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Erratum: Thermal mass transport mechanism of an adatom on a crystalline surface

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Additional simulations have brought us to the conclusion that an approximation that we did in Ref. 1 is not justified, questioning several quantitative and qualitative results.

The probability of presence of the adatom at position x_0 is driven by the thermodynamic potential Φ :

$$p(x_0) \propto e^{-\Phi(x_0)} \quad (1)$$

The derivative of the thermodynamic potential (Eq. A7 of 1) reads:

$$\frac{\partial \Phi}{\partial x}(x_0) = - \left\langle \left[\frac{\vec{p}_a^2}{2m_a} + \sum_i \frac{1}{2} E_{LJ}(r_a^0, r_i^0) \right] \frac{1}{T(x_0)^2} \frac{\partial T}{\partial x}(x_0) \right\rangle_{x_0} + \left\langle \sum_i \frac{1}{2} \frac{\partial E_{LJ}}{\partial x_a}(r_a^0, r_i^0) \left[\frac{1}{T(x_0)} + \frac{1}{T(x_i)} \right] \right\rangle_{x_0}, \quad (2)$$

In order to evaluate it, we have approximated $\frac{1}{T(x_i)} \simeq \frac{1}{T(x_0)}$ when a substrate atom at abscissa x_i interacts with the adatom at abscissa x_0 ¹. Within this approximation, we found the following expression of the derivative of the thermodynamic potential:

$$\frac{\partial \Phi}{\partial x} = - \left\langle \left[\frac{\vec{p}_a^2}{2m_a} + \sum_i \frac{1}{2} E_{LJ}(r_a^0, r_i^0) \right] \frac{1}{T(x_0)^2} \frac{\partial T}{\partial x}(x_0) \right\rangle_{x_0} + \left\langle \frac{1}{T(x_0)} \sum_i \frac{\partial E_{LJ}(r_a^0, r_i^0)}{\partial x_a} \right\rangle_{x_0} \quad (3)$$

We have recently run further simulations to check the validity of this approximation. Fig. 1 shows both the derivative and the thermodynamic potential computed from Eq. (2) and Eq. (3). The approximation appears to just slightly alter the values of $\frac{\partial \Phi}{\partial x}(x_0)$ in Fig. 1(a): both Eq. (2) and Eq. (3) seem to provide similar results, but the two curves are offset by a tiny quantity almost invisible to the naked eye on Fig. 1(a). The integration of this offset results in a significant difference on the thermodynamic potentials given by Eqs. (2) and Eqs. (3) in Fig. 1(b).

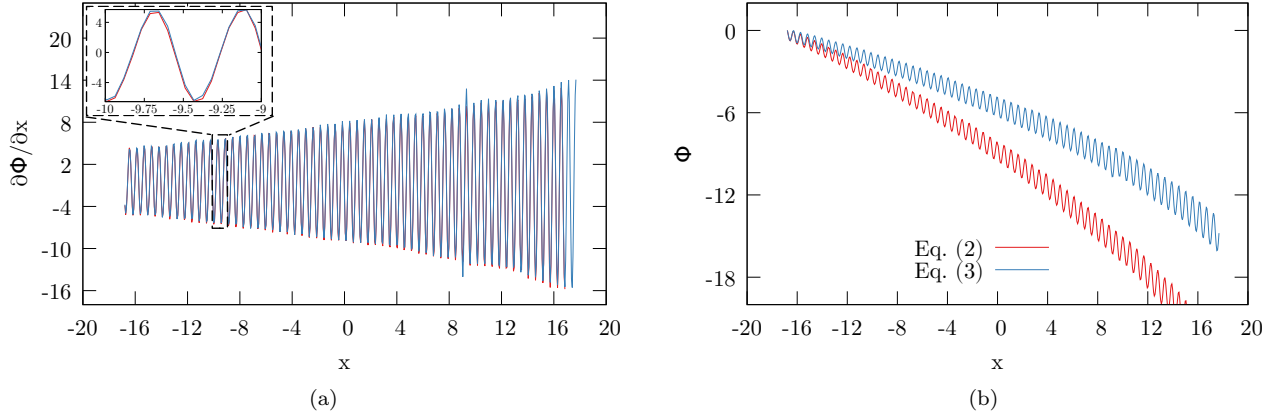


FIG. 1. (a) Derivative and (b) thermodynamic potential computed using Eq. (2) (solid red line) and Eq. (3) (solid blue line) for a thermal gradient $\langle \frac{\partial T}{\partial x} \rangle = 0.0038$;

Using Eq. (2) instead of Eq. (3), the thermodynamic potential is again a linear function of $1/T$ but the potential $\Phi_{TGIP}(1/T) = -\frac{Q}{T} + \Phi_0$ presents a slope $Q = 3.45$. The use of the incorrect approximation yielding to Eq. (3) and erroneous values of Q led us to an improper interpretation of the thermodynamic potential. Indeed, the thermodynamic potential reads

$$\Phi(x_0) = -\ln[Z(x_0)] \quad (4)$$

$$Z(x_0) = \frac{1}{h^{3N+3}} \int \delta\left(\frac{\sum_k^M x_k}{M} - x_0\right) e^{-\int \frac{\mathcal{H}(\vec{r})}{T(\vec{r})} d^3\vec{r}} \prod_{k=1}^M d^3\vec{r}_k d^3\vec{p}_k^3 \prod_{i=1}^N d^3\vec{r}_i d^3\vec{p}_i \quad (5)$$

