Many-Body Nature of the Meyer-Neldel Compensation Law for Diffusion

Ghyslain Boisvert,[1,*] Laurent J. Lewis,[1,†] and Arthur Yelon[2,‡]

[1]*Département de Physique et Groupe de Recherche en Physique et Technologie des Couches Minces (GCM),*
Université de Montréal, Case Postale 6128, Succursale Centre-Ville, Montréal, Québec, Canada H3C 3J7
[2]*Département de Génie Physique et Groupe de Recherche en Physique et Technologie des Couches Minces (GCM),*
École Polytechnique de Montréal, Case Postale 6079, Succursale Centre-Ville, Montréal, Québec, Canada H3C 3A7

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We present the results of a detailed embedded-atom-method molecular-dynamics study of diffusion on metallic surfaces with a view of establishing the validity of the compensation (Meyer-Neldel) law for phonon-activated Arrhenius processes. We find, indeed, that surfaces with large activation barriers for diffusion compensate by increasing their effective attempt-to-diffuse frequencies. The Meyer-Neldel energy we obtain agrees very well with bulk diffusion data. Our results confirm the role played by phonons in the activation, as well as the many-body nature of the excitations leading to diffusion and, therefore, to the Meyer-Neldel rule.

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The compensation law, or Meyer-Neldel rule (MNR) [1], is observed in a wide range of phenomena in physics, chemistry, and biology [2–4]. It appears to be a fundamental property of many families of activated processes following an Arrhenius dependence on temperature,

$$X = X_0 e^{-\Delta/kT}. \tag{1}$$

It is frequently found that, when the activation energy Δ is varied within a family of processes (related chemical reactions, for example), then the prefactor X_0 in Eq. (1) obeys the (empirical) relation

$$X_0 = X_{00} e^{\Delta/\Delta_0}. \tag{2}$$

Here, X_{00} is a constant, and Δ_0 is the Meyer-Neldel energy (MNE) for the processes in question. Thus the increase in the prefactor X_0 when Δ increases, Eq. (2), "compensates" for the decrease in the activation factor, Eq. (1), so that the processes actually take place at a rate larger than would be expected from a knowledge of Δ alone. In view of the ubiquitous character of this important phenomenon, and its relevance in the interpretation of experimental data for activated processes (e.g., diffusion), it is important to understand its origin in detail.

In the past, the MNR has frequently been attributed to activation into exponentially varying densities of states [5–8]. However, it has been shown [2–4,9] that the MNR arises naturally for kinetic processes for which Δ is large compared to the energies of the excitations which contribute to the activation, as well as to kT. The exponential in Eq. (2), which is *not* at the origin of the effect, results, rather, from the entropy of combining *multiple* excitations (or fluctuations [10,11]) in the thermal reservoir available for the kinetic processes. The MNE, Δ_0, therefore, is expected to be of the order of the energy of the excitations in the reservoir, times a logarithmic correction term [2,3,9], which is frequently found to be of the order of unity, as discussed below.

Among the phenomena which have been found to exhibit the MNR is diffusion in bulk solids [12–14]. In this case, the thermal reservoir contains the excitations of the lattice, i.e., the phonons. There presently exists no analytical model, in the case of diffusion, where the circumstances appropriate for the MNR, i.e., the combination of multiple excitations in the realization of the kinetic process, are treated fully. However, we expect atomistic models which do include such multiple excitations, such as molecular dynamics (MD), to yield the compensation law; indeed, MD provides an essentially exact solution to the problem of determining the trajectory in time of an ensemble of dynamically interacting particles. It is therefore of considerable interest to establish the validity and ubiquity of the MNR, and its origin in multiple-excitation effects, through the study of a phenomenon for which an exact solution is available.

In view of this, we present here the results of a series of MD calculations of diffusion on various metallic surfaces. Diffusion proceeds more readily on surfaces than in bulk material (because of the generally smaller activation energies), making them more amenable to detailed MD simulations. More precisely, we have calculated the Arrhenius parameters for diffusion on the (100) and (111) surfaces of Au, Ag, Pd, and Ni, using the embedded-atom method (EAM) [15,16] to describe the interactions between the atoms. The rate of diffusion [17] can be expressed as

$$\Gamma = \Gamma_0 e^{-E_A/kT}, \tag{3}$$

where E_A is the activation energy and the prefactor Γ_0 is an effective "attempt-to-diffuse" frequency. The activation energy was varied by considering different types of diffusion (see below) on the various surfaces. We indeed find, as will be shown below, the prefactor Γ_0 to follow the MNR, Eq. (2). The MNE we obtain is in excellent agreement with bulk diffusion data. Our results confirm the validity of the Meyer-Neldel law for phonon-activated processes, as well as the many-body nature of the excitations leading to it, since there is nothing resembling an exponential single-particle density of states in our model.

