

## Surface diffusion coefficients: Substrate dynamics matters

LingTi Kong\* and Laurent J. Lewis†

Département de Physique et Regroupement Québécois sur les Matériaux de Pointe (RQMP), Université de Montréal, Case Postale 6128, Succursale Centre-Ville, Montréal, Québec, Canada H3C 3J7

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The pre-exponential factors for Cu adatom diffusion on Cu(001), (110), and (111) are examined within the framework of the harmonic transition-state theory and the embedded-atom method in order to precisely assess the role of the substrate dynamics. We find that the substrate cannot be ignored for an accurate determination of the prefactors: its contribution to the Helmholtz vibrational free energy is typically of the same order as that of the adatom and often of opposite sign so that significant cancellation may occur. These results provide a convenient pathway for the proper calculation of prefactors by using, e.g., *ab initio* methods.

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Detailed knowledge of diffusion processes is of utmost importance for the understanding of a number of nonequilibrium phenomena, such as nucleation and growth.<sup>1</sup> On surfaces, for instance, the rates at which particles diffuse determine the equilibrium shape of islands and, on macroscopic time scales, the morphology of films.

Diffusion may be characterized in terms of “diffusion coefficients,” derived from the Einstein relation as follows:

$$D = \lim_{t \rightarrow \infty} \frac{\langle \Delta r^2(t) \rangle}{2dt}, \quad (1)$$

where  $t$  is the time,  $d$  is the dimension of the space in which diffusion takes place, and  $\langle \Delta r^2(t) \rangle$  is the mean square displacement of the diffusing particle.  $D$  may be expressed in the Arrhenius form,

$$D = D_0 \exp\left(-\frac{E_d}{k_B T}\right), \quad (2)$$

where  $D_0$  is the prefactor and  $E_d$  is the energy barrier opposing diffusion; these may be obtained “brute force” by running molecular-dynamics (MD) simulations at several temperatures, by calculating  $D$  using Eq. (1), and by fitting to Eq. (2) (see, for instance, Ref. 2). However, because this approach is not very efficient, alternative schemes based on the transition-state theory<sup>3,4</sup> (TST) are frequently employed. The energy barrier is often approximated by the difference in energies between the transition state (TS—saddle-point site) and the equilibrium state (ES—binding or stable site); the prefactor is given by

$$D_0 = \frac{n\nu_0 l^2}{2d}, \quad (3)$$

where  $n$  is the number of equivalent diffusion channels,  $l$  is the distance between neighboring binding sites (jump length), and  $\nu_0$  is the prefactor for the attempt-to-diffuse frequency. Within the harmonic TST, this is given by

$$\nu_0 = \frac{k_B T}{h} \exp\left(-\frac{\Delta F_{\text{vib}}}{k_B T}\right), \quad (4)$$

where  $\Delta F_{\text{vib}}$  is the vibrational Helmholtz free-energy (VFE) difference between the TS and the ES, and  $k_B$  and  $h$  are

Boltzmann’s and Planck’s constants, respectively. An alternative (TST-based) expression was proposed by Vineyard,<sup>4</sup>

$$\nu_0 = \frac{\prod_{i=1}^{3N} \nu_i}{\prod_{j=1}^{3N-1} \nu'_j}, \quad (5)$$

where  $\nu_i$  and  $\nu'_j$  are the  $\Gamma$ -point vibrational frequencies at the ES and TS, respectively; Eq. (5) is actually the high-temperature limit of the harmonic TST, as shown in Ref. 5.

The evaluation of  $\nu_0$  may be further simplified—from a computational viewpoint—by limiting the number of atoms that are considered in the calculation of  $\Delta F_{\text{vib}}$  in Eq. (4) or the number of normal-mode frequencies in Eq. (5). For example, in a recent paper, Yildirim, Kara, and Rahman (YKR)<sup>6</sup> argued that the substrate plays a minor role and can actually be ignored—only the adatom needs to be considered. This is at variance with a recent publication of ours<sup>7</sup> where we showed that the dynamics of both adatom and substrate are important: neglecting the contribution from the substrate can lead to prefactors that are underestimated by factors as large as  $\sim 8$ . It is true that such “errors” are not dramatic in view of the exponential temperature dependence of the diffusion coefficient. However, an accurate evaluation of the prefactors is important for a proper identification of the relevant mass transport mechanisms.<sup>2,8</sup> Most important, perhaps, is the need to clarify some of the issues pertaining to the calculation of prefactors: one ultimately hopes to be able to calculate prefactors for diffusion (and other processes) by using first-principles approaches, in which accuracy is in a sense “built in.” Indeed, because such calculations are computationally very demanding, it is important to understand the factors that determine the diffusion constants.

