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Reply to ''Comment on 'Chemically frozen phase separation in an adsorbed layer' ''

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In a previous paper [Phys. Rev. E **52**, R4616 (1995)] we proposed a simple model to illustrate a basic mechanism for the formation of adsorbate islands on a surface. In the preceding paper [Phys. Rev. E **55**, 4826 (1997)] it was claimed that this model was not realistic because it assumed a desorption rate constant independent of coverage, therefore neglecting the effect of interadsorbate interactions on the desorption rate. In view of numerous experimental results and microscopic simulations, we argue that, at least in some temperature ranges, this assumption is fully justified. Moreover, it does not compromise the model's ability to capture the crucial features of the system under consideration. [S1063-651X(97)11003-0]

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In the preceding Comment [1], Zhdanov criticizes our paper [2] stating that the treatment of the kinetic terms is not realistic since the influence of adsorbate-adsorbate interactions on the desorption rate was neglected. He argues that the Landau-Ginzburg approach used in the treatment of mass transport terms should be complemented by the use of the mean-field approximation to account for the effect of lateral interactions on the desorption rate. We strongly disagree with his view, according to which such a treatment would make the model more ''realistic'' in contrast to our assumption of a desorption rate constant independent of coverage, referred to as ''not realistic.''

The Arrhenius law for the desorption rate constant reads (setting $k_B=1$)

$$\ln k_d(\theta)=\ln\nu(\theta)-E_d(\theta)/T. \tag{1}$$

In real adsorbate systems, the apparent Arrhenius parameters strongly depend on surface coverage, but this is true for *both* the activation energy $E_d(\theta)$ and the preexponential factor $\nu(\theta)$. The variation of $\nu(\theta)$ is far from being marginal. Indeed, variations by factors of 10^3-10^6 have often been observed [3,4]. As a rule, $\nu(\theta)$ and $E_d(\theta)$ vary sympathetically, leading to the well-known but not well-understood *compensation effect* [3,4]. Although this phenomenon is in no way exclusive to heterogeneous reactions, it is nevertheless in this field that it has been most widely observed and its consequences are the most expressive. At present, conceivable explanations follow two trends [4]. Some rely on the statistical thermodynamics of the adlayer alone and give the variations in the distribution of local configurations of reactive molecules, as a function of temperature and surface coverage, responsible for compensation. Others emphasize the role of the substrate, sustaining that interadsorbate interactions can significantly alter the potential-energy surface and therefore influence both the activation energy and the preexponential factor. The latter opinion is endorsed by the fact that models that incorporate adsorbate-induced changes in the surface phonon spectrum predict a large compensation effect. Nevertheless, statistical models of the overlayer, including the relatively simple lattice gas, treated in the quasichemical approximation [5], also predict a coverage dependence of the preexponential factor. However, such a dependence is weak compared to that measured for real rate processes. Recent Monte Carlo simulations [6,7], performed at different temperatures, have also shown strong variations in the preexponential factor and compensation, for both attractive and repulsive interadsorbate interactions. In sharp contrast with these studies, the mean-field approximation, by predicting a constant preexponential factor, is in strong disagreement with experimental results even at a qualitative level. On the contrary, the assumption of a k_d independent of coverage seems to be a phenomenologically well-justified option at least in some temperature ranges, as we shall now briefly explain.

The plots of the logarithm of the reaction rate versus the inverse temperature, at different surface coverages, often yield a family of straight lines with different slopes that approximatively intersect at a common point, defining the so-called compensation or isokinetical temperature T_{iso} through the equation [4]

$$\ln\nu(\theta)=E_d(\theta)/T_{\text{iso}}+\text{const}. \tag{2}$$

Substitution of Eq. (2) into Eq. (1) yields

$$k_d(\theta)\sim\exp[-(1/T-1/T_{\text{iso}})E_d(\theta)], \tag{3}$$

so that, for $T\simeq T_{\text{iso}}$, which is often of the same order of magnitude as temperatures at which surface reactions are usually studied, one has simply $k_d\simeq$const. Complete compensation throughout an extended temperature region is certainly an idealized situation. However, full compensation is not required to guarantee the *qualitative* conclusions drawn from the linear analysis performed in [2] under the assumption $k_d\simeq$const, particularly the damping of a band of long-wavelength modes. In fact, these modes will be linearly stable if the derivative

