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Thermally activated processes near a second-order phase transition of the reservoir*

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Where the degrees of freedom of particles in thermally activated motion are coupled to the order parameter associated with a phase transition of the bath, fluctuations in that parameter cause a modulation of the activation barrier, and hence an anomalous rate near T_C.

Various heterogeneously catalyzed reactions display anomalies in their rates as functions of the temperature near phase transitions of the catalysts. In some cases the slope of the Arrhenius plot (logarithm of rate vs reciprocal temperature) changes at a transition; in others the slope is not appreciably changed, but an enhancement or diminution of rate occurs in a fairly narrow temperature range around the transition.

We argue that a contributory factor to these anomalies is a coupling of the order parameter characterizing the transition to the degrees of freedom of the reacting atoms or ions. Inasmuch as most chemical reactions are thermally activated processes, it suffices to state the argument for the simple case of thermally activated motion of a massive particle over a potential barrier starting from an initial energy minimum (see Fig. 1). This particle is imagined coupled to the order parameter.

The rate of escape over the barrier (the reaction rate) may be found by solving a Fokker-Planck (FP) equation for the momentum (P) and position (R) dependent distribution function of an ensemble of such particles. This Fokker-Planck equation is essentially one dimensional, since for energetic reasons the particles move very close to the line of steepest ascent over the barrier [which is always a saddle point of the potential energy surface $V(R)$]. The result of such a calculation for the rate K is

$$K=\nu \exp(-\Delta V/k_B T) \tag{1}$$

(T is temperature and k_B Boltzmann's constant.) Here ΔV is the height of the barrier measured from the originating potential minimum. The prefactor ν is an "attempt" frequency which depends on some salient features of the "reaction path," and on the "friction constant" η occurring in the FP equation. The course of ν as a function η has been described by Kramers.[1] For small η it rises linearly, then saturates and remains constant for a range of η's, and for large η decreases again (as $1/\eta$). The η-independent range is referred to as the range of applicability of the so-called absolute rate theory (ART). In that range the effect of propulsion by the random forces (of which η is a measure) is in balance with their friction effect (of which η is also a measure).

The reasoning underlying the FP equation is based on the hypothesis of two time scales, a slow one, on which the position and speed of the massive particle changes, and a rapid one characteristic of the motion of the "bath" degrees of freedom. Stated crudely, the former motion involves the "average" force of the bath on the chemicals. The latter motion determines η, which for large mass is expressible in terms of an autocorrelation function of the force fluctuation about that average force. As shown in earlier publications,[2,3] η may be expressed in terms of electromagnetic response characteristics of the bath. This response becomes anomalous near a transition and thus causes an anomaly in the rate of the reaction wherever that rate depends on η, i.e., outside the range of applicability of ART.

However, near the transition some of the substrate degrees of freedom also vary slowly and must be treated on the same footing as the massive particle. In particular, the order parameter (or parameters) associated with the transition must be so treated, if, as will generally be the case, some of the effective coupling of the particle to the bath involves the order parameter. The appropriate Fokker-Planck equation then is for a joint distribution functional of the order parameter *and* the particle variables.

The free-energy functional F consistent with a given order-parameter field $\vec{\mathfrak{M}}(\vec{r})$ is defined as $e^{-\beta F}=\mathrm{Tr}_{b(\mathfrak{M})}e^{-\beta H}$, where H is the full Hamiltonian, $\beta=1/k_B T$, and the trace is over all bath variables consistent with $\vec{\mathfrak{M}}(\vec{r})$. (For definiteness we shall henceforth speak of a ferromagnetic transition, with $\vec{\mathfrak{M}}$ denoting magnetization density.) F has the form

$$F=F_s+F_c+F_{sc}\,, \tag{2}$$

where the substrate free energy F_s is

$$F_s=F_0+\int\left[\tfrac{1}{2}a\vec{\mathfrak{M}}^2+\tfrac{1}{4}b(\vec{\mathfrak{M}}^2)^2+\tfrac{1}{2}c(\nabla\vec{\mathfrak{M}})^2\right]dv$$

and that of the particle is

$$F_c=(1/2M)P^2+V(R)\,,$$

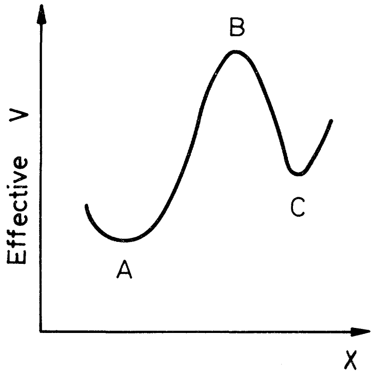

FIG. 1. Path for the reaction A to C.

where M is the effective mass and $V(R)$ the potential energy.