With this objective in mind, we report in this short paper further calculations of the prefactors for Cu adatom self-diffusion on the (001), (110), and (111) surfaces of Cu, within the harmonic approximation (HA) and using two different computational approaches. We demonstrate, in particular, that the contribution of the substrate dynamics cannot be neglected for accurately determining the adatom self-diffusion prefactors. These can be safely calculated by using

the present computational scheme as long as the systems remain closely harmonic; when this is not the case, the exact TST must be solved (by using, e.g., thermodynamic integration<sup>9</sup>) or brute-force MD calculations must be performed.

Computational details are as follows: Supercell surface models were constructed in slab geometry with an adatom on one side of the slab; the two bottom layers on the other side were held fixed in order to mimic the presence of the bulk. All other atoms were free to move except the adatom at the TS, whose  $x$  and  $y$  coordinates (in plane) were fixed so as to keep it from returning to the binding site. Periodic boundary conditions were applied in the  $x$  and  $y$  directions, while the  $z$  direction was free. The size of all models was  $\sim 20 \times 20 \times 25 \text{ \AA}^3$ ; for Cu adatom on Cu(001), e.g., the substrate consisted of  $8 \times 8 \times 14$  atoms. The interactions among atoms were described by the semiempirical embedded-atom method (EAM-FBD)<sup>10</sup> potential cutoff at  $4.95 \text{ \AA}$ . Each model was first subjected to a conjugate-gradient relaxation phase in order to take it to its lowest energy state. The full spectra of phonon frequencies were then calculated within the HA, from which the total VFEs may be obtained by summing over all frequencies and integrating over reciprocal space,

$$F_{\text{vib}} = k_B T \sum_{\mathbf{q}} w_{\mathbf{q}} \sum_i \ln \left[ 2 \sinh \left( \frac{\hbar \nu_{i\mathbf{q}}}{2k_B T} \right) \right], \quad (6)$$

where  $w_{\mathbf{q}}$  is the weight of a particular  $\mathbf{q}$  point and  $\nu_{i\mathbf{q}}$  is the  $i$ th eigenfrequency at  $\mathbf{q}$ . The *local* density of states (LDOS) for a specific atom (say  $l$ ) in a specific direction (say  $\alpha$ ) can be evaluated by using

$$n_{l\alpha}(\nu) = \sum_{i,\mathbf{q}} \frac{\gamma}{\pi} |u_{l\alpha}(\nu_{i,\mathbf{q}})|^2 e^{-\gamma^2(\nu - \nu_{i\mathbf{q}})^2}, \quad (7)$$

where  $u_{l\alpha}$  is the eigenvector of the dynamical matrix that corresponds to the  $\alpha$  direction of atom  $l$  in mode  $\nu_{i\mathbf{q}}$ . In practice,  $\delta$  functions are replaced by the Gaussian functions of width  $\gamma$ ; this method will be referred to as “full-phonon LDOS” (FPLD) hereafter. In order to unambiguously validate our calculations, and following YKR,<sup>6</sup> we also employed the real-space Green’s function (RSGF) approach to calculate the LDOS,<sup>6,11,12</sup>

$$n_{l\alpha}(\nu) = -4 \lim_{\epsilon \rightarrow 0^+} \text{Im} \mathbf{G}_{l\alpha,l\alpha}(4\pi^2\nu^2 + i\epsilon), \quad (8)$$

where  $\text{Im} \mathbf{G}_{l\alpha,l\alpha}(4\pi^2\nu^2 + i\epsilon)$  represents the imaginary part of the on-site phonon Green’s function for an atom  $l$  in direction  $\alpha$ . From the LDOS, the local (i.e., site-specific) VFEs are given by

$$f_{\text{vib}}^{\alpha} = k_B T \int_0^{\nu_{\text{max}}} n_{l\alpha}(\nu) \ln \left[ 2 \sinh \left( \frac{\hbar \nu}{2k_B T} \right) \right] d\nu, \quad (9)$$

where  $\nu_{\text{max}}$  is the maximum phonon frequency.