$$h=-\frac{\partial}{\partial\theta}[P(1-\theta)-k_d(\theta)\theta^2]_{\theta=\theta_s} \tag{4}$$

is positive, θ_s being the solution of

$$P(1-\theta_s)-k_d(\theta_s)\theta_s^2=0. \tag{5}$$

Expanding Eq. (4) and solving the above equation for P, one obtains

$$h=\left[\frac{\theta_s{}^2}{(1-\theta_s)}+2\theta_s+[\ln k_d(\theta_s)]'\theta_s^2\right]k_d(\theta_s). \qquad (6)$$

As $0<\theta_s<1$, it is clear that h can only become negative if $[\ln k_d(\theta)]'<0$. Somehow unexpectedly for attractive interactions, simulations suggest that in certain temperature domains this may not even be the case, i.e., k_d may increase with θ [7]. Anyhow, h will remain positive provided $\ln k_d$ is a slowly varying function of θ, which is expected for systems where compensation is appreciable, that is, when the two terms on the right-hand side of Eq. (1) balance each other to a large extent. In particular, the variation of $\ln k_d$ is likely to be significantly more moderate than predicted by the mean-field theory. This expectation is confirmed by experiments, showing that although the Arrhenius plots at different coverages are usually nonlinear, the curves often remain close to each other through a significant temperature range.

Phase separation in adsorbed overlayers is obviously a highly cooperative phenomenon, introducing dramatic distortions in the diffusion field (see also [8]), leading to the formation of sharp interfaces and the subsequent coarsening process. In this vein, Zhdanov's premise that the effect of attractive adsorbate-adsorbate interactions on the desorption rate ''is even expected to be stronger than that on the rate of diffusion because the former process involves two particles'' makes little sense. Rather, in adsorbates that undergo phase separation, a powerful compensation effect is expected. Indeed, in such cases, compensation was shown to be so effective that it has been suggested, generally, as a valuable signature of an underlying phase transition [9].

The decoupling scenario assumed in [2] is justified by the presence of two disparate energy scales: in chemisorbed layers, the energy of adsorption is typically much higher than the energy of diffusion or the energy of interaction between adsorbed molecules. Besides, since the system is driven into a far-from-equilibrium state by the kinetic exchange processes between the surface and the gas, kinetics and mass transport evolving on different time scales may be treated as two independent nonequilibrium processes [10]. Therefore, from our viewpoint, it is unwise to ignore experimental evidence, in a pointless quest of mutually compatible approximation schemes for kinetic and diffusive terms.

Finally, in the last two sentences of his Comment the author makes the conclusion that ''the perturbations with small wave numbers are not stable ... indicates that formation of frozen islands is hardly possible.'' We find this statement unfounded because, while the damping of small wave numbers is *possibly* a sufficient condition for pinning in these circumstances (although this conjecture awaits proof), it is *certainly not* a necessary condition. Anyway, no decisive information concerning the formation and stability of nonequilibrium structures can be drawn from linear analysis alone, since by definition it neglects nonlinear couplings ultimately responsible for the eventual saturation of the amplitudes of excited modes. In order to reach a settlement on this issue, a nonlinear analysis is always required, desirably done in parallel to the numerical integration of the evolution equation as in [2].

In conclusion, interadsorbate interactions are responsible for the coverage dependence not only of the energy of desorption but also of the preexponential factor. The mean-field approximation, being unable to account for this effect on the preexponential factor, does not provide us with a valid option for the treatment of desorption terms and must therefore be discarded. In the absence of a theory that predicts such large coverage variations in $\nu(\theta)$ as those observed in most experiments, a phenomenological approach in the spirit of Eq. (3) should be preferred. In a certain domain around T_{iso}, determined by the magnitude of the compensation effect, k_d may be taken independent of coverage without major