



Quantum Markovian activated surface diffusion of interacting adsorbates

R. Martínez-Casado, A. S. Sanz, and S. Miret-Artés

Citation: *J. Chem. Phys.* **129**, 184704 (2008); doi: 10.1063/1.3009624

View online: <http://dx.doi.org/10.1063/1.3009624>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v129/i18>

Published by the [American Institute of Physics](http://www.aip.org).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



physicstoday

Comment on any
Physics Today article.

Physics Today / Volume 65 / July 2012
Previous Article | Next Article

Measured energy in Japan
David von Seggern
(vonseg@seismo.unr.edu) University of Nevada
July 2012, page 10
DIGITAL OBJECT IDENTIFIER
<http://dx.doi.org/10.1063/PT.3.1619>

The article by Thorne Lay and Hiroo Kanamori is an interesting one. It discusses the energy released by the 1964 Chilean earthquake. While that of a 100-megaton nuclear detonation is approximately five times as much energy as that of a 100-megaton atmospheric explosion, the 1964 Chilean earthquake had still more energy by a factor of about 3 or 4. This is because the seismic energy released is proportional to the volume of rock that is broken, rather than to the volume of the nuclear device. I believe the authors used the relation for seismic energy release rather than total strain energy release. The seismic energy underestimates the total strain energy release by a variable that depends on friction on the fault plane. Accounting for total strain energy release would increase the earthquake energy number by orders of magnitude.

Despite the catastrophic damage potential of nuclear bombs, the forces of nature occasionally unleash much larger energy releases. Although the nuclear bombs are under our control, earthquakes, volcanic eruptions, and extreme weather events are not. However, by judicious preparation and avoidance measures, humans can significantly diminish the damage of natural events.

The article does not have any references.

Comment on this article

By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck team. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.

Written by Edgar McCarvill, 14 July 2012 19:59

Quantum Markovian activated surface diffusion of interacting adsorbates

R. Martínez-Casado,^{a)} A. S. Sanz,^{b)} and S. Miret-Artés^{c)}

Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas, Serrano 123, 28006 Madrid, Spain

(Received 24 July 2008; accepted 2 October 2008; published online 13 November 2008)

A quantum Markovian activated atom-surface diffusion model with interacting adsorbates is proposed for the intermediate scattering function, which is shown to be complex-valued and factorizable into a classical-like and a quantum-mechanical factor. Applications to the diffusion of Na atoms on flat (weakly corrugated) and corrugated-Cu(001) surfaces at different coverages and surface temperatures are analyzed. Quantum effects are relevant to diffusion at low surface temperatures and coverages even for relatively heavy particles, such as Na atoms, where transport by tunneling is absent. © 2008 American Institute of Physics. [DOI: 10.1063/1.3009624]

In 1954, van Hove¹ introduced the space-time correlation function G (a generalization of the well-known pair-distribution function from the theory of liquids) as a tool to study the scattering of probe particles off quantum systems consisting of ensembles of interacting particles. Within the Born approximation in scattering theory, the nature of the scattered particles, as well as the details of the interaction potential, is largely irrelevant. Hence, following Lovesey,² the scattering processes with interacting particles essentially reduce to a typical problem of statistical mechanics. The linear response function of the interacting particles, also known as *dynamic structure factor* or *scattering law*, is then related to the spontaneous-fluctuation spectrum of such particles (measured from G) by the fluctuation-dissipation theorem and can be expressed in terms of particle density-density correlation functions.² In general, G is a complex-valued function, which can be considered as a signature of the quantum nature of the problem. The imaginary part of G is important at small values of time (of the order of $\hbar\beta$, with $\beta = 1/k_B T$), extending its range of influence by decreasing the temperature. This dynamical regime takes place when the thermal de Broglie wavelength $\lambda_B = \hbar/\sqrt{2mk_B T}$ (m is the adsorbate mass) is of the order of or greater than the typical interparticle distances. The quantum system is then assumed to obey the fundamental condition of stationarity and the scattering problem satisfies the detailed balance principle, displaying the *recoil effect*. Here, we study the quantum observable effects of Na-atom diffusion on flat (weakly corrugated) and corrugated-Cu(001) surfaces probed by He atoms at different values of the Na coverage (θ) and the surface temperature. For simplicity, in our model only coupling to substrate phonons (phonon friction) and not to low-lying electron-hole pair excitations (electronic friction) is considered. Nevertheless, as an extension of this stochastic model, the electronic friction could be accounted for by simply adding it to the total friction coefficient. Moreover, diffusion by tunneling will not be considered in this work.