We present in Table I the static energy barriers obtained by taking the difference between relaxed transition and equilibrium configurations; they perfectly agree with previous investigations,<sup>5,13</sup> but they are of no particular interest here as we are concerned, rather, with prefactors. To this end, we

TABLE I. Static energy barriers  $E_d$  (eV) and VFE differences (meV) for the whole system ( $\Delta F_{\text{vib}}$ ) and for the adatom only ( $\Delta f_{\text{vib}}$ ; two different approaches are used—see text) for Cu adatom hopping on Cu(001), (110), and (111) surfaces. The subscript  $\parallel$  denotes diffusion along the [110] direction, while  $\perp$  is across; for the (111) surface,  $f$  and  $h$  are for the ES at an fcc or an hcp site, respectively.

	(001)	(110) $_{\parallel}$	(110) $_{\perp}$	(111) $_f$	(111) $_h$
$E_d$	0.505	0.230	1.146	0.030	0.027
300 K					
$\Delta F_{\text{vib}}$	-9.5	0.3	2.5	44.3	41.4
$\Delta f_{\text{vib}}^{\text{FPLD}}$	14.8	28.1	13.9	48.3	48.6
$\Delta f_{\text{vib}}^{\text{RSGF}}$	14.9	29.3	15.1	46.7	46.9
600 K					
$\Delta F_{\text{vib}}$	18.1	36.8	41.2	124.6	119.1
$\Delta f_{\text{vib}}^{\text{FPLD}}$	65.8	93.2	65.1	132.6	133.2
$\Delta f_{\text{vib}}^{\text{RSGF}}$	66.0	94.6	66.6	129.4	129.7

also present in Table I the VFE differences between TS and ES, both local (that is, for the adatom alone) and global (adatom plus full substrate), at two temperatures and by using both the FPLD and the RSGF methods. These results call for several remarks. First, and evidently, the FPLD and RSGF local VFE differences agree very well—the small discrepancies are numerical errors. Second, the *global* VFE differences  $\Delta F_{\text{vib}}$  are, in general, quite different from the local ones  $\Delta f_{\text{vib}}$ , except perhaps for hopping on the (111) surface. As a particular example, consider the (001) surface at 300 K for which  $\Delta F_{\text{vib}} = -9.5$  meV, while  $\Delta f_{\text{vib}} \approx 14.8$  meV; this indicates that the absolute change in VFE for the substrate is even greater than that for the adatom alone under these specific conditions. Third,  $\Delta F_{\text{vib}}$  is in all cases smaller than  $\Delta f_{\text{vib}}$ , implying that the change in VFE for the substrate is always *negative*, thus compensating for, or reducing, the contribution from the adatom. Last but not least, the magnitude of the contribution of the substrate to  $\Delta F_{\text{vib}}$ —that is the difference between  $\Delta F_{\text{vib}}$  and  $\Delta f_{\text{vib}}$ —is generally of the same order as  $\Delta f_{\text{vib}}$ , implying that it cannot, in general, be neglected. The (111) surface is special: because of its close-packed nature, the substrate dynamics is hardly affected by the adatom and, therefore, its contribution to  $\Delta F_{\text{vib}}$  is negligibly small.

To further refine the argument, we present in Table II the layer-resolved contributions to  $\Delta F_{\text{vib}}$ . It is clearly seen that (i) the adatom’s contribution to  $\Delta F_{\text{vib}}$  is major, as expected, (ii) the topmost layer (right underneath the adatom) contributes almost the same as the adatom, and (iii) the contributions from other layers are small. These results are fully consistent with Cohen and Voter.<sup>14</sup> Thus, it is already clear at this stage that the substrate does play an important role in determining the diffusion parameters of an adatom on a surface.

We now turn to the prefactors, which are presented in Table III; they evidently exhibit a behavior that is consistent with that of the VFE differences: the prefactors extracted from the LDOS (either FPLD or RSGF, which almost exactly agree) are, in general, significantly different from those

TABLE II. Layer-resolved contributions to the global VFE difference  $\Delta F_{\text{vib}}$  (in meV) for Cu adatom hopping on Cu(001) by using the RSGF method and the FPLD method (in parentheses).

