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Physisorption Kinetics from Mean-Field Theory: Compensation Effect near Monolayer Coverage

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Based on a set of nonlinear rate equations with phonon-mediated transition rates calculated from mean field theory, the coverage-dependent isothermal desorption time for ³He on graphite up to a coverage of 1.5 adlayers is determined. Prefactors in the Arrhenius parametrization drop by 2 orders of magnitude as the heat of adsorption decreases for increasing coverage, establishing a compensation effect in physisorption kinetics.

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A gas is said to physisorb onto the surface of a solid if the net interaction between a gas particle and the solid is accounted for by an effective surface potential $V_s(\vec{r})$ which for an inert gas is well approximated by a sum $V_s(\vec{r}) = \sum_i V(\vec{r} - \vec{r}_i)$ where $V(\vec{r} - \vec{r}_i)$ is the two-body potential between a gas particle at \vec{r} and a constituent particle of the solid at lattice site \vec{r}_i .¹ Particles trapped into the bound states of $V_s(\vec{r})$ form the adsorbate. At very low (submonolayer) coverages θ , we may neglect the interactions between the adparticles. However, as θ approaches unity and the average separation of gas particles in the adsorbate approaches that of a liquid, their mutual interaction potential plays a crucial role in ensuring saturation in a (mobile) fluid adsorbate or causing crystallization in the adsorbed film. We have recently developed a mean-field theory^{2,3} to describe an adsorbate of nonzero coverage in equilibrium with the gas phase. Such a theory is

eminently suited to study the adsorption and desorption kinetics in such systems, a task that two-dimensional theories,⁴ in which the adsorbate is totally decoupled from the gas phase, have difficulty in tackling. For the study of adsorption kinetics it is important, for example, to know what changing environment additional particles arriving from the gas phase will experience as the coverage on the surface builds up. In a single-particle picture this necessitates the construction of an effective coverage-dependent surface potential given by $V_s(\vec{r}, \theta) = V_s(\vec{r}) + V_{mf}(\vec{r}, \theta)$, where $V_s(\vec{r})$ is the interaction of a single gas particle with the solid, referred to from now on as the bare surface potential. $V_{mf}(\vec{r}, \theta)$ is the potential arising from the mean field experienced by a gas particle in the presence of all other gas particles already in the surface region at a given coverage θ . It can be calculated as a Slater average from the self-consistent solutions of the temperature-dependent Hartree-Fock equations

$$\begin{aligned} & [-(\hbar^2/2m)d^2/d\vec{r}^2 + V_s(\vec{r}) - E_{\vec{r}}] \psi_{\vec{r}}(\vec{r}) + \sum_{\vec{r}'} n_{\vec{r}'} \int dr' V_{eff}(|\vec{r} - \vec{r}'|) \psi_{\vec{r}'}^*(\vec{r}') \\ & \times [(2s+1)\psi_{\vec{r}}(\vec{r}')\psi_{\vec{r}}(\vec{r}) \mp \psi_{\vec{r}}(\vec{r}')\psi_{\vec{r}}(\vec{r}')] = 0, \end{aligned} \quad (1)$$

where $n_{\vec{r}}$ is the occupation function of the \vec{r} th state; s is the spin of the adsorbing gas particle, obeying Fermi-Dirac (minus sign) or Bose-Einstein (plus sign) statistics. V_{eff} is the effective two-body interaction between gas particles whose short-range repulsion is suitably softened which, for gas particles obeying Fermi-Dirac statistics, can be done by employing Brueckner theory in the local density approximation.^{2,3} For mobile

adsorbates the bare surface potential can be approximated by a function of the distance z from the surface only, i.e., $V_s(\vec{r}) \equiv V_s(z)$, so that an Ansatz $\psi_{\vec{r}}(\vec{r}) = \varphi_{\vec{r}}(z) \exp[i\vec{q} \cdot \vec{\rho}]$ is justified [$\vec{r} = (\vec{\rho}, z)$; \vec{q} is the particle momentum in the surface plane] reducing (1) *cum grano salis* to a one-dimensional theory for the wave functions $\varphi_{\vec{r}}(z)$ and the energies $\epsilon_i = E_{\vec{r}} - \hbar^2 q^2/2m$ and re-

