

Microscopic Explanation of the Compensation (Meyer-Neldel) Rule

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We propose that the Meyer-Neldel compensation rule can be understood as arising naturally for assisted processes in which the energy for the process is much larger than that of a typical excitation. In this case, the total energy is provided by multiple excitations. The prefactor is then proportional to the number of ways of assembling these excitations. This number increases exponentially with the energy for the process, yielding the Meyer-Neldel rule.

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A great many activated processes, including solid-state diffusion in crystals¹ and polymers,² dielectric relaxation and conduction in polymers,³ thermally stimulated processes in polymers,⁴ and electronic conduction in amorphous semiconductors,⁵ obey the compensation law, or Meyer-Neldel rule.⁶ This rule states that if a process X obeys the equation

$$X = X_0 e^{-E/kT}, \quad (1)$$

the X_0 and E obey the equation

$$\ln X_0 = a + bE, \quad (2)$$

where a and b are constants.

That is, for a relaxation frequency ν , for example, if the activation energy increases, the attempt frequency ν_0 increases exponentially. This poses two problems. First, one obtains values for the apparent attempt frequency which are difficult to interpret physically. This has been a great problem in the field of variable-range hopping,⁷ in which ν_0 is found to vary between about 10^3 and 10^{28} s⁻¹. Second, it has been difficult to understand, from a microscopic point of view, why this rule should be so general.

A phenomenological approach to the problem has been taken by Keyes,¹ Lawson,² and Crine.⁸ This may be envisaged as beginning from the Eyring theory⁹ of the activated state. In this model, the reaction rate is proportional to $e^{\Delta G/kT}$, where ΔG is the difference between the free energy of the state at the peak of an activation barrier and that of the initial state. Since

$$\Delta G = \Delta H - T\Delta S, \quad (3)$$

it is evident that

$$\nu \propto e^{\Delta S/k} e^{-\Delta H/kT}. \quad (4)$$

Thus, the compensation law follows if the activation entropy is proportional to the activation enthalpy. For processes involving an activation volume, Keyes¹ and Lawson² presented arguments as to why this should be so, arguing for a constant ratio between them. Crine⁸ has argued for a ratio which will be different for dif-

ferent materials.

Three objections to this approach can be invoked. First, it can be looked at as merely restating the Meyer-Neldel rule in terms of the Eyring equation. Second, it seems difficult to understand why it should apply to a process, such as electronic conduction in amorphous semiconductors, in which we do not anticipate that an activation volume will play a role. Finally, it is not immediately obvious what a macroscopic entropy will signify in such a single-electron process.

Nonetheless, such a concept is very appealing. One possible microscopic interpretation would be that as the activation energy (or enthalpy) increases, the number of paths to the activated state increases. In fact, this is what we should expect when the activation energy for a process becomes large compared to the energy of the typical fluctuations of a system. In that case, a substantial fluctuation is necessary to provide the required energy. While this has not been generally recognized, it should be clear that, in a phonon-assisted electron hop, for example, the electron is far more likely to encounter a large number of small phonons than one very large phonon. The number of ways of assembling these phonons will obviously increase as the total energy increases. In order to obtain the Meyer-Neldel rule, it is only necessary to show that this number increases exponentially.

For this purpose we consider a simple yet very general model: that of a two-level system with energies ϵ_1 , ϵ_2 , and $\epsilon_1 - \epsilon_2 = \Delta$ and couple this system to an abstract multimode Bose field. The Hamiltonian can be written

$$H = \epsilon_1 c_1^\dagger c_1 + \epsilon_2 c_2^\dagger c_2 + \sum_{\mathbf{q}, \mu} (\hbar \omega_{\mathbf{q}}^\mu) [\lambda_{\mathbf{q}}^{\dagger \mu} \lambda_{\mathbf{q}}^\mu + \frac{1}{2}] \\ + \sum_{\mathbf{q}, n, \mu} \gamma_{n, \mathbf{q}}^\mu c_n^\dagger c_n (\lambda_{\mathbf{q}}^{\dagger \mu} + \lambda_{-\mathbf{q}}^\mu) + \{J_{12} c_1^\dagger c_2 + J_{21} c_2^\dagger c_1\}. \quad (5)$$

In Eq. (5), $n=1,2$, γ is the electron-Bose-field coupling, \tilde{c} and $\tilde{\lambda}$ are electron and field operators, respectively. $\hbar \omega_{\mathbf{q}}^\mu$ is the dispersion of the μ th mode, and J is the field-free coupling term.