Layer	300 K	600 K
0 (Adatom)	14.9 (14.8)	66.0 (65.8)
1	-19.6 (-19.9)	-38.6 (-39.3)
2	-1.9	-3.7
3	-0.7	-1.3
4	-0.4	-0.7
5	-0.7	-1.3
6	-0.3	-0.6
7-14	0	0

based on the global VFE differences. This again is a manifestation of the important contributions from the substrate. The discrepancies are in some cases as large as a factor of 3, while the prefactors are all of the order of  $10^{-3}$  cm<sup>2</sup>/s. Incidentally, the prefactors have a rather weak temperature dependence, as reported in our previous publication,<sup>7</sup> and this is a consequence of using the harmonic approximation.

While we have obtained a consistent set of data by using two different approaches, our results are at variance with those reported by YKR,<sup>6</sup> as can be seen in Table III, in spite of the fact that we have used exactly the same computational approach—same parametrization of EAM (viz., FBD<sup>10</sup>), same simulation setup, etc. As an additional validation, we have calculated the distances between the adatom and its nearest neighbors in the ES and in the TS and found 2.417 and 2.309 Å, respectively, which are exactly the values reported by YKR.<sup>6</sup> In order to understand better the origin of the discrepancies, we compare in Table IV our local RSGF results to YKR result for the particular case of the (001) surface; the atoms are labeled by following YKR (see Fig. 1). Clearly, the two sets of data agree when the adatom is at the ES; however, significant differences appear when it is at the TS. This translates into serious errors in the values of the

TABLE III. Prefactors  $D_0$  for Cu adatom hopping on Cu (001), (110), and (111) surfaces in units of  $10^{-4}$  cm<sup>2</sup>/s. For YKR, prefactors are calculated by using the VFE data of Table I (Ref. 6).

Method	(001)	(110) <sub>  </sub>	(110) <sub>⊥</sub>	(111) <sub>f</sub>	(111) <sub>h</sub>
300 K					
Global	59	40	74	1.84	2.06
Local/FPLD	23	14	48	1.57	1.56
Local/RSGF	23	13	46	1.67	1.66
YKR/Local/RSGF	11				
600 K					
Global	58	40	74	1.83	2.04
Local/FPLD	23	13	46	1.57	1.55
Local/RSGF	23	13	45	1.67	1.66
YKR/Local/RSGF	11				
Vineyard/Global	60	42	73	1.83	2.03

TABLE IV. Local VFEs (in meV) for Cu adatom hopping on Cu(001) by the RSGF method. ES and TS refer to the equilibrium and transition sites, respectively, and  $\Delta$  is the difference between the two. The atoms are labeled as follows: Ad is the adatom, 1–8 are the eight nearest neighbors (see YKR and Fig. 1), and 9- $N$  are all of the others. Also listed are the total VFE [Eq. (6)] differences and prefactors  $D_0$  (in unit of  $10^{-4}$  cm<sup>2</sup>/s) that are calculated by using Eq. (3). The results are given for three different levels of approximation: (i) considering only the adatom (Ad), i.e., ignoring the substrate; (ii) the adatom and the eight nearest neighbors (Ad & 1–8); (iii) the adatom and the full substrate (Ad & 1- $N$ ). NI means “not included.”

Atom	Present work				YKR			
	ES	TS	$\Delta$	$D_0$	ES	TS	$\Delta$	$D_0$
(300 K)								
1 & 2	-34	-42	-7		-35	-40	-5	
3 & 4	-34	-30	+4		-35	-26	+9	
5 & 6	-39	-42	-3		-40	-40	0	
7	-22	-20	+2		-23	-20	+3	
8	-20	-20	0		-20	-20	0	
1-8			-9				+11	
9- $N$			-15		NI	NI	NI	
1- $N$			-24					
Ad	-54	-40	+15	23	-52	-18	+34	11
Ad & 1-8			+5.8	33			+45	7
Ad & 1- $N$			-8.7	57				
Eq. (6)			-9.5	59				
(600 K)								
1 & 2	-179	-193	-14		-180	-189	-9	
3 & 4	-179	-171	+8		-180	-163	+17	
5 & 6	-188	-193	-5		-189	-189	0	
7	-154	-150	+4		-156	-150	+6	
8	-151	-150	0		-150	-150	0	
1-8			-18				+22	
9- $N$			-29		NI	NI	NI	
1- $N$			-47					
Ad	-218	-152	+66	23	-214	-111	+103	11
Ad & 1-8			+48	32			+125	7
Ad & 1- $N$			+19	56				
Eq. (6)			+18	58				

prefactors, as can be seen in Table IV and will be discussed next.