Near T_C, a varies like $T - T_C$. Finally, the lowest order significant terms in the coupling energy are, with $\vec{n}$ denoting a unit vector in a preferred direction (if any) occurring in the system (e.g., the normal to the surface of a solid in the case of a surface reaction),

$$F_{sc} = \sum_{\alpha\beta} A_{\alpha\beta}\mathfrak{M}^{\alpha}(R)\mathfrak{M}^{\beta}(R) + B\vec{\mathfrak{M}}(R)(\vec{\mathrm{P}}\times\vec{\mathrm{n}})$$

$$+D[\vec{\mathrm{P}}\cdot\nabla\times\vec{\mathfrak{M}}(\vec{\mathrm{R}})] \; . \tag{3}$$

The first term will arise, for example, from exchange coupling of the conduction electrons of a metal substrate to any residual free spin of the massive particle. The second will arise from spin orbit coupling of the particle in the field of force of the bath. The last term is a crude local approximation to the interaction of the adatoms with the magnetic field due to $\vec{\mathfrak{M}}$. (The simplest way to verify these statements is by considering a well defined local spin $\vec{\mathrm{S}}$ interacting with $\vec{\mathfrak{M}}$ through exchange. Since it has some susceptibility, $\vec{\mathrm{S}}$ becomes proportional to $\vec{\mathfrak{M}}$.)

We retain only the first (generally largest) term of (3). If the fluctuations in $\mathfrak{M}$ are slow compared with those of P and R, the observed reaction rate will obviously be equal to the time average of the instantaneous rate, or, equivalently, equal to $\nu e^{-\beta(\Delta V+\Delta F_{sc})}$, averaged over the fluctuations with a weight proportional to $e^{-\beta F_s}$. Here ΔF_{sc} is the increment in F_{sc} between saddle point and minimum. Fluctuations in the reaction path itself may be neglected. The reader not interested in the more general case may now proceed with the text following Eq. (8).

In the general case, we assume a simple exponential type regression for $\mathfrak{M}$:

$$\frac{\partial\vec{\mathfrak{M}}}{\partial t} = D\not{\nabla}_{\mathfrak{M}}F + \text{random force} \; , \tag{4}$$

where D is a constant and $\not{\nabla}_{\mathfrak{M}}$ is the functional gradient of F with components $\delta F/\delta\mathfrak{M}_x$, $\delta F/\delta\mathfrak{M}_y$, $\delta F/\delta\mathfrak{M}_z$. With this hypothesis, the Fokker-Planck equation becomes

$$\frac{\partial f}{\partial t} + \left(\frac{\vec{\mathrm{P}}}{M}\frac{\partial f}{\partial\vec{\mathrm{R}}} - \frac{\partial V'}{\partial\vec{\mathrm{R}}}\frac{\partial f}{\partial\vec{\mathrm{P}}}\right) = \frac{\partial}{\partial\vec{\mathrm{P}}}\,\eta\left(\vec{\mathrm{P}} + Mk_BT\frac{\partial}{\partial\vec{\mathrm{P}}}\right)f$$

$$+D\int dv\,\not{\nabla}_{\mathfrak{M}}\circ(\not{\nabla}_{\mathfrak{M}}F + k_BT\not{\nabla}_{\mathfrak{M}})f \; , \tag{5}$$

where

$$V' = V + F_{sc} \; ;$$

η is, as before, the friction coefficient arising from the rapid, nonthermodynamic fluctuations. Because the motion hugs the reaction path, Eq. (5) reduces to one-dimensional form along this path:

$$\frac{\partial f}{\partial t} + \frac{P}{M}\frac{\partial f}{\partial X} - \frac{\partial V'}{\partial X}\frac{\partial f}{\partial P} = \eta\frac{\partial}{\partial P}\left(P + Mk_BT\frac{\partial}{\partial P}\right)f$$

$$+D\int dv\,\not{\nabla}_{\mathfrak{M}}\cdot(\not{\nabla}_{\mathfrak{M}}F + k_BT\not{\nabla}_{\mathfrak{M}})f \; , \tag{6}$$

where M is an effective mass, P an effective momentum, and X the position along the reaction path. To test the internal consistency of this formalism, the case in which $\mathfrak{M}$ is rapidly varying (D large) is examined in Appendix A. Here we examine only the case of slowly varying $\mathfrak{M}$.

In the ART range the rate does not materially depend on η, which may thus be equated to zero (as a mathematical device only). Let us further suppose that the fluctuations in $\mathfrak{M}$ are even slower than those in $\vec{\mathrm{R}}$ and $\vec{\mathrm{P}}$. Then D may be equated to zero also. We seek a solution of Eq. (6) with $\eta = D = 0$, which satisfies $f \sim e^{-\beta F}$ well to the left of the barrier, and $f = 0$ well to the right of it.

That solution has the form

$$f = C\theta\{P - [2M(V'_{\max} - V)]^{1/2}\}$$

$$\times\exp[-(P^2/2M + V' - V'_{\max} + F_s)/k_BT] \; , \tag{7}$$

where θ is the step function, and $(X^2)^{1/2}$ means X. [(7) satisfies (6) because $X\delta(X) = 0$.] $V'_{\max}$ is the height of the saddle point of $V' = V + F_{sc}$. We find C by assigning a fixed current to this solution, and then calculate the total number of particles n in the originating well (A in Fig. 1). The rate is then $K = j/n$.

The current may be evaluated at $V' = V'_{\max}$, and the result is

$$C = \beta j\Big/\int\exp(-\beta F_s/k_BT)\,\delta M \; .$$

(Here $\int\delta M$ denotes functional integration.) Near A, f is nearly equal to

$$C \exp -\beta [P^2/2M + V_{\min} - V_{\max} + \tfrac{1}{2} M \omega_A^2 (X - X_A)^2 + F_{sc}(X) - F_{sc}(0) + F_s] ,$$

where $X = 0$ has been chosen as the coordinate of the top of the barrier, and ω_A is the natural frequency around $V_{\min}$. The rate is thus

$$K = (1/\beta) \int dX \, dP \langle \exp -[F_{sc}(X) - F_{sc}(0)] \rangle \times \exp -\{[P^2/2M + \tfrac{1}{2} M \omega_A^2 (X_A)^2 / k_B T\} \times \exp -[(V_{\max} - V_{\min})/k_B T], \quad (8)$$

where $\langle \cdots \rangle$ denotes the functional average of the argument, with $e^{-\beta F_s} / \int e^{-\beta F_s} \delta M$ as weight factor. The average in (8) may be written as a cumulant average (denoted by subscript c):

$$\langle e^{-\beta G(M)} \rangle = \exp(\langle e^{-\beta G(M)} \rangle_c - 1) .$$

Thus the rate has the Eyring ART form:

$$K = (\omega_A'/2\pi) \, e^{-\Delta V / k_B T} ,$$

with

$$\Delta V = V_{\max} - V_{\min} + k_B T \times \{\langle \exp -[F_{sc}(X_A) - F_{sc}(0)]/k_B T \rangle_c - 1\}$$

and

$$\omega_A'^2 = \omega_A^2 + k_B T \, (d^2 \langle \ldots \rangle_c / d X_A^2)/M .$$

Keeping only the lowest-order cumulant average has the effect of replacing $V(X)$ by $V(X) + \langle F_{sc}(X) \rangle$, as one would expect.