In the most common practical situation of the transfer and excitation in solids the Bose field is just the phonon

field, so that Eq. (5) represents the two-level version of the Holstein-Emin Hamiltonian.¹⁰

The usual approach to systems described by this Hamiltonian is the Miller-Abrahams approximation.¹¹ It is assumed that the behavior of the system is dominated by one-phonon processes. However, Emin¹² has shown that this approximation is not always valid for Δ large compared to kT . He performed an exact calculation for acoustic-phonon-assisted hopping of electrons between two sites, including multiphonon processes. He showed that the rate characterizing a hop between sites g and g' is given by

$$R_{gg'} = (J_{g'g} e^{-S/\hbar})^2 e^{-\Delta/2kT} \times \sum_{n=1}^{\infty} \left(\frac{1}{n!} \right) \int_{-\infty}^{\infty} dt [F(t)]^n \cos \left(\frac{\Delta t}{\hbar} \right). \quad (6)$$

In Eq. (6), J is the transfer integral between sites, Δ is a positive activation energy for upward hops, and S and F are sums involving phonon frequencies ω and the coupling γ [see Eqs. (2) and (3) of Ref. 12]. The parameter n corresponds to the total number of phonons emitted and absorbed in the jump. Assuming a cutoff frequency ω_m , Emin showed that when

$$\hbar \omega_m > \Delta \gg kT \quad (7)$$

then Eq. (6) yields

$$R = (J e^{-S_0})^2 e^{-\Delta/kT} (2\pi/\hbar\Delta) \sum_{n=1}^{\infty} B^n(\Delta)/n!(2n-1)!, \quad (8)$$

where

$$S_0 = \frac{3}{2} \gamma (\omega_m/\omega_D)^2 \quad (9)$$

and

$$B(\Delta) = 3\gamma(\Delta/\hbar\omega_D)^2. \quad (10)$$

In Eqs. (9) and (10), ω_D is the Debye frequency. When $B(\Delta)$ is small, Emin finds that only the first term in the series of Eq. (8) need be considered (that is, the Miller-Abrahams approximation is valid) so that

$$R \propto e^{-\Delta/kT}. \quad (11)$$

However, when $B \gg 1$, he finds that the series yields a term $\exp(\Delta/\Delta_0)^{2/3}$, where $\Delta_0 = \frac{2}{9} \gamma^{-1/2} \hbar \omega_D$. That is,

$$R = \nu(T) e^{(\Delta/\Delta_0)^{2/3}} e^{-\Delta/kT}, \quad (12)$$

where $\nu(T)$ is a temperature-dependent prefactor.¹⁰ When Δ is large, the number of different paths to the final state, via multiphonon processes, increases "exponentially" with Δ .

Thus, at low activation energies there is no compensation rule, but one is predicted, with a slightly different form from the empirical rule, for large activation energy. This is physically what we should anticipate. All of the processes cited as showing a Meyer-Neldel rule involve

large activation energies (on the order of an electron volt), whereas no one has reported such a rule for shallow dopants in crystalline semiconductors, for example. It is also very satisfying, in that it does not require physically unreasonable phonon frequencies to produce very large frequency prefactors. The fact that this particular process yields a prefactor which varies as $\exp(\Delta^{2/3})$ rather than $\exp(\Delta)$ is not of great concern, as it is notoriously difficult¹³ to prove which value of α in an $\exp(\Delta^\alpha)$ law provides the best straight-line fit to experimental data. The optical-phonon model has also been considered by Emin, in Ref. 10. The expression for the prefactor contains an exponential scaling factor which behaves as $\exp(\Delta/\hbar\omega_0) \ln(2E_b/\hbar\omega_0)$, where ω_0 is the optical-phonon frequency and E_b describes the strength of the local electron-phonon coupling ($E_b \gg \hbar\omega_0$). Thus, we see that the dispersion does not greatly modify the result, except to change the value of α .