The observable magnitude in this type of scattering experiments is the so-called *differential reflection coefficient*, which gives the probability that the He atoms reach a certain solid angle Ω with an energy exchange $\hbar\omega = E_f - E_i$ and wave-vector transfer parallel to the surface $\Delta\mathbf{K} = \mathbf{K}_f - \mathbf{K}_i$ after probing the quantum system, which consists of an ensemble of interacting Na atoms on the surface. This magnitude reads as

$$\frac{d^2\mathcal{R}(\Delta\mathbf{K}, \omega)}{d\Omega d\omega} = n_d \mathcal{F}S(\Delta\mathbf{K}, \omega), \quad (1)$$

where n_d is the concentration of Na atoms on the surface, \mathcal{F} is the *atomic form factor*, which depends on the He–Na interaction potential, and $S(\Delta\mathbf{K}, \omega)$ is the dynamic structure factor or scattering law, which gives the line shape and provides a complete information about the dynamics and structure of the adsorbates. Experimental information about long-distance correlations is obtained from the dynamic structure factor for small values of $\Delta\mathbf{K}$, while information on long-time correlations is provided at small energy transfers, $\hbar\omega$.

The dynamic structure factor can be expressed as

$$\begin{aligned} S(\Delta\mathbf{K}, \omega) &= \frac{1}{2\pi\hbar} \int \int e^{i(\Delta\mathbf{K}\cdot\mathbf{R} - \omega t)} G(\mathbf{R}, t) dt d\mathbf{R} \\ &= \frac{1}{2\pi} \int e^{-i\omega t} I(\Delta\mathbf{K}, t) dt, \end{aligned} \quad (2)$$

where \mathbf{R} denotes the adatom position on the surface and

$$I(\Delta\mathbf{K}, t) = \langle e^{-i\Delta\mathbf{K}\cdot\mathbf{R}(0)} e^{i\Delta\mathbf{K}\cdot\mathbf{R}(t)} \rangle. \quad (3)$$

In the Heisenberg representation, the trajectories $\mathbf{R}(t)$ are replaced by linear position operators $\hat{\mathbf{R}}(t)$ and, therefore, the brackets in Eq. (3) will denote the average of the expectation value of the operators enclosed. The so-called *intermediate scattering function*, $I(\Delta\mathbf{K}, t)$, is the space Fourier transform of the van Hove G -function. Within the context of ³He spin-echo experiments, this function is also known as *polarization*,³ its real and imaginary parts being observable magnitudes [for instance, in Cs diffusion on a corrugated-Cu(001) surface⁴]. An exact, direct calculation of $I(\Delta\mathbf{K}, t)$ is

^{a)}Electronic mail: ruth@imaff.cfmac.csic.es.

^{b)}Electronic mail: asanz@imaff.cfmac.csic.es.

^{c)}Electronic mail: s.miret@cfmac.csic.es.

difficult to carry out due to the noncommutativity of the particle position operators at different times. Nonetheless, this calculation can be alternatively performed after postulating^{5,6} that the adatom position operators $\hat{\mathbf{R}}(t)$ obey a standard Langevin equation (i.e., the associated stochastic dynamics is Markovian) and the product of the two exponential operators in Eq. (3) can then be evaluated according to a special case of the Baker–Hausdorff theorem (*disentangling theorem*), namely, $e^{\hat{A}}e^{\hat{B}}=e^{\hat{A}+\hat{B}}e^{[\hat{A},\hat{B}]/2}$, which only holds when the corresponding commutator is a c -number. As shown below, this expression allows us to interpret $I(\Delta\mathbf{K},t)$ as the product of a classical-like and a quantum-mechanical intermediate scattering function associated with the exponentials of $\hat{A}+\hat{B}$ and the commutator $[\hat{A},\hat{B}]$, respectively. Expressing now the thermal average implicit in Eq. (3) and the corresponding position operators in terms of the system Hamiltonian, and replacing t by $t+i\hbar\beta$, the so-called *detailed balance condition* reads as⁷

$$S(-\Delta\mathbf{K},-\omega)=e^{\hbar\beta\omega}S(\Delta\mathbf{K},\omega). \quad (4)$$