To assess these results for $T > T_c$, we go into Fourier representation

$$\vec{\mathfrak{M}}(\vec{r}) = (2\pi)^{-3/2} \int \vec{m}(\vec{q}) \sin q^z Z \, e^{i \vec{q}^t \cdot \vec{r}^t} d\vec{q} ,$$

and assume $\vec{\mathfrak{M}}$ to vanish for $z > 0$. For simplicity we take all three components of A to be equal and consider desorption of a particle from a surface. Also, we omit the quartic terms in F_s and thus cannot expect to obtain the precise values of the indices in the critical behavior near T_C. More accurate approximations are possible, but of no concern in this preliminary assessment. Then

$$\langle F_{sc} \rangle = \frac{k_B T A}{4\pi^3} \int \frac{\sin^2 q^z R^z(X)}{c q^2 + a} d\vec{q} .$$

The integral formally diverges, but this is due to the neglect of terms such as $(\nabla^2 M)^2$, etc., in F_s, which are equivalent to an upper cutoff $q_{\max}$ to the q integration. The integral thus consists of an a-independent part

$$\frac{k_B T A}{2\pi^2} \frac{1}{c} \int_0^{q_{\max}} [1 - (\sin 2 q R^z)/2 q R^z] q^2 \, dq ,$$

which may be interpreted as contributing a constant activation entropy (the coefficient of T) and a more interesting a-dependent part which is

$$\langle F_{sc}(X) \rangle_a = k_B T \, (A/4\pi c) \sqrt{a/c} \, (1 - \{1 - \exp[-2R^z(X)\sqrt{a/c}]\}/2R^z(X)\sqrt{a/c})]\} ,$$

which tends to zero like a, i.e., like $T - T_C$ as $T \rightarrow T_C$. The effective barrier height will be changed as the result of the fluctuations by an amount (see Fig. 1)

$$\langle F_{sc}(X_B) \rangle_a - \langle F_{sc}(X_A) \rangle_a = k_B T (A/8\pi c) \{[1 - \exp(-2R_A^z \sqrt{a/c})]/R_A^z - [1 - \exp(-2R_B^z \sqrt{a/c})]/R_B^z\} ,$$

which likewise goes to zero like a as $T \rightarrow T_C$. Substitution into (1) shows that if this effect is interpreted as a change of prefactor with temperature, we have an anomaly of amount

$$\Delta \nu = |\nu_{T=\infty} - \nu_{TC}| / \nu_{\max}(\infty, T_C) = 1 - \exp - |A(1/R_A^z - 1/R_B^z)/8\pi c| .$$

For a $J \vec{S} \cdot \vec{s}$ model of the adatom, A is of order $-(J^2/\text{bandwidth}) \times (\text{atomic volume})$. Taking c to be of order $k_B T_C \times (\text{lattice spacing})^2$ and $1/R_A - 1/R_B$ of order of a reciprocal-lattice spacing, then with $T_C \sim 1000$ °K, $J \sim 0.4$ eV, the bandwidth approximately 3 eV we find that $\Delta\nu$ is about 5%. Substantially larger anomalies are sometimes observed.[4] (A brief resume of the experiment in Ref. 4 is given in Appendix II.) This may be due to less smoothing of the fluctuations near the surface (for example, as the result of c having a reduced value there).

When $T < T_C$, the same analysis may be repeated, but with $\mathfrak{M}$ expanded around the appropriate mean value.

Anomalies of the kind described here should be observable also in the diffusion rate of atoms through solids near phase transitions; also in the interactions between adatoms or impurities. (The formalism is trivially generalized to many heavy particles.)

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APPENDIX A

In the usual derivation of the Fokker-Planck equation for Brownian particles, the friction coefficient arises from the coupling to those degrees of freedom of the bath that vary rapidly on the scale of motion of the particles. In the case of large D, the magnetization field can be regarded as such a set of degrees of freedom. Hence in the limit of large D one should recover the FP equation for the adparticle alone, with the friction coefficient determined by coupling to the magnetization field (assuming any other source of friction to be absent). Thus for large D the solution of the functional equation (5) should have the form of a product of the solution of that new FP equation, multiplied by the equilibrium distribution of the magnetization field. (Such a result is somewhat analogous to the approximate solution of the usual FP equation for large friction, which reduces to a product of a solution of the Smoluchowski equation and the Maxwell velocity distribution.) It is desirable to perform such a check, since essentially the same formalism should apply in the case of coupling to other fields: For example, the strain field and the electromagnetic field in the case of physisorption. To make our point we shall neglect other sources of friction on the adparticle ($\eta = 0$). Writing