To further clarify the issue,  $\Delta F_{\text{vib}}$  was computed by summing up the full set of RSGF local, atomic VFEs; the results are given in Table IV (Ad & 1- $N$ ) and found to be in almost perfect agreement with the global VFE differences from Eq. (6); likewise, the prefactors coincide. However, significant discrepancies appear when only the adatom is included in the calculation (Ad) or when only the adatom and substrate atoms 1–8 are included (Ad & 1–8), the error in  $D_0$  being as large as a factor of 2.5 ( $59 \times 10^{-4}$  vs  $23 \times 10^{-4}$  cm<sup>2</sup>/s). A comparison to the YKR results reveals even more serious differences ( $59 \times 10^{-4}$  vs  $11 \times 10^{-4}$  cm<sup>2</sup>/s when only the

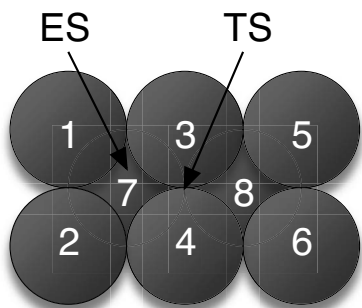


FIG. 1. Geometry of a jump between the ES and the TS on the (001) surface and labels of the atoms in the vicinity.

adatom is considered, and  $vs \times 10^{-4} \text{ cm}^2/\text{s}$  when atoms 1–8 are also considered). As a test, we have also calculated the prefactors by using the ( $\Gamma$ -point) Vineyard method;<sup>4</sup> the results, provided in Table III, precisely agree with the global results—as they should since both methods take the whole system into account. Further, our numbers for Cu(100) agree with those calculated with other parametrizations of the EAM<sup>15–17</sup> by using either the free-energy approach,<sup>7</sup> the full MD approach,<sup>8,9,18</sup> and/or the Vineyard method.<sup>19</sup> Note that, as demonstrated by YKR and Durukanoglu,<sup>5</sup> the Vineyard prefactor is the high-temperature limit of the TST within the HA; the agreement with our results provides additional evidence for the validity of our approach.

Our results clearly show, therefore, that the substrate cannot be ignored when evaluating the prefactors if accurate values are to be obtained. The contribution of the substrate is often comparable to that of the adatom and frequently of opposite sign; as a result, the total VFE difference  $\Delta F_{\text{vib}}$  may decrease significantly and even change sign. Since  $\Delta F_{\text{vib}}$  is the small difference between two relatively large numbers and since it enters the definition of the prefactor through an exponential term, accuracy is evidently needed when computing the free energies. This is clearly demonstrated in Table IV for the case of Cu/Cu(100). Of course, in some situations, including only the atoms neighboring the adatom may provide an adequate description of the dynamics of the system, but our calculations show that this is not in general possible; the problem should really be handled on a case to case basis.

The origin of the differences between our data and those of YKR—especially for the local VFEs at the TS (cf. Table IV)—remains unclear and may possibly lie in an inaccurate numerical approach in the latter; what is clear, however, is that the LDOS must be handled with care as numerical errors easily occur. We note in passing that in YKR, *local* refers to the adatom alone and *global* means the adatom plus its eight nearest neighbors (cf. Fig. 1); atoms in the substrate other than 1–8 are not included (cf. Table IV). Also, to dissipate a possible confusion, YKR stated that the contribution of the substrate to the VFE is always *positive* and, thus, reduces the prefactor when included; this statement is contradicted even by their own data, e.g., Tables IV and V in Ref. 6, which show the prefactors in most cases to increase upon taking the substrate into account (and, of course, the change is small as the substrate is partially included in the calculation).