Recently, it has been shown^{8,9} that results obtained from a standard Langevin equation with two different noncorrelated noise sources compare fairly well with the experimental data available. These noise sources are a Gaussian white noise accounting for the surface friction and a white shot noise replacing the pairwise interaction potential that simulates the adsorbate-adsorbate collisions. In this context, the double Markovian assumption holds because the substrate excitation time scale is much shorter than the characteristic times associated with the adatom motion (the maximum frequency of the substrate excitation is around 20–30 meV and the characteristic vibrational frequency of the adatom is about 4–6 meV). Moreover, the time involved in a collision process is shorter than the typical time between two consecutive collisions. Thus, memory effects can be neglected. Within this framework, called the *interacting single adsorbate* (ISA) approximation, the total friction η thus consists of the substrate friction γ and the *collisional friction* λ (i.e., $\eta=\gamma+\lambda$). The collisional friction can be related¹⁰ to the surface coverage θ as $\lambda=(6\rho\theta/a^2)\sqrt{k_B T/m}$, where a is the length of an assumed surface lattice with square unit cells and ρ is the effective radius of an adparticle. Thus, the stochastic single-particle trajectories $\mathbf{R}(t)$ running on the surface are assumed to obey the Langevin equation

$$\ddot{\mathbf{R}}(t)=-\eta\dot{\mathbf{R}}(t)+\mathbf{F}(\mathbf{R}(t))+\delta\mathbf{N}(t), \quad (5)$$

where $\mathbf{F}(\mathbf{R}(t))$ is the adiabatic force per mass unit derived from the periodic surface interaction potential, $\delta\mathbf{N}(t)=\delta\mathbf{N}_G(t)+\delta\mathbf{N}_S(t)$ is the two-dimensional fluctuation of the total noise acting on the adparticle (the G and S subscripts stand for Gaussian and shot, respectively). In the Heisenberg representation, Eq. (5) still holds, its formal solution being

$$\hat{\mathbf{R}}(t)=\hat{\mathbf{R}}_0+\frac{\hat{\mathbf{P}}_0}{m\eta}\Phi(\eta t)+\frac{1}{\eta}\int_0^t\Phi(\eta t-\eta t')[\hat{\mathbf{F}}(\hat{\mathbf{R}}(t'))+\delta\hat{\mathbf{N}}(t')]dt', \quad (6)$$

where $\hat{\mathbf{R}}_0$ and $\hat{\mathbf{P}}_0$ are the adparticle position and momentum operators at $t=0$, respectively, and $\Phi(x)=1-e^{-x}$. From Eqs. (3) and (6), and considering the disentangling theorem, $I(\Delta\mathbf{K},t)$ can be expressed as

$$I(\Delta\mathbf{K},t)\simeq I_q(\Delta\mathbf{K},t)I_c(\Delta\mathbf{K},t), \quad (7)$$

which is a product of a quantum intermediate scattering function, $I_q(\Delta\mathbf{K},t)$, and a classical-like one, $I_c(\Delta\mathbf{K},t)$. The quantum contribution, governed by the commutator, is the same for any type of surface regardless of its relative corrugation. For weakly corrugated surfaces, which can be assumed as flat, the commutator between the position and momentum operators is a c -number, and the relation (7) is exact. However, in general, the presence of the adiabatic force introduces an additional commutator, $[\hat{\mathbf{R}}_0,\hat{\mathbf{F}}(\hat{\mathbf{R}}(t))]=(i\hbar)\partial\hat{\mathbf{F}}(\hat{\mathbf{R}}(t))/\partial\hat{\mathbf{P}}_0$, where the dependence of the adiabatic force on the initial state $(\hat{\mathbf{R}}_0,\hat{\mathbf{P}}_0)$ is through $\hat{\mathbf{R}}(t)$. Assuming a Markovian regime (fast memory loss on the initial conditions), the previous commutator is going to be negligible. Thus, in both cases, I_q will read as

$$I_q(\Delta\mathbf{K},t)\simeq\exp\left[\frac{i\hbar\Delta\mathbf{K}^2}{2\eta m}\Phi(\eta t)\right]=\exp\left[\frac{iE_r}{\hbar}\frac{\Phi(\eta t)}{\eta}\right], \quad (8)$$

where $E_r=\hbar^2\Delta\mathbf{K}^2/2m$ is the *adsorbate recoil energy*. As expected, the argument of I_q becomes less important as the adparticle mass and the total friction increase (and, therefore, as the coverage also increases). Furthermore, for $\hbar=0$, we recover the standard classical function: $I=I_c$. In Eq. (8), the time dependence arises from $\Phi(\eta t)$. Thus, at short times ($\lesssim\hbar\beta$), we find $\Phi(\eta t)\approx\eta t$ and the argument of I_q becomes independent of the total friction, increasing linearly with time. On the contrary, in the long-time limit, this argument approaches a constant phase.