$$F_1 = F_s + F_{sc}$$

and

$$f = \tilde{f} e^{-\beta F_1/2} ,$$

we obtain from (6)

$$\frac{\partial f^2}{\partial t} + \frac{\vec{\mathrm{P}}}{M}\frac{\partial \tilde{f}}{\partial \vec{\mathrm{R}}} - \frac{\partial V}{\partial \vec{\mathrm{R}}}\frac{\partial \tilde{f}}{\partial \vec{\mathrm{P}}} - \frac{\beta}{2}\frac{\vec{\mathrm{P}}}{M}\frac{\partial F_1}{\partial \vec{\mathrm{R}}}\tilde{f} - \frac{\partial F_1}{\partial \vec{\mathrm{R}}}\frac{\partial \tilde{f}}{\partial \vec{\mathrm{P}}} = D\int dv\,[\vec{\nabla}^2_{\mathfrak{M}} + \tfrac{1}{2}\beta\vec{\nabla}^2_{\mathfrak{M}}F_1 - \tfrac{1}{4}\beta^2(\vec{\nabla}_{\mathfrak{M}}F_1)^2]\tilde{f} \ . \tag{A1}$$

For simplicity, let A be diagonal: $A_{\alpha\beta} = \delta_{\alpha\beta}A_\alpha$. Then up to terms bilinear in $\mathfrak{M}$ we have:

$$F_1 = \int \left(a\vec{\mathfrak{M}}^2(r) + \tfrac{1}{2}c[\nabla\vec{\mathfrak{M}}(r)]^2 + \sum_\alpha A_\alpha \mathfrak{M}^2_\alpha(r)\delta(\vec{\mathrm{r}} - \vec{\mathrm{R}})\right) dv \ .$$

This may be rewritten in terms of "normal modes," which we chose to be real: If $\{\varphi_{q\alpha}(r, R)\}$ is the orthonormal set that satisfies

$$-c\nabla^2_r\varphi_{q\alpha}(\vec{\mathrm{r}}, \vec{\mathrm{R}}) + a\varphi_{q\alpha}(\vec{\mathrm{r}}, \vec{\mathrm{R}}) + A_\alpha\varphi_{q\alpha}(\vec{\mathrm{R}}, \vec{\mathrm{R}})\delta(\vec{\mathrm{r}} - \vec{\mathrm{R}}) = \omega_{q\alpha}(\vec{\mathrm{R}})\varphi_{q\alpha}(\vec{\mathrm{r}}, \vec{\mathrm{R}}) \ , \tag{A2}$$

then

$$F_1 = \frac{1}{2}\sum_q \omega_{q\alpha} m^2_{q\alpha} \ ,$$

where

$$m_{q\alpha} = \Omega^{-1/2}\int \mathfrak{M}_\alpha(r)\varphi_{q\alpha}(r, R)\, dv \ , \tag{A3a}$$

$$\mathfrak{M}_\alpha(r) = \Omega^{-1/2}\sum_q m_{q\alpha}\varphi_{q\alpha}(r, R) \ . \tag{A3b}$$

The normalization is $\int \varphi_{q\alpha}\varphi_{q'\alpha}\, dv = \Omega\delta_{qq'}$ and Ω denotes the sample volume. Henceforth we incorporate the α index in q. Writing

$$\mu_q = m_q(\tfrac{1}{2}\beta\omega_q)^{1/2} \tag{A4}$$

and substituting (A4) and (A3b) into (A1) converts that equation into:

$$\frac{\partial \tilde{f}}{\partial t} + \frac{\vec{\mathrm{P}}}{M}\frac{\partial \tilde{f}}{\partial \vec{\mathrm{R}}} - \frac{\partial V}{\partial \vec{R}}\frac{\partial \tilde{f}}{\partial \vec{\mathrm{P}}} - \sum \mu^2_q \frac{\partial \nu_q}{\partial \vec{\mathrm{R}}}\left(\frac{\vec{\mathrm{P}}}{2\vec{\mathrm{M}}}f^2 - \frac{1}{\beta}\frac{\partial \tilde{f}}{\partial \vec{\mathrm{P}}}\right) = D\frac{\beta}{2}\sum_q\left(\frac{\partial^2 f^2}{\partial \mu^2_q} + (1 - \mu^2_q)\tilde{f}\right) , \tag{A5}$$

where $\nu_q = \ln(\omega_q)$.