To model the surfaces, we constructed "slabs" containing 8 to 11 layers, of which the bottom two were held fixed in order to mimic the bulk. Periodic boundary conditions were used parallel to the slab, but not perpendicular to it. Each layer consisted of either 64 or 72 atoms [for the (111) and (100) surfaces, respectively]. We note that the systems are fairly small: Because diffusion decreases rapidly with decreasing temperature, it was necessary to keep the size to a minimum so as to afford sufficiently long runs (2–12 ns), necessary for statistically reliable results [18]. We have verified that the systems are large enough to ensure convergence of the calculated properties.

The simulations were performed in the (N,V,T) ensemble, except for a series of runs on the bulk materials carried out in the (N,P,T) ensemble in order to determine the temperature dependence of the lattice parameters; these were used in the slabs to set the two fixed layers to their proper bulklike equilibrium configuration. As mentioned above, the atoms were chosen to interact via the EAM potentials of Foiles, Baskes, and Daw [15], using the parameters optimized by Adams, Foiles, and Wolfer [16]. The EAM is known to provide a realistic description of the energetics of fcc metals, including surface properties [19].

For each choice of metal and geometry, a series of runs in temperature was carried out in order to determine the Arrhenius parameters for diffusion. In Fig. 1 we show typical results for three different cases, namely, Ni/Ni(100)-*X*, Pd/Pd(100)-*J*, and Pd/Pd(100)-*X*. Here, *J* and *X* stand for "jump" and "exchange," respectively. On the (100) surface, diffusion can proceed either by jumps or via an exchange mechanism [but only by jumps on the close-packed (111) surface]. The straight lines represent the Arrhenius fits to the MD data. It should be noted that as temperature is lowered diffusion slows down rapidly [exponentially, and depending on the activation energy; cf. Eq. (3)], to the point where it becomes impractical, or impossible, to properly simulate the process. At high temperatures, on the other hand, disordering of the surface sets in and diffusion becomes very complicated. These considerations impose limitations on the range of temperatures that can be examined. For Ni/Ni(100)-*X*, for instance, we were limited to the range $1000 \leq T \leq 1150$ K. We have demonstrated, however, by comparing the MD data with the predictions of a simple transition-state model, that temperature ranges such as those used in Fig. 1 are sufficient to yield converged diffusion parameters [18].

In all, ten different cases were considered; they are listed in Table I where we give, for each, the mechanism for diffusion (*J* or *X*), the activation energy E_A, and the prefactor Γ_0. Some of the data discussed here are particular to the present study, while others were generated in the context of a detailed investigation of diffusion processes on metallic surfaces [18,20,21].

In Fig. 2 we present a Meyer-Neldel plot of the data of Table I; i.e., we plot $\ln\Gamma_0$ as a function of E_A. The MNR is obeyed if the data follow a straight line with positive slope. [The form $\exp(E_A/\Delta_0)^\alpha$, with $1/2 \leq \alpha \leq 1$, is also possible [2,3]; we shall return to this point below.] Evidently, a straight line fits the data very well. The MNE Δ_0 is the inverse of the slope; the best fit to the data is obtained with $\Delta_0 = 190 \pm 20$ meV. (The fit excludes point number 1, which may or may not obey the MNR—see

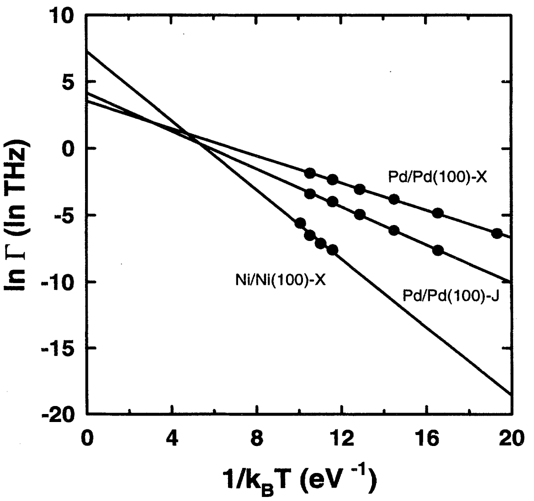

FIG. 1. Arrhenius plot of the diffusion rates for Ni/Ni(100)-*X*, Pd/Pd(100)-*J*, and Pd/Pd(100)-*X*, as indicated. The full circles are the MD values and the lines correspond to the Arrhenius fits.