For flat or weakly corrugated surfaces, I_c reads as

$$I_c(\Delta\mathbf{K},t)=e^{-\chi^2[\eta t-\Phi(\eta t)]}, \quad (9)$$

where the so-called *shape parameter* χ is given by $\chi^2=\Delta\mathbf{K}^2\langle\mathbf{v}_0^2\rangle/\eta^2$ and, therefore, the total intermediate scattering function (8) can be expressed as

$$I(\Delta\mathbf{K},t)=e^{\alpha\chi^2}e^{-\chi^2[\eta t+\alpha\Phi(\eta t)]}, \quad (10)$$

where $\alpha=1+i\hbar\eta/2k_B T$ if the thermal square velocity is $\langle\mathbf{v}_0^2\rangle=k_B T/m$. Equation (10) is the generalization of the intermediate scattering function for the quantum motion of interacting adsorbates on a flat surface. The dependence of this function on $\Delta\mathbf{K}^2$ through the shape parameter is the same as in the classical theory.¹⁰ Note that the total intermediate scattering function issued from Eqs. (7)–(10) is exact for Gaussian quantum processes and no information about the velocity autocorrelation function is needed. However, classically the intermediate scattering function is usually obtained from

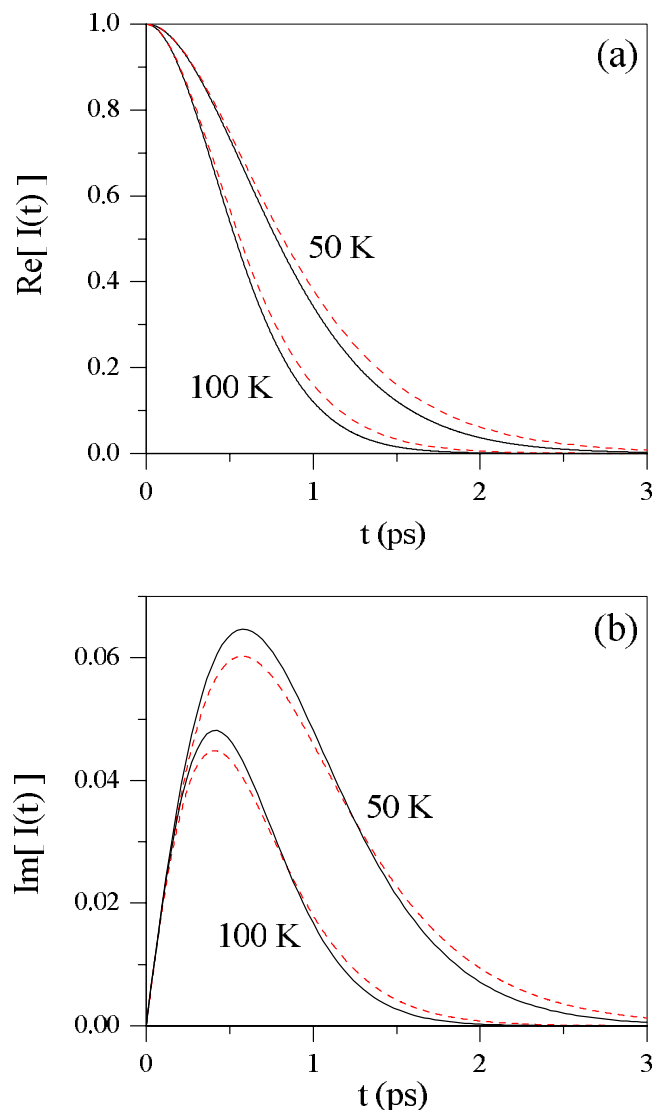


FIG. 1. (Color online) Quantum intermediate scattering function [Eq. (10)] for Na diffusion on a flat surface at 50 and 100 K: (a) real part and (b) imaginary part. Two coverages are considered: $\theta=0.028$ (black solid line) and $\theta=0.18$ (red/dark gray dashed line).

Doob's theorem, which states that the velocity autocorrelation function for a Gaussian, Markovian stationary process decays exponentially with time.¹¹ Furthermore, two regimes are clearly distinguishable: free diffusion or ballistic and diffusive. The former is dominant at very low times, $\eta t \ll 1$, while the latter rules the dynamics at very long times, $\eta t \gg 1$. In the diffusive regime, the mean square displacement, $\langle \mathbf{R}^2(t) \rangle$, is also linear with time, the slope giving the diffusion coefficient according to Einstein's law, $D = k_B T / m \eta$ (which ensures that the adparticle velocity distribution becomes Maxwellian asymptotically). Therefore, since tunneling is absent, the quantum diffusion coefficient follows Einstein's law as in the classical case.

