diffusive mechanism like divacancy motion or interstitial jumps are often activated processes, at least at temperatures well below the melting point. Their contribution to the diffusion coefficient can be computed by means of the reactive flux formalism if one is able to define a suitable reaction coordinate.

Acknowledgments

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