The eigenvalues and eigenfunctions of the term in paranthesis on the right-hand side of (A.5) are $-2n_q$ and

$$\Psi(n_q) = (\pi^{1/2}2^{n_q}n_q!)^{-1/2}H_{n_q}(\mu_q)\exp(-\tfrac{1}{2}\mu^2_q),$$

where the n_q are positive integers or zero, and the H_{n_q} are Hermite polynomials. In deriving (A.5) we have used the fact that because of the orthonormality of the φ, (A3a) and (A3b) give $\partial m_q/\partial\vec{\mathrm{R}} = 0$, whereas from (A4) $\partial\mu_q/\partial\vec{\mathrm{R}} = \frac{1}{2}\mu_q\,\partial\nu_q/\partial R$.

Noting that the left-hand side of (A5) links only Ψ states whose n_q's differ by ± 2, we attempt a solution

$$\tilde{f} = \tilde{f}_0(\vec{\mathrm{R}}, \vec{\mathrm{P}}, t)\,\Psi(0) + \sum_q \tilde{f}_q(R, P, t)\,\Psi(2_q) \ , \tag{A6}$$

in an obvious rotation. The second term on the right is expected to be of order $1/D$. Terms with four, six, etc. quanta have been dropped as they will be of order $1/D^2$, $1/D^3$, etc. $\Psi(0)$ [or, more precisely $\Psi(0)\,e^{-\beta F_1/2}$] corresponds to thermal equilibrium of the field for a given fixed position of the adparticle. Substituting (A6) in (A5), using (A4), dropping terms with four or more quanta, and equating coefficients of $\Psi(0)$ and $\Psi(2_q)$, we find

$$\frac{\partial \tilde{f}_0}{\partial t}+\frac{\vec{P}}{M}\frac{\partial \tilde{f}_0}{\partial \vec{R}}-\frac{\partial V}{\partial \vec{R}}\frac{\partial \tilde{f}_0}{\partial \vec{P}}-\sum_q \frac{\partial \nu_q}{\partial \vec{R}}\frac{\partial f_q}{\partial \vec{P}}\Big/\sqrt{2}\,\beta-\frac{1}{2}\sum_q \frac{\partial \nu_q}{\partial \vec{R}}\left(\frac{\vec{P}}{M}\tilde{f}_0+\beta^{-1}\frac{\partial \tilde{f}_0}{\partial \vec{P}}\right)=0$$

$$\frac{\partial \tilde{f}_q}{\partial t}+\frac{\vec{P}}{M}\frac{\partial \tilde{f}_q}{\partial \vec{R}}-\frac{\partial V}{\partial \vec{R}}\frac{\partial \tilde{f}_q}{\partial \vec{P}}-\frac{\partial \nu_q}{\partial \vec{R}}\left(\frac{\vec{P}}{M}\tilde{f}_0+\beta^{-1}\frac{\partial f_0}{\partial \vec{P}}\right)-\frac{5}{2}\frac{\partial \nu_q}{\partial R}\left(\frac{\vec{P}}{M}f_q+\beta^{-1}\frac{\partial f_q}{\partial \vec{P}}\right)+\frac{\vec{P}}{M}\frac{\partial \nu_q}{\partial \vec{R}}\tilde{f}_q=-2D\omega_q\tilde{f}_q$$

To order D^{-1} the solution of the latter equation is

$$\tilde{f}_q=(2\sqrt{2}D\omega_q)^{-1}\frac{\partial \nu_q}{\partial \vec{R}}\left(\frac{\vec{P}}{M}f_0+\beta^{-1}\frac{\partial \tilde{f}_0}{\partial \vec{P}}\right)\ .$$

Substituting this in the former equation and setting

$$f_0=f_0\exp\frac{1}{2}\sum \nu_q$$

gives

$$\frac{\partial f_0}{\partial t}+\frac{\vec{P}}{M}\frac{\partial f_0}{\partial \vec{R}}-\frac{\partial V'}{\partial \vec{R}}\frac{\partial f_0}{\partial \vec{P}}=\sum_{\alpha\beta}\eta_{\alpha\beta}\frac{\partial}{\partial P_\alpha}\left(P_\beta f_0+M\beta^{-1}\frac{\partial f_0}{\partial P_\beta}\right), \tag{A7}$$

where

$$\eta_{\alpha\beta}=(4\beta DM)^{-1}\sum_q \frac{\partial \nu_q}{\partial R_\alpha}\frac{\partial \nu_q}{\partial R_\beta}$$

is the effective friction coefficient and

$$V'=V+(2\beta)^{-1}\sum_q \nu_q$$

is the effective potential.

(A7) has indeed the form of the FP equation. It is interesting to note that $2^{-1}\sum_q \nu_q$ is the position-dependent part of the entropy associated with the field fluctuations [as is checked from the relation: entropy $= k(\ln Z - T\partial \ln Z/\partial T)$ where $Z=\int \Pi_q e^{-\beta F_1}$]. Thus in solving (A1) for a reaction one finds that the activation energy ΔV will be replaced by the activation *free* energy $\Delta V'$ as required by general reaction kinetics. Note that these results apply for all coupling strengths.

APPENDIX B

In the experiments on initial oxidation rate of iron in Ref. 4, the investigators plotted that rate over the first two minutes of exposure of the pure sample by recording the change of weight. From about fifty-five seconds onwards, they found the rate to be diffusion limited. That is to say, the rate of change of weight varies as $(\text{time})^{-1/2}$ at long times. Presumably, the bottleneck of the reaction is then diffusion of oxygen through the growing oxide layer. Up to about forty seconds, a marked deviation from diffusive behavior is observed. The rate in that range declines experimentally with time, and the oxidation reaction at the oxide-metal interface should then be the rate-limiting step. Extrapolation to zero time of the logarithmic rate curve then gives the oxidation rate. The first measurements became possible after twenty seconds of exposure, and so the extrapolation to zero time had to be based on the data between twenty and forty seconds. However, barring any changes of mechanism between zero and twenty seconds, the investigators claim a reproducibility of ±5%.

An Arrhenius plot of their data (log rate versus reciprocal temperature) shows a pronounced cusp at 755 °C, the Curie temperature of pure iron, and a smooth behavior on either side of the cusp. Also, the activation energies above and below the Curie point were found to differ substantially, by about $\frac{1}{2}$ eV, on the basis of a plot of log (rate/temperature) versus reciprocal temperature, thus assuming applicability of absolute rate theory to the reaction. The theory given in the present paper will indeed yield such a change in slope, obtainable by replacing $\mathfrak{M}$ by its average value in the expression for F_{sc}. Evidently $F_{sc}(\langle\mathfrak{M}\rangle)=0$ above the Curie point and finite below. The exchange mechanism discussed at the end of the main text will only give about one tenth of the observed change in activation energy. It is possible that the mechanism discussed by Measor and Afzulpurkar (change of density of states at the Fermi level upon spontaneous magnetic polarization below T_C) is responsible for the observations. Such a mechanism, at the phenomenological level, can likewise be described by the present theory, with a possibly much larger value of A. This would explain both the large anomaly near the transition, and the large difference in activation energies.

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[1] H. A. Kramers, Physica 7, 284 (1940).

[2] E. G. d'Agliano, W. L. Schaich, P. Kumar, and H. Suhl, in *Nobel Symposium* 24, *Medicine and Natural Sciences*, *Collective Properties of Physical Systems*, edited by B. Lundqvist and S. Lundqvist (Academic, New York, 1973), pp. 200–208.

[3] E. G. d'Agliano, P. Kumar, W. Schaich, and H. Suhl (unpublished).

[4] M. R. Shanabarger (private communication) has observed a large prefactor anomaly in the desorption rate of hydrogen from a nickel film near T_C. Measor and Afzulpurkar [Philos. Mag. 10, 817 (1964)] observed a large anomaly of the initial oxidation rate of iron at T_C.