In Fig. 1, the real and imaginary parts of Eq. (7) for Na diffusion on a flat surface are plotted at two different surface temperatures, 50 and 100 K, and two coverages, 0.028 and 0.18. As can be clearly seen, the real part of $I(t)$ decreases faster with temperature and slower with coverage. On the other hand, the imaginary part of $I(t)$ displays maxima be-

tween 4% and 6% of the corresponding real part, depending on the temperature. It starts linearly with time and, after passing through a maximum, decays smoothly to zero. The corresponding quasielastic line shapes (around the zero energy exchange) will then display narrowing with the coverage and broadening with the surface temperature. This behavior could be experimentally confirmed for those systems where the diffusion barrier is smaller than the thermal energy $k_B T$. For light particles, the imaginary part is expected to be much more important keeping the same shape.

Let us now consider the case of nonzero corrugation. For Na atoms, the pairwise interaction potential is repulsive and the mean interparticle distance should be greater than λ_B most of time. Thus, the classical-like part of Eq. (7) could be replaced, at a first approximation, by the classical counterpart. Obviously, if diffusion is mediated by tunneling, this procedure is no longer valid. The error comes from small times, but since diffusion is a long-time process, the influence on the quasielastic peak (wave-vector dependence) and the quantum diffusion constant (Einstein's law) will be very small for massive particles. In Figs. 2 and 3, plots for Na diffusion on Cu(001) at the same surface temperatures and coverages as in Fig. 1 are shown. The numerical values corresponding to I_c have been obtained from classical Langevin simulations in a nonseparable adsorbate-substrate interaction potential.¹² The global time behavior of the real and imaginary parts of the intermediate scattering function [see Figs. 2(a) and 3(a), respectively] displays important differences for high and low temperatures. At 50 K, the thermal energy is not enough to surmount the diffusion barrier of the Cu(001) surface and adsorbates will remain for relatively long times inside potential wells. On the contrary, at 100 K, the intermediate scattering function decreases asymptotically to zero according to a more or less exponential function,¹⁰ as happens in a regime characterized by surface diffusion. The maxima displayed by the imaginary part are, again, around the same percentage as before [see Fig. 3(b)]. In principle, these imaginary parts should also be observable at least at 100 K in spin-echo experiments. With coverage, this time behavior means that the quasielastic peaks, given by the scattering law, will undergo broadening, as observed experimentally.¹³ Quantum jump mechanisms can also be extracted from that peak in a similar way as the classical procedure.¹⁰ The rapid oscillations displayed by the intermediate scattering function at short times [see Figs. 2(b) and 3(b)] indicate bound motions inside the potential wells, which become less pronounced as temperature increases. These oscillations are associated with the lowest frequency mode or frustrated translational mode.

In Fig. 4, we show the effects of the quantum correction on the diffusion process studied here at two different surface temperatures for a coverage of 0.028. To compare, both the classical intermediate scattering function and the real part of its quantum analog are displayed in the figure. As seen, although the Na atom is a relatively massive particle, at low temperatures the *plateau* is lower for the quantum case. This implies an initially (relatively) faster decay arising from the strong influence of the quantum behavior at short time scales. It is therefore the real part of the intermediate scatter-