The prefactor  $D_0$  is often found to be  $\sim 10^{-3} \text{ cm}^2/\text{s}$ , and in practice, it is often assumed to be  $= 10^{-3} \text{ cm}^2/\text{s}$ . One may justify this value by a simple back-of-the-envelope calculation based on the fact that the adatom loses 1 degree of freedom upon going from the ES to the TS. Substituting Eq. (4) into Eq. (3), the prefactor  $D_0$  becomes

$$D_0 = \frac{k_B T n l^2}{h \ 2d} \exp\left(-\frac{\Delta F_{\text{vib}}}{k_B T}\right), \quad (10)$$

and  $\Delta F_{\text{vib}}$  is given by

$$\Delta F_{\text{vib}} = k_B T \int_0^{\nu_{\text{max}}} \Delta N(\nu) \ln \left[ 2 \sinh\left(\frac{h\nu}{2k_B T}\right) \right] d\nu, \quad (11)$$

where  $\Delta N(\nu)$  is the difference in the total phonon density of states between the TS and the ES that satisfies

$$\int_0^{\nu_{\text{max}}} \Delta N(\nu) d\nu = -1. \quad (12)$$

When the temperature  $T$  is high enough,  $h\nu/k_B T \rightarrow 0$  and we therefore have

$$\begin{aligned} \Delta F_{\text{vib}} &\approx k_B T \int_0^{\nu_{\text{max}}} \Delta N(\nu) \ln\left(\frac{h\nu}{k_B T}\right) d\nu \\ &\approx k_B T \ln\left(\frac{h\bar{\nu}}{k_B T}\right) \int_0^{\nu_{\text{max}}} \Delta N(\nu) d\nu \\ &= -k_B T \ln\left(\frac{h\bar{\nu}}{k_B T}\right), \end{aligned} \quad (13)$$

where  $\bar{\nu}$  is some weighted average frequency. Consequently, at a high temperature,

$$\begin{aligned} D_0 &= \frac{k_B T n l^2}{h \ 2d} \exp\left(-\frac{\Delta F_{\text{vib}}}{k_B T}\right) \\ &= \frac{k_B T n l^2}{h \ 2d} \exp\left[\ln\left(\frac{h\bar{\nu}}{k_B T}\right)\right] \\ &= \frac{k_B T n l^2}{h \ 2d} \frac{h\bar{\nu}}{k_B T} = \frac{n l^2}{2d} \bar{\nu}. \end{aligned} \quad (14)$$

With appropriate values for  $l$ ,  $\bar{\nu}$ ,  $n$ , and  $d$ , one finds, indeed, that  $D_0 \sim 10^{-3} \text{ cm}^2/\text{s}$ .

This order-of-magnitude value is convenient for assessing the contributions of different mass transport mechanisms since these are more strongly determined by the diffusion barriers than the prefactors. Yet, the prefactors affect the various transport mechanisms differently and can, in fact, lead to crossovers as a function of temperature (cf., for instance, Refs. 2 and 8). Furthermore, the connection between prefactors and energy barriers—the Meyer–Neldel (compensation) rule<sup>20</sup>—has been unambiguously established:<sup>13,18,21</sup> prefactors are evidently not universally equal to the canonical (“harmonic”) value of  $10^{-3} \text{ cm}^2/\text{s}$ . This is a consequence of the fact that a harmonic theory is, by definition, incomplete as it neglects the anharmonicity of the potentials, nonlinear many-body contributions, etc., which deeply affect the thermodynamics.<sup>22</sup> A thorough description of diffusion thus

requires the exact TST to be solved or full MD calculations to be performed. In many cases, however, the harmonic TST is perfectly adequate and, as shown above, the Vineyard approximation provides an acceptable estimate of the prefactors. There is, however, no general “recipe” for determining *a priori* whether the harmonic TST and/or the Vineyard formula is appropriate and this, of course, also depends on the desired accuracy.

To conclude, local approximations in the evaluation of diffusion prefactors may be appropriate in some cases, but they are not in general. Our calculations clearly show that the contribution of the substrate, in the case of surface diffusion, cannot be ignored. The present work, furthermore, provides a convenient framework for the precise evaluation of (harmonic) diffusion prefactors by using, e.g., *ab initio* methods. Evidently, for specific materials, convergence tests must be

performed as many factors determine diffusion. Likewise, the HA will break down at some point, in particular, at elevated temperatures; in such case, one must resort to either MD calculations or the exact TST, which can be solved by using, e.g., thermodynamic integration.<sup>9</sup>

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\*Present address: Department of Applied Mathematics, University of Western Ontario, London, Ontario, Canada N6A 5B7.

†Corresponding author; laurent.lewis@umontreal.ca

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