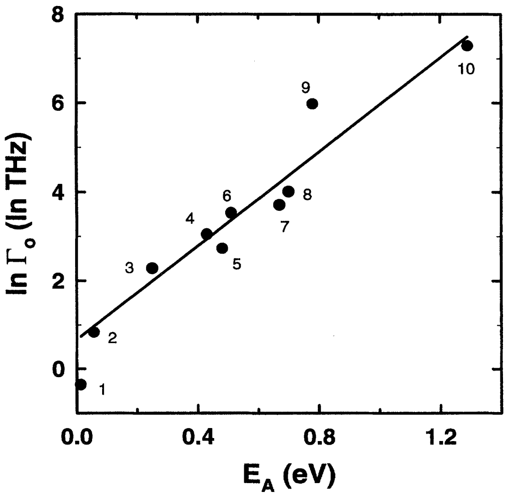

FIG. 2. Meyer-Neldel plot of the prefactor ("effective attempt-to-diffuse frequency") Γ_0 versus the activation energy E_A. The points are labeled as indicated in Table I. The straight line is a fit to the MNR, Eq. (2). The inverse of the slope is the MNE, $\Delta_0 = 190$ meV.

TABLE I. The various cases of surface diffusion considered. J and X refer to diffusion by jumps and by an exchange mechanism, respectively. E_A is the activation energy, and Γ_0 is the attempt-to-diffuse frequency.

Label	Surface	E_A (meV)	$\ln\Gamma_0$ (THz)
1	Au/Au(111)-J	13	−0.36
2	Ag/Ag(111)-J	55	0.83
3	Au/Au(100)-X	250	2.28
4	Au/Au(100)-J	430	3.05
5	Ag/Ag(100)-J	480	2.73
6	Pd/Pd(100)-X	510	3.53
7	Ni/Ni(100)-J	670	3.71
8	Pd/Pd(100)-J	700	4.01
9	Ag/Ag(100)-X	780	5.97
10	Ni/Ni(100)-X	1290	7.28

below; point number 9 carries a large error bar because of severe limitations on the range of temperatures that could be investigated.) That the MNR is obeyed by surface diffusion was, in fact, already visible in Fig. 1: The temperature at which the three lines cross (*modulo* statistical error) is the isokinetic temperature, $T_0 = \Delta_0/k \approx 2200$ K.

These results lead to several observations. First, the MD model *does* predict the MNR for all the diffusion processes represented in Fig. 2. The calculated MNE, 190 meV, is in excellent agreement with the available experimental data: We are not aware of measurements of the MNE for surface diffusion; however, bulk diffusion experiments yield values of Δ_0 on the order of 150–200 meV [12–14].

Second, both experimental (for bulk diffusion) and calculated (for surface diffusion) values of Δ_0 are larger than one might have expected on the basis of previous observations of the MNR. In the EAM, all electronic effects are incorporated into the potentials. Thus the only excitations available to provide the bath from which the thermal fluctuations are drawn are phonons. We may then take, as the characteristic energy of the excitations, the Debye energy, which is of the order of 25 meV [22], i.e., Δ_0 is 7–8 times larger than this energy. This is in contrast to other cases which have been studied [2,3,23], for which Δ_0 is no more than a factor of 2–3 different from the characteristic energy of the excitations involved—optical phonons [2–4] or infrared excitations [23]. Why this difference should exist is unclear; however, one possibility is worth discussing here.

As noted above, the theoretical model for the MNR predicts a prefactor of the form $\exp(E_A/\Delta_0)^\alpha$, with $1/2 \leq \alpha \leq 1$, depending on the nature of the excitations that give rise to the activated processes [2,3]. For optical phonons, for instance, both a model which considers the bath of phonons in a phenomenological manner [3] and a detailed calculation of electron-phonon interactions [2,24] predict $\alpha = 1$, in agreement with the usual empirical result. For acoustic phonons, on the other hand, the simple phenomenological model [3] predicts 3/4, while we expect 2/3 with detailed electron-phonon interactions [2,25]. In the simple systems considered here, optical phonons are absent. While neither of the above two models provides a perfectly adequate guide for atomic motions induced by acoustic phonons, they suggest α might be closer to 0.7 than to 1. In Fig. 3, we have plotted $\ln\Gamma_0$ vs Δ_0^α, with $\alpha = 0.7$. The fit is quite comparable to that of Fig. 2. From the slope b we obtain $\Delta_0 = (1/b)^{1/\alpha} = 74 \pm 15$ meV, i.e., *3 times the characteristic excitation energy*, in line with other observations of the MNR [2,3,23]. Even though an analytical microscopic model would be needed to verify this analysis, it reinforces the view that acoustic phonons can, by themselves, provide the fluctuations necessary for the MNR. It would be of considerable interest that experimental bulk diffusion data [12–14] be reinterpreted in a corresponding manner.