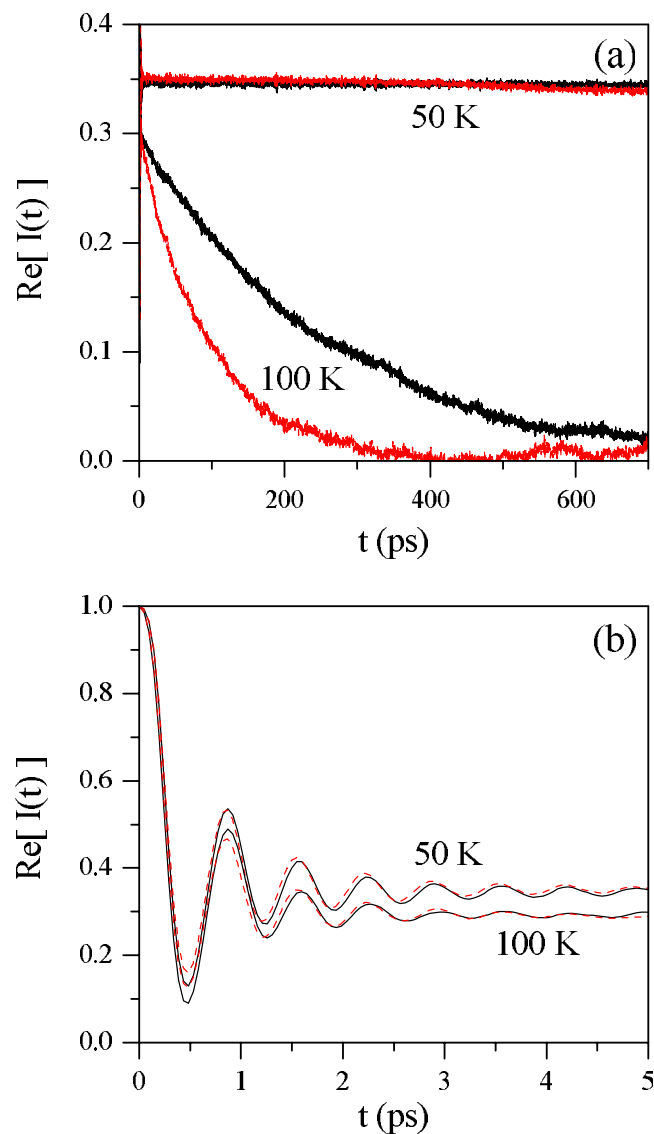


FIG. 2. (Color online) Real part (a) of the quantum intermediate scattering function [Eq. (7)] for Na diffusion on a corrugated-Cu(001) surface at 50 and 100 K. An enlargement at short time scales is shown in part (b). Two coverages are considered: $\theta=0.028$ (black solid line) and $\theta=0.18$ (red/dark gray dashed line).

ing function that one should compare to the experiment rather than I_c , as is usually done. Obviously, this effect will be less pronounced at high coverages.

It is remarkable that within the Markovian approach presented here the quantum intermediate scattering function I_q is independent of the relative corrugation of the surface and, at short times, also independent of the friction. At low surface temperatures, the I_q factor will be responsible for a higher contribution of the imaginary part of I , given by Eq. (7), modifying substantially the response in the diffusion process. Despite the fact that we have termed I_c the classical-like intermediate scattering function, strictly speaking it is not a classical magnitude because it involves position operators. Nevertheless, for relatively heavy particles and at very long times (diffusion time scales), operators can be replaced by variables since λ_B is very small. As far as we know, an exact quantum calculation for a corrugated surface is not possible and some approximations have to be invoked, e.g., the

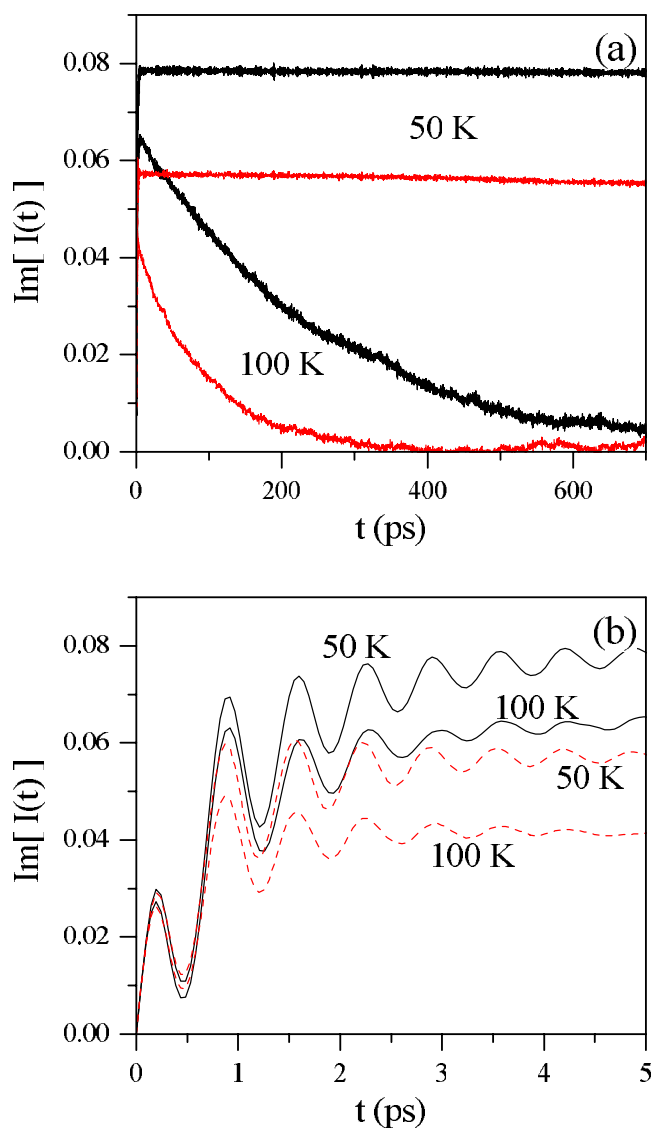


FIG. 3. (Color online) Imaginary part (a) of the quantum intermediate scattering function [Eq. (7)] for Na diffusion on a corrugated-Cu(001) surface at 50 and 100 K. An enlargement at short time scales is shown in part (b). Two coverages are considered: $\theta=0.028$ (black solid line) and $\theta=0.18$ (red/dark gray dashed line).