The many body microscopic hamiltonian $\mathcal{H}(\vec{r})$ mainly involves two types of interactions. The substrate-substrate $\mathcal{H}_{sub-sub}$ and the adatom-substrate \mathcal{H}_{ad-sub} interactions. Among them, only the adatom-substrate interaction mainly depends on the position of the adatom. Hence, we note that if the adatom is in a metastable state of the crystalline potential and the thermal gradient weak, then:

$$\int \frac{\mathcal{H}(\vec{r}, x_0)}{T(\vec{r})} d^3\vec{r} \approx \frac{-E_{ad-sub}}{T(x_0)} + \int \frac{\mathcal{H}_{sub-sub}(\vec{r})}{T(\vec{r})} d^3\vec{r} \quad (6)$$

With E_{ad-sub} a free energy of the adatom-substrate interaction (we use the convention $E_{a-sub} > 0$). We conclude that minima of the thermodynamic potential (or equivalently $\Phi_{TGIP}(1/T)$) should follow:

$$\Phi(x_0)|_{min} \approx -\frac{E_{ad-sub}}{T(x_0)} + \dots \quad (7)$$

This interpretation is more natural since, if the thermal gradient is infinitely small, the probability of presence of the adatom should follow a Boltzmann law:

$$P(x_0) \propto e^{-\frac{A(x_0)}{T(x_0)}} \quad (8)$$

with $A(x_0)$ the free energy of the adatom at position x_0 . Combining Eqs 1 and 8, $\phi_{TGIP}(\frac{1}{T})$ should linearly vary with $1/T(x_0)$ with a slope equal to the free energy of the adatom. We found $Q = 3.45$ slightly smaller than the binding energy 4.17 of the adatom with the substrate calculated at 0K: Q indeed involves some entropic effects while the binding energy at 0K does not.

Adatom trajectories are calculated following

$$\frac{dx}{dt} = \alpha \frac{D_0}{a} \left[e^{-[\Phi(x_m + \frac{a}{2}) - \Phi(x_m)]} - e^{-[\Phi(x_m + \frac{a}{2}) - \Phi(x_m + a)]} \right], \quad (9)$$

$$\approx -\alpha D[T] \frac{Q}{T^2} e^{-\frac{(Q-E_m)a}{2T^2} \frac{dT}{dx}} \frac{dT}{dx}. \quad (10)$$

With $D[T] = D_0 e^{-\frac{E_m}{T}} = \nu_0 a^2 e^{-\frac{E_m}{T}}$ and α an adjustable parameter. Using the numerical parameters Q derived from Eq. (2), the approximation used to obtain Eq. (10) from Eq. (9) is no longer satisfied in our simulations for which the thermal gradient is very high. Therefore, we compute the adatom trajectory solving Eq. (9). MD simulations and predictions of Eq. (9) (with $\alpha = 1$) do not agree. We need to adjust the parameter $\alpha = \frac{1}{8}$ to find a good agreement as shown in Fig. 2. We have checked that the parameter α does not depend on the thermal gradient. If the agreement between MD simulations and model is not perfect, a coefficient $\alpha = \frac{1}{8}$ is reasonable knowing the simplicity of the model that we used. We emphasize that this study is, to our knowledge the first one proposing a quantitative microscopic model of thermomigration with a direct comparison with MD simulations.

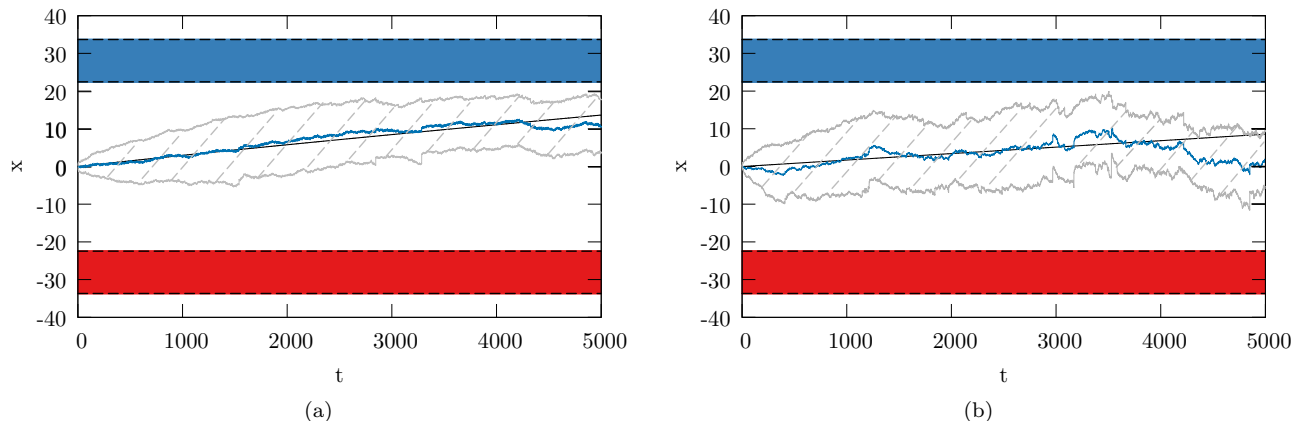


FIG. 2. Trajectories (solid black line) computed from integration of Eq. (9) with $\alpha = 1/8$ compared to the average MD trajectories (solid blue line) of the adatom for (a) $\langle \frac{\partial T}{\partial x} \rangle = 0.0038$ and (b) $\langle \frac{\partial T}{\partial x} \rangle = 0.0027$; Grey lines and dashed regions design the standard deviations of the average MD trajectories.

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¹ A. Roux and N. Combe, Phys. Rev. B **108**, 115410 (2023).