Third, and perhaps most important, the condition of large activation energy, compared to the characteristic energy of the excitations, is certainly obeyed for all points in Fig. 2 except the lowest: The point labeled "2" has $E_A = 55$ meV, about 3 times the Debye (or characteristic excitation) energy for Ag. For point "1," in contrast, $E_A = 13$ meV, and the MNR should not be observed; Γ_0, further, is somewhat less than the Debye frequency for the material (3.4 THz), whereas it is larger for all other points. The MD model, now, contains no exponential single-particle density of states, excluding such an explanation for the observed Meyer-Neldel behavior; *compensation, therefore, must arise from multiple excitations.* The hopping adatom (or the atoms involved in the exchange mechanism) plus the accumulated phonons provide the fluctuations which are necessary in order for the activated diffusion to take place, thus leading to an effective, many-body, exponential

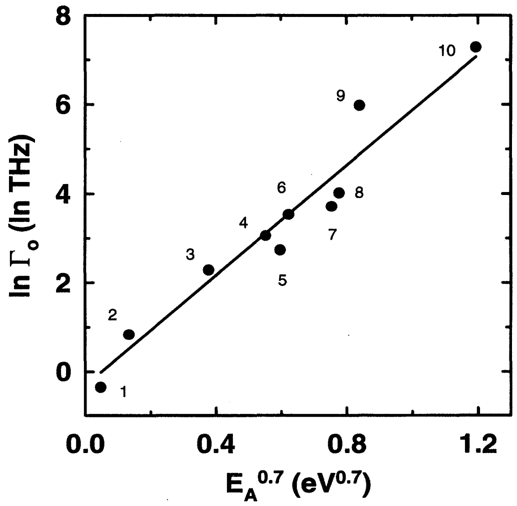

FIG. 3. Plot of $\ln\Gamma_0$ vs $E_A^{0.7}$. The points are labeled as indicated in Table I. The line indicates the best linear fit, and leads to the MNE $\Delta_0 = 74$ meV.

density of states [11]. *This, however, is a result of the compensation effect, not its cause.*

As a fourth and last point, our findings have important consequences for the experimental interpretation of surface diffusion data. Because a systematic study of diffusion as a function of temperature is both difficult and time consuming, the prefactor for diffusion, D_0, is often assumed to be known; the value of E_A, then, can be deduced from a single diffusion-constant measurement. Since E_A depends logarithmically on D_0, errors arising from such an approximation will be small provided E_A does not depart too much from the actual value corresponding to D_0. For instance, taking $D_0 = 1 \times 10^{-3}$ cm^2/s (or $\Gamma_0 \approx 2-3$ THz, i.e., typical phonon frequencies), a value commonly used for surface diffusion (see, e.g., [26,27]), we find, from Fig. 2, that the assumption of a constant prefactor will be approximately valid if $E_A \approx 0.1$ eV. For exchange diffusion of Pt on Pt(100), however, the low-temperature diffusion data yield $E_A = 0.47$ eV [26]. Taking due account of the variation of D_0 with E_A, i.e., the MNR, we obtain $E_A = 0.51$ eV. In view of the activated form of the diffusion constant this is a sizable difference that cannot be neglected; at 800 K, for instance, the estimated value for the diffusion coefficient is in error by a factor of 4. Likewise, for jump diffusion of Pd on Pt(100), experiment gives $E_A = 0.70$ eV [27], while the MNR-corrected value is 0.77 eV; at 800 K the diffusion constant is here in error by a factor of 10. Clearly, therefore, it is important, in order to extrapolate diffusion data to high temperatures, to fully take into account the compensation, by the prefactor, of large activation barriers.

In summary, on the basis of detailed MD calculations of diffusion on metallic surfaces, we have unambiguously established the validity of the Meyer-Neldel law for phonon-activated Arrhenius processes. We find, indeed, that surfaces with large activation barriers for diffusion compensate the difficulty in overcoming these barriers by increasing their attempt-to-diffuse frequencies. The Meyer-Neldel energy we obtain agrees very well with bulk diffusion measurements. Our results confirm the role of phonons in the activation, as well as the many-body nature of the excitations leading to diffusion and, therefore, to the Meyer-Neldel law.

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*Electronic mail address: boisver@physcn.umontreal.ca

†Electronic mail address: lewis@physcn.umontreal.ca

‡Electronic mail address: artyelon@css.phys.polymtl.ca

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