damped harmonic oscillator, which has been applied by some of us¹⁴ within the same context. Of course, other different alternative theoretical approaches can also be found in literature (see, for instance, Ref. 15) within the single adsorbate approximation. The theoretical formalism that we propose here should also be very useful to avoid extrapolations at zero surface temperature when trying to extract information about the frustrated translational mode. Diffusion experiments at low temperatures are very difficult to perform (or even unaffordable). However, the type of theoretical calculations needed in this formalism is easy to carry out and they would provide a simple manner to go to very low temperatures with quite reliable results, thus allowing to extract confident values of magnitudes such as friction coefficients and oscillation frequencies. By decreasing the surface temperature, quantum effects are extended at higher values of time. Going from 100 to 50 K, the time where the quantum dynamics is important increases from 0.07 to 0.15 ps. The stan-

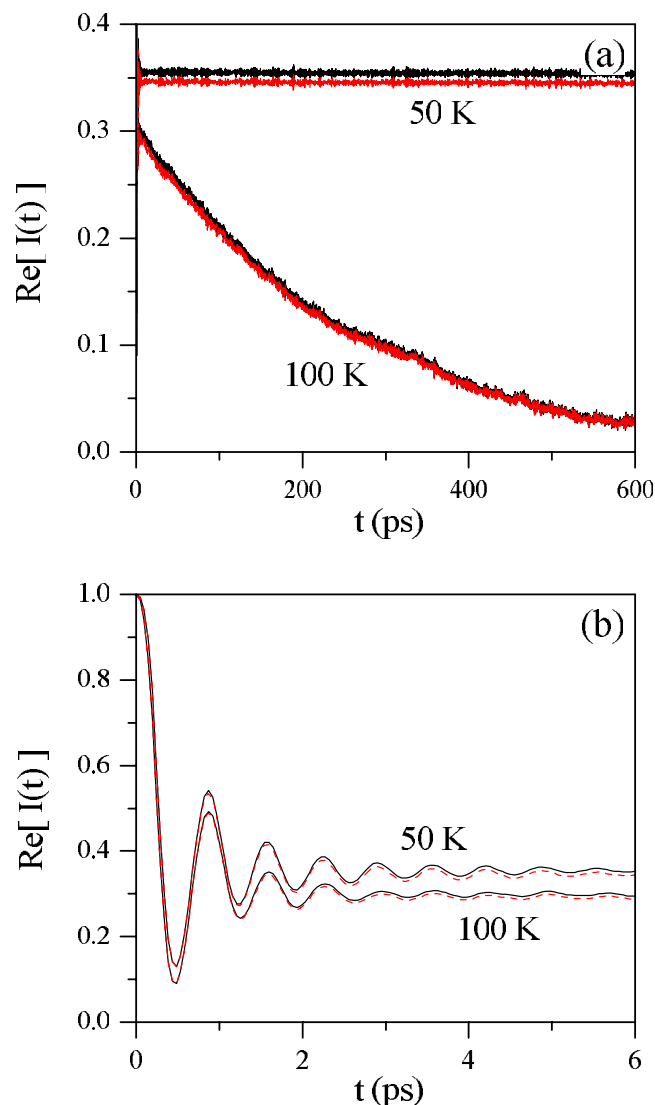


FIG. 4. (Color online) Classical intermediate scattering function for Na diffusion on a corrugated-Cu(001) surface at 50 and 100 K (black solid lines) and the real part of its quantum-mechanical analog (7) (red/dark gray dashed lines). An enlargement at short time scales is shown in part (b). The surface coverage considered here is 0.028.

dard propagation time for diffusion is greater than 400 ps, as can be seen in Figs. 2 and 3. In our opinion, the range of applicability of this quantum theory should be around or below 10 K and with coverages up to 20%. Clearly, tunneling-mediated diffusion, where the isotopic effect and the so-called crossover temperature have been first observed by Gomer *et al.*¹⁶ is not accounted for by our model. This is a very important aspect that deserves further consideration, in particular, regarding the new observations of Zhu *et al.*¹⁷ concerning the coverage dependence of tunneling diffusion and the works by Ho *et al.*¹⁸ and Sundell and Wahnström.¹⁹

