Critical Magnetic Field Dependence of Thermally Activated Surface Processes

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Activated processes at surfaces such as desorption or sublimation may exhibit a thermal anomaly at the Curie point of a magnetic substrate. We propose to measure this anomaly with an applied magnetic field H, and we predict a decrease in the reaction rate proportional to H^x with $x(T>T_c)=2$, $x(T<T_c)=1$, and $x(T=T_c)=2/\delta_1$, where $\delta_1 \cong 1.9$ is an exponent for ordinary phase transitions. In the case of a surface transition, or if the substrate is a film with two-dimensional Ising behavior, the anomaly is significantly enhanced.

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In this Letter we examine the behavior of thermally activated surface processes in an applied magnetic field. In the vicinity of a continuous magnetic phase transition these processes may exhibit anomalies in their reaction rate, $r(T)$, known as the Hedvall effect.[1,2] The experimentally observed deviation from the Arrhenius law

$$r(T)=k\exp(-Q/k_BT) \tag{1}$$

depends not only on the type of the process—desorption,[3] sublimation,[4] oxidation,[5,6] or catalytic reaction[7]— but also on the specific substrate-adsorbate combination and on features such as oxide-layer thickness[6] or on details of the surface preparation.[8]

This variety complicates the theoretical understanding of the Hedvall effect considerably. An important contribution was made by Suhl and co-workers some years ago.[9,10] Combining the Kramers approach[11] to activated processes with linear-response theory, these authors expressed the activation energy Q and the attempt frequency k in Eq. (1) in terms of those static and dynamic degrees of freedom in the substrate which are coupled to the spin of the adsorbed particles. This coupling leads to a temperature dependence in $k(T)$ and $Q(T)$ which reflects the critical behavior of the substrate and thus causes deviations from a straight line in the Arrhenius plot $\ln(r)$ vs $(1/T)$ near T_c.

It has recently been shown[12] that the anomaly in k, as well as in Q, is significantly weaker than predicted in earlier work for two reasons. (1) The relevant critical behavior of the substrate is that of its surface.[13] In the case of the so-called ordinary transitions where the surface orders simultaneously with the bulk, the critical near-surface effects are weaker than those in the bulk. Only the bulk behavior was taken into account in Ref. 14. (2) The critical slowing down in the substrate invalidates a naive use of the Kramers approach since a clear-cut separation in the time scales is no longer possible. Memory effects lead to a renormalized attempt frequency k which involves a dynamic correlation function at nonzero frequencies. Its anomaly turns out to be reduced compared to that of the zero-frequency limit employed in previous work.[14,15]

Such a weak anomaly appears to be in qualitative agreement with experiments.[3-8] However, the uncertainties in the available data inhibit a quantitative comparison with the theory. Furthermore, these measurements of the rate, with temperature as the only control parameter, do not provide enough information to allow for stringent tests of crucial model assumptions. Therefore, we suggest Hedvall experiments be performed with an applied magnetic field H. This field is an additional parameter which can be varied reversibly in a controlled fashion during a measurement on a particular sample. We predict a decrease in the rate with increasing field as

$$r(T,0)-r(T,H)\sim\begin{cases} H^2, & \text{for } T>T_c, \\ H^{2/\delta_1}, & \text{for } T=T_c, \\ H, & \text{for } T<T_c. \end{cases} \tag{2}$$

In (2), δ_1 denotes a surface exponent characterizing the magnetic field dependence of the surface magnetization $m_1 \sim H^{1/\delta_1}$. For ordinary transitions,[16] $\delta_1 \cong 1.9$. The arguments leading to this result are as follows.

Let us consider a desorption process occurring along the coordinate z perpendicular to the surface $z=0$ in a potential $V(z)$ (see inset in Fig. 1). The substrate fills the half-space $\{\mathbf{R}=(\mathbf{r},z\geqq 0)\}$. Initially, the adparticle is bound in a metastable adsorption well at $z_A<0$. Desorption takes place if the adparticle is thermally excited to cross the desorption barrier at $z_B(<z_A<0)$ from where it escapes to infinity. The energy $\mathcal{H}$ of the adparticle's spin $\mathbf{S}$ is given by the Zeeman term $\mathcal{H}^z=-g\mu_B\mathbf{H}\cdot\mathbf{S}$ and the interaction[12,14,15] $\mathcal{H}^{\text{int}}$ with the local magnetic order parameter of the substrate, which is taken as a scalar field $s(\mathbf{R})$,

$$\mathcal{H}^{\text{int}}=-\mathbf{S}\cdot\mathbf{l}\int d\mathbf{R}'J(\mathbf{R}-\mathbf{R}')s(\mathbf{R}'). \tag{3}$$

Here, $\mathbf{l}$ denotes the direction of the easy axis of the Ising-type substrate. $\mathcal{H}^{\text{int}}$ depends on the position $\mathbf{R}_0=(0,z)$ of the adparticle. The thermal average over the substrate field $s(R)$ yields the magnetic contribution to

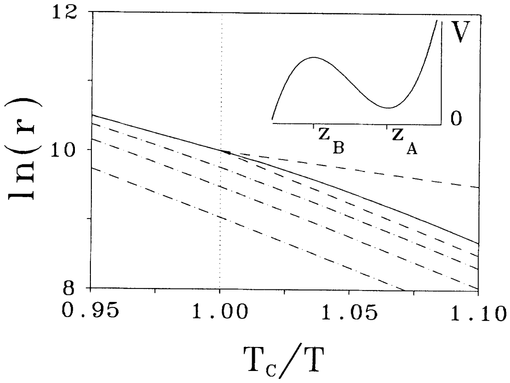

FIG. 1. Arrhenius plot of the rate (9). (——) $h=0$; (-·-·-) $h=0.01$, 0.02, 0.04; (---) the two branches before averaging. $q_0^- = 5$, $Q_0 = g\mu_B |\mathbf{H}_0 \cdot \mathbf{S}| = 10 k_B T_c$ and $a=2$. Inset: Kramers potential $V(z)$ for the adparticle.

the potential for the adparticle

$$V_\sigma^{\text{int}}(z) = \sigma \bar{V}(z) = \sigma \bar{V}(z) = \sigma |\mathbf{S}\cdot\mathbf{l}| \int_0^\infty dz' J_0(z-z') \langle s(z') \rangle , \quad (4)$$

where $\sigma = -\text{sgn}(\mathbf{S}\cdot\mathbf{l})$. We also assume the ferromagnetic exchange coupling $0 \leqq J_0(z-z') = \int d\mathbf{r}' J(\mathbf{R}_0 - \mathbf{R}')$ to be of short range, z_0. The spin-density profile $\langle s(z)\rangle$ varies on the scale of the bulk correlation length $\xi = \xi_0 |\tau|^{-\nu}$, with $\xi_0 = 0(1\text{ Å})$, $\tau = (T-T_c)/T_c$, and the bulk exponent $\nu = 0.6$. The critical behavior of $\langle s(z)\rangle$ is embodied in a scaling form[13,17] which specializes to

$$\langle s(z)\rangle = |\tau|^{\beta_1} (z/\xi_0)^{(\beta_1-\beta)/\nu} g(|h|/|\tau|^\Delta) , \quad (5)$$

when $z \ll \xi$. Here, $\beta_1 \cong 0.8$ and $\beta \cong 0.3$ are the exponents of the surface and bulk magnetization, whereas $\Delta = \beta_1 \delta_1 \cong 1.6$ is known to be the bulk gap exponent.[13] h denotes the reduced magnetic field $h = H/H_0$ with $H_0 = k_B T_c / g\mu_B S$, where g is the g factor of the substrate spins s. Equation (5) yields a scaling expression for the magnetic contribution to the activation energy,

$$Q_\sigma = V_\sigma^{\text{int}}(z_B) - V_\sigma^{\text{int}}(z_A) = -\sigma \bar{Q}(\tau,h) = -\sigma k_B T_c |\tau|^{\beta_1} q^{\pm}(|h|/|\tau|^\Delta) . \quad (6)$$

In the critical regime, the shape functions $q^{\pm}(x)$ behave asymptotically as

$$q^{\pm}(x) \sim q_\infty x^{1/\delta_1}, \quad \text{for } x \gg 1 ,$$
$$q^{+}(x) \sim q_0^{+} x , \quad \tau > 0, \qquad \text{for } x \ll 1 . \quad (7)$$
$$q^{-}(x) \sim q_0^{-} , \quad \tau < 0 ,$$