sulting in a one-dimensional effective coverage-dependent surface potential $V_s(z, \theta)$. For details we refer the reader to Refs. 2 and 3. To illustrate the main results for the ^3He -graphite system, relevant to the following discussion of physisorption kinetics, we turn to Fig. 1. The upper panel gives the bare surface potential $V_s(z)$ at zero coverage constructed by averaging the ^3He -C two-body Lennard-Jones interaction laterally along the graphite surface and summing over the lattice planes.¹ Indicated are the four bound-state energies; also given are the (squared) wave functions of the lowest two bound states. As the coverage builds up to a monolayer (center panel in Fig. 1) $V_s(z, \theta)$ develops a repulsive barrier that keeps additional particles confined to a second adlayer. Whereas the (squared) wave functions $|\varphi_0|^2$ and the energy ϵ_0 of the ground state remain more or less unchanged, the excited states get modified considerably in that their energies move up and their wave functions move out into the position of the second [$|\varphi_1(z)|^2$] and third [$|\varphi_2(z)|^2$] adlayer; see lower panel in Fig. 1.

At very low ("zero") coverage physisorption kinetics is, in systems like helium on graphite, controlled by a set of linear rate equations for the occupation function $n_{\vec{i}}$.⁵ This is no longer the case at nonzero coverage as one must account for the fact that transitions into some state will now depend on whether this state is occupied or not. Thus the time evolution of the occupation function is controlled by⁶

$$\frac{dn_{\vec{i}}}{dt} = \sum_{\vec{j}} R_{\vec{i}\vec{j}} n_{\vec{j}} (1 \pm n_{\vec{i}}) - \sum_{\vec{j}} R_{\vec{j}\vec{i}} n_{\vec{i}} (1 \pm n_{\vec{j}}), \quad (2)$$

where the plus (minus) sign applies if the adsorbing particles obey Bose-Einstein (Fermi-Dirac) statistics. The index \vec{i} is a set of quantum numbers characterizing a gas particle; e.g., in a mobile adsorbate we have $\vec{i} = (i, \vec{q})$. The transition probabilities $R_{\vec{i}\vec{j}}$ describe bound-state-bound-state, bound-state-continuum, and continuum-bound-state transitions. In weakly coupled physisorbed gas-solid systems they are calculated in perturbation theory as one-phonon processes so that⁵ (for $E_{\vec{i}} < E_{\vec{j}}$)

$$R_{\vec{i}\vec{j}} = (\pi/M_s N_s) \sum_{\vec{p}} \omega_{\vec{p}}^{-1} \left| \int dr \psi_{\vec{i}}^*(r) \frac{\partial V_s(z)}{\partial z} \psi_{\vec{j}}(r) \right|^2 \delta(E_{\vec{i}} - E_{\vec{j}} + \hbar\omega_{\vec{p}}) (n_{\vec{p}}^{(\text{ph})} + 1). \quad (3)$$

Here $n_{\vec{p}}^{(\text{ph})}$ is the Bose-Einstein occupation function for a phonon of energy $\hbar\omega_{\vec{p}}$. N_s is the number of atoms of mass M_s in the solid.

Isothermal desorption is phenomenologically described by a simple rate equation $d\theta/dt = -\theta/t_d(\theta)$ where $t_d(\theta)$ is the, in general coverage-dependent, desorption time. To calculate the latter we employ the following procedure: (1) For a gas-solid system in equilibrium at a pressure P and a temper-