Finally, it is well known that the broadening is due to the increase in coverage. As we have shown in Ref. 10, better

agreement with the experimental results is found with the ISA model (classical theory) than with the previous calculations where the repulsive lateral interaction is taken into account in Langevin molecular dynamics simulations. This leads us to conclude that a stochastic description of the broadening should be good enough to describe it since the statistical limit (central limit theorem) in the number of collisions should be reached in the very long-time propagation describing the diffusion process. This conclusion is still valid in this quantum theory since the adparticle is massive and the small quantum effects are mainly observed in the short time limit. What this quantum theory has showed is the complex character of the intermediate scattering function whose real and imaginary parts are observable⁴ even for massive adparticles (Cs atoms).

We would like to thank the Cambridge Surface Physics group for very interesting and stimulating discussions. This work has been supported by the Ministerio de Ciencia e Innovación (Spain) under Project with Reference No. FIS2007-62006. R. Martínez-Casado and A. S. Sanz acknowledge the Consejo Superior de Investigaciones Científicas for a predoctoral contract and a JAE-Doc contract, respectively.

¹L. van Hove, *Phys. Rev.* **95**, 249 (1954).

²S. W. Lovesey, in *Theory of Neutron Scattering from Condensed Matter* (Clarendon, Oxford, 1986), Vol. 1.

³G. Alexandrowicz, A. P. Jardine, H. Hedgeland, W. Allison, and J. Ellis, *Phys. Rev. Lett.* **97**, 156103 (2006).

⁴A. P. Jardine, G. Alexandrowicz, H. Hedgeland, R. D. Diehl, W. Allison, and J. Ellis, *J. Phys.: Condens. Matter* **19**, 305010 (2007).

⁵S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943).

⁶G. H. Vineyard, *Phys. Rev.* **110**, 999 (1958).

⁷P. Schofield, *Phys. Rev. Lett.* **4**, 239 (1960).

⁸R. Martínez-Casado, J. L. Vega, A. S. Sanz, and S. Miret-Artés, *Phys. Rev. Lett.* **98**, 216102 (2007).

⁹R. Martínez-Casado, J. L. Vega, A. S. Sanz, and S. Miret-Artés, *Phys. Rev. B* **77**, 115414 (2008).

¹⁰R. Martínez-Casado, J. L. Vega, A. S. Sanz, and S. Miret-Artés, *J. Phys.: Condens. Matter* **19**, 305002 (2007).

¹¹H. Risken, *The Fokker-Planck Equation* (Springer, Berlin, 1984).

¹²A. P. Graham, F. Hofmann, J. P. Toennies, L. Y. Chen, and S. C. Ying, *Phys. Rev. B* **56**, 10567 (1997).

¹³J. Ellis, A. P. Graham, F. Hofmann, and J. P. Toennies, *Phys. Rev. B* **63**, 195408 (2001).

¹⁴J. L. Vega, R. Guantes, S. Miret-Artés, and E. Pollak, *J. Chem. Phys.* **120**, 10768 (2004); J. L. Vega, R. Guantes, S. Miret-Artés, and D. A. Micha, *ibid.* **121**, 8580 (2004).

¹⁵P. Hänggi, P. Talkner, and M. Borkovec, *Rev. Mod. Phys.* **62**, 251 (1990); L. Y. Chen and S. C. Ying, *Phys. Rev. Lett.* **73**, 700 (1994); Y. Georgievskii and E. Pollak, *Phys. Rev. E* **49**, 5098 (1994).

¹⁶R. DiFoggio and R. Gomer, *Phys. Rev. B* **25**, 3490 (1982); T.-S. Lin and R. Gomer, *Surf. Sci.* **225**, 41 (1991).

¹⁷X. D. Zhu, A. Lee, A. Wong, and U. Linke, *Phys. Rev. Lett.* **68**, 1862 (1992); G. X. Cao, E. Nabighian, and X. D. Zhu, *ibid.* **79**, 3696 (1997).

¹⁸L. J. Lauhon and W. Ho, *Phys. Rev. Lett.* **85**, 4566 (2000); J. Kua, L. J. Lauhon, W. Ho, and W. A. Goddard III, *J. Chem. Phys.* **115**, 5620 (2001).

¹⁹P. G. Sundell and G. Wahnström, *Phys. Rev. B* **70**, 081403(R) (2004).