We do not wish to suggest here that all of the processes which yield a compensation law must be phonon activated, although this is a reasonable mechanism for many of them. If the phonon field is replaced by a more general boson field, the result will be essentially the same. Intuitively, one would not be surprised (although this needs to be demonstrated) if processes assisted by electron-electron interaction yielded a not dissimilar result, since the electron field can be replaced by a photon field representing the vacuum polarization.

This picture can be generalized, as follows: Imagine an electron in the valence band of a large-band-gap semiconductor at $t=0$. How long will it take until the particle is excited to the conduction band? In general, both particle and energy can diffuse freely in the system with their own characteristic diffusion equations. In order to reach the highly excited state ($\Delta \gg kT$), (1) the particle has to encounter a fluctuation strong enough to promote it to the excited state, and (2) once encountered, the interaction with the thermal fluctuation (phonons, electrons, photons, . . .) has to promote the particle to the excited state. If the characteristic time for the encounter is τ_Δ and the process of excitation τ_e and $\tau_\Delta \gg \tau_e$, it is the former which determines the transition rate ($1/\tau_\Delta$).

Given an excitation energy Δ , the transition rate $1/\tau_\Delta$ will obviously depend upon the total number of ways a fluctuation larger than Δ can organize itself within the interaction volume, V . This is the microscopic meaning of the Meyer-Neldel rule.

If V is the interaction volume (volume in which the particle can effectively couple to the excitations), then the total number of excitations with the total energy in excess of Δ is given by

$$n(\Delta) = \left[\frac{\sum_{\tilde{\Delta} \geq \Delta} e^{-\beta \tilde{\Delta}}}{\sum_{\tilde{\Delta}} e^{-\beta \tilde{\Delta}}} \right] V \quad (13)$$

at any time, by conservation of energy. If D_e is the diffusivity of the particle and $D_e > D_t$, where D_t is the thermal diffusion rate, then the transition rate is given by¹⁴

$$1/\tau_d = C[D_e/a^2](V/a^3)^{1/3}n(\Delta). \quad (14)$$

In Eq. (14) C is a constant of order unity, and a is an interatomic distance. Clearly $n(\Delta)$ depends on the total number of ways an energy in excess of Δ can be organized within an effective interaction volume.

For a stationary particle (localized state), as in the two hopping models discussed above, the rate of transition is determined by the local coupling to the thermal bath and the number of configurations which generate the threshold energy Δ . Therefore, for both cases, the transition rate is determined by the thermal factor $\exp(-\Delta/kT)$ multiplied by a term which measures the number of configurations (the entropy term).

An interesting exception might be provided by considering glassy systems when neither particle nor excitation can diffuse freely. If the diffusion of energy is hindered by local barriers (spin diffusion in spin glass), then only the available modes can be counted for the transition in question and this, of course, has to be taken into account when evaluating the transition rate.

In processes involving an activation volume, such as diffusion and dipole relaxation in polymers, the microscopic model will be very different. But the basic idea is the same: The generation of the activation volume is likely to be a multiphonon process. The larger this volume and the activation enthalpy are, the more pho-

nons will be required, and the more paths there will be to the final result. This is a microscopic justification for the proportionality among ΔV , ΔS , and ΔH .

We therefore propose that, except for glassy systems, as discussed above, the compensation law is to be expected as a consequence of assisted activation whenever large activation energies compared to typical excitations are involved. This should be a very general result.

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