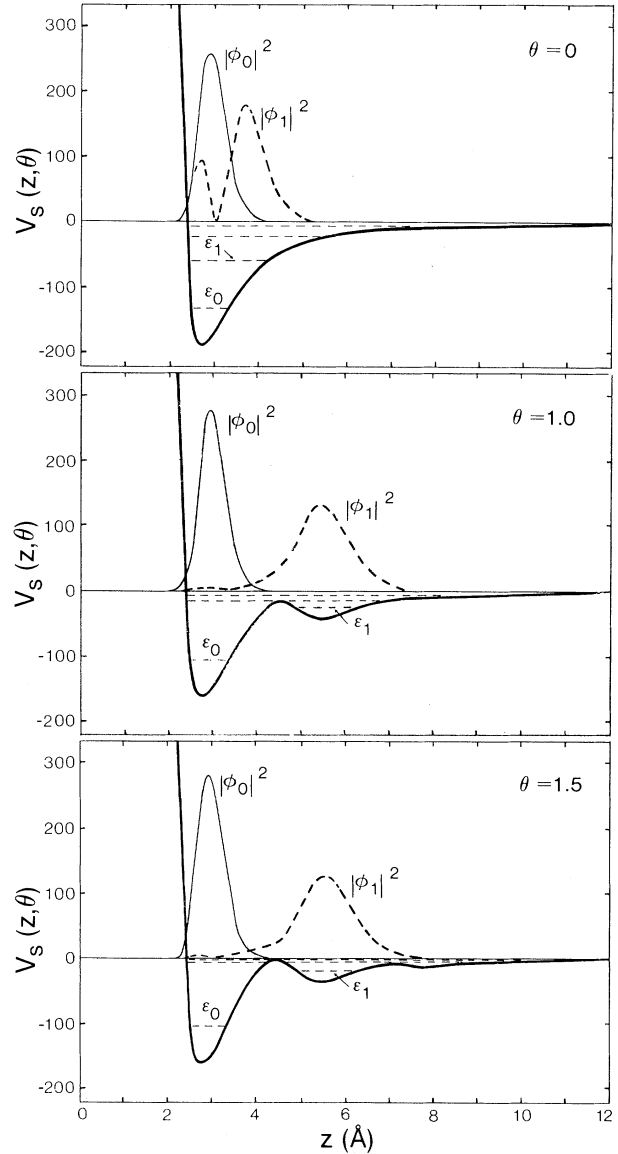


FIG. 1. Effective surface potential, single-particle wave functions, and bound-state energies for ^3He on graphite at $T = 12$ K and different coverages θ , calculated in Hartree-Fock approximation. Maximum monolayer coverage 0.107 \AA^{-2} . $V_s(z, \theta)$ in kelvins.

ature T , i.e., with occupation functions $n_{\vec{i}} = \{\exp[\beta(E_{\vec{i}} - \mu)] + 1\}^{-1}$ for fermionic gas particles (^3He) where μ is the chemical potential of an ideal (classical) gas in front of the solid, the Hartree-Fock equations (1) are solved yielding single-particle wave functions $\psi_{\vec{i}}(\vec{r}) = \varphi_i(z) \exp(i\vec{q} \cdot \vec{\rho})$ and energies $E_{\vec{i}} = \epsilon_i + \hbar^2 q^2 / 2m$ at a coverage $\theta = \sum_{\vec{i}} n_{\vec{i}} / n_{\vec{i}}(\text{max})$ where $n_{\vec{i}}(\text{max})$ is the maximum occupation of the \vec{i} th state corresponding to monolayer density. To ensure saturation in our theory we introduced a cutoff q_c for the summation over the two-dimensional lateral momentum \vec{q} in the surface plane. (2) The transition probabilities $R_{\vec{i}\vec{j}}$ are calculated according to Eq. (3). (3) To account for the removal of the gas phase in an isothermal desorption experiment we drop continuum-bound-state transitions from Eq. (2) and integrate these equations for a small time increment Δt with the right-hand side determined by the initial conditions. (4) With the new occupation functions $n_{\vec{i}}(\Delta t)$ (all continuum states are empty!),

$$t_d^{-1} = (\pi / M_s N_s) \sum_{\vec{i}} \sum_{\vec{p}} \sum_{\vec{c}} \omega_{\vec{p}}^{-1} \left| \int dr \psi_{\vec{i}}^*(\vec{r}) [\partial V_s(z) / \partial z] \psi_{\vec{c}}(\vec{r}) \right|^2 \delta(E_{\vec{i}} - E_{\vec{c}} + \hbar \omega_{\vec{p}}) n_{\vec{i}} n_{\vec{p}}^{(\text{ph})} / \sum_{\vec{j}} n_{\vec{j}}, \quad (4)$$

where \vec{c} is the momentum of a gas particle in the continuum. For a graphical representation of our results we use the Frenkel-Arrhenius parametrization $t_d = \nu^{-1} \exp[Q/k_B T]$ where $Q = k_B T^2 \times [\partial(\ln P) / \partial T]_{\theta}$ is the isosteric heat of adsorption with P the gas pressure necessary to maintain a transient coverage at a temperature T .

In Fig. 2 we plot $\log_{10} \nu$ and Q versus θ . Q drops from a value $Q \approx -\epsilon_0 + 2.5 k_B T$ at $\theta = 0$, where $\epsilon_0 / k_B = -135$ K is the lowest-energy state in the bare surface potential, to $Q \approx \epsilon_g + 2.5 k_B T$ at $\theta \approx 1.5$ where ϵ_g is the depth of the He-He interaction potential! This trend simply reflects the fact that a He atom is more tightly bound to the graphite surface than to a monolayer of helium on graphite.³ The prefactor drops from $\nu = 10^{13} \text{ s}^{-1}$ at $\theta = 0$ to $\nu = 10^{10} \text{ s}^{-1}$ at $T = 12$ K and $\nu = 10^{11} \text{ s}^{-1}$ at $T = 18.5$ K for $\theta > 1$.⁸ The rapid decrease in ν as a monolayer gets completed can be readily understood from the expression (3) for $R_{\vec{i}\vec{j}}$ and the fact that, according to the lower panel of Fig. 1, the second bound state is moving out for $\theta > 0$ into the region of the second adlayer where the coupling to the phonons gets very weak. The overall desorption time gets faster with increasing coverage, e.g., at $T = 12$ K from $t_d = 1.2 \times 10^{-7}$ s at $\theta = 0$ to $t_d = 3.3 \times 10^{-9}$ s at $\theta = 1.5$, and at $T = 18.5$ K from $t_d = 10^{-9}$ s at $\theta = 0$ to $t_d = 4.2 \times 10^{-10}$ s at $\theta = 1.2$.

corresponding to a reduced coverage $\theta(\Delta t)$, we enter the Hartree-Fock equations (1) and recalculate $\psi_{\vec{i}}(\vec{r})$ and $E_{\vec{i}}$ self-consistently, after which we can return to step (2) above. In this way we generate the time evolution $\theta(t)$ from which we can extract the time scale $t_d(\theta)$ of desorption. The implicit assumption in the above procedure is, of course, that the internal readjustment of the adsorbate during the desorption process is much faster than the desorption process itself. Note that in addition to the explicit nonlinearity of the rate equations (2) there is a much stronger implicit one through the dependence of the initial and final states in $R_{\vec{i}\vec{j}}$ on the $n_{\vec{i}}$'s in (1). The above calculation can be simplified considerably after the realization that the He-graphite and similar systems remain in a quasiequilibrium during the desorption process in a temperature regime where the desorption time is much larger than the time characterizing bound-state-bound-state transitions justifying the use of perturbation theory on (3) to calculate the desorption time as⁷

The fact that the prefactor ν changes in the same direction as the heat of adsorption is referred to, generally for thermally activated processes, as a compensation effect and has been observed in many chemisorbed systems.⁹

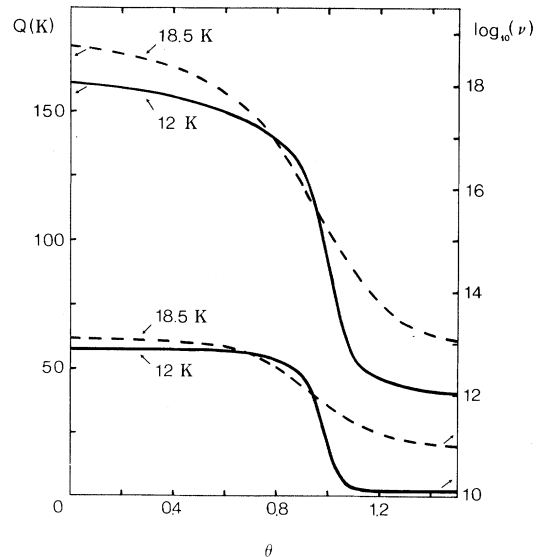


FIG. 2. Heat of adsorption Q and $\log_{10} \nu$ vs coverage θ at two temperatures from desorption time $t_d = \nu^{-1} \times \exp(Q/k_B T)$.

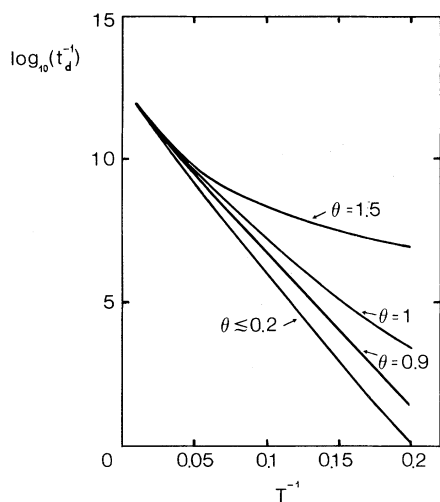


FIG. 3. $\log_{10} t_d^{-1}$ vs T for various coverages θ .

Figure 3 shows that the curves of $\log_{10} \nu$ versus T^{-1} for various coverages θ indeed converge at high temperature but do not cross.⁸ We also note that the entropy lost by transferring a particle from the adsorbate to the gas phase rises, not quite linearly, with Q .

In summary, we have reported a fully microscopic (mean-field theory plus nonlinear rate equations) calculation of the (phonon mediated) desorption time in the ^3He -graphite system up to a coverage $\theta \sim 1.5$. A compensation effect is predicted around monolayer coverage in gas-solid systems where the phonon density of states

in the surface region is not changed appreciably by the presence of the adsorbate and in the absence of strong coupling to collective excitations in the adsorbate itself.

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