With the coupling (3), the attempt frequency k is determined by the dynamical autocorrelation function of the normal derivatives of the surface spin density[12] and is independent of the orientation σ. In the adsorption well, σ will be distributed according to

$$P_\sigma = \frac{\exp\{-\sigma[\bar{V}(z_A) + |\mathbf{H}\cdot\mathbf{S}|]/k_B T\}}{2\cosh\{[\bar{V}(z_A) + |\mathbf{H}\cdot\mathbf{S}|]/k_B T\}]} , \quad (8)$$

with $\mathbf{H}$ taken to be parallel to $\mathbf{l}$. The observable rate is the average over the two branches r_σ,

$$r = \sum_{\sigma=\pm 1} P_\sigma r_\sigma = k e^{-Q_0/k_B T} \frac{\cosh\{[(a-1)\bar{Q} + |\mathbf{H}\cdot\mathbf{S}|]/k_B T\}}{\cosh[(a\bar{Q} + |\mathbf{H}\cdot\mathbf{S}|)/k_B T]} . \quad (9)$$

This is our main result. Q_0 denotes the activation energy in the absence of the magnetic interaction; a is defined by

$$a = \bar{V}(z_A)/\bar{Q} = \bar{V}(z_A)/[\bar{V}(z_A) - \bar{V}(z_B)] .$$

The critical anomaly in the rate r arises from Q as given in equations (6) and (7) and from $k(\tau,h)$. The asymptotic form of $k(\tau,0)$ for $|\tau| \to 0$ is known[12] to be

$$k(\tau,0) \cong k(0,0)(1 + c_1\tau - c_2|\tau|^{2-\alpha}) , \quad (10)$$

with the bulk specific-heat exponent $\alpha \cong 0.1$. The magnetic field dependence at T_c for $|h| \to 0$ is given by[18]

$$k(0,h) \cong k(0,0)(1 - c_3|h|^{(2-\alpha)/\beta_1\delta_1}) , \quad (11)$$

with $(2-\alpha)/\beta_1\delta_1 \cong 1.2$.

Consequently, we obtain the following asymptotics for the rate $r(T,H)$:

(1) $H=0$, $\tau \to 0$:

$$r \cong k(0,0) e^{-Q_0/k_B T} \times \begin{cases} (1 + c_1\tau - c_2|\tau|^{2-\alpha}) , & \tau \geqq 0 \\ [1 + c_1\tau - (a-\tfrac{1}{2})(q_0^-)^2 |\tau|^{2\beta_1}] , & \tau < 0 . \end{cases} \quad (12)$$

Note that the averaging over σ causes a significant reduction of the singularity in r, which behaves as $|\tau|^{\beta_1}$ for $\tau < 0$ for each branch r_σ separately.[12]

(2) $\tau = 0$, $H \to 0$:

$$r \cong k(0,0) e^{-Q_0/k_B T_c} [1 - (a - \tfrac{1}{2}) q_\infty^2 |h|^{2/\delta_1} - c_3 |h|^{(2-\alpha)/\beta_1\delta_1}] . \quad (13)$$

(3) For $T \neq T_c$, the H dependence is given by Eq. (2). The general analytic form of the scaling function for the

profile $\langle s(z)\rangle$ is not known explicitly for $T\neq T_c$ and $H\neq 0$. In order to get an idea about the global features of the rate $r(T,H)$ in the critical regime we adopted the mean-field expression[13] for m_1 to compute the curves shown in Fig. 1. The mean-field surface exponents are $\beta_1=1$ and $\delta_1=\frac{3}{2}$. Furthermore, since the dominant contribution to the Hedvall anomaly arises from statics, we neglected dynamic effects by replacing $k(\tau,h)$ with $k(0,0)$.

The above results were derived for the ordinary transition, which are expected to be the rule. However, the theory applies equally well to the so-called surface transition,[19] where the top layers of the substrate order at higher transition temperature than the bulk. The only difference is in the values of the surface exponents, which are those of the two-dimensional Ising model. Hence, $\beta_1^{\rm surf}=\frac{1}{8}$ and $\delta_1^{\rm surf}=15$. The singularities in the rate are now considerably stronger: $r(0,0)-r(\tau,0)\sim|\tau|^{1/4}$ for $\tau<0$ and $r(0,0)-r(0,h)\sim|h|^{2/15}$. This enhancement of the signal is enforced if one uses a thin-film substrate, which exhibits a two-dimensional magnetic Ising transition.

In conclusion, we pointed out that an experimental study of thermally activated rate process in a magnetic field provides new insight into the Hedvall effect and, in particular, the interaction mechanisms which govern the rate of these ubiquitous processes. Furthermore, with some optimism, one may contemplate employing the magnetic Hedvall effect to measure critical surface exponents such as δ_1, which are difficult to access by conventional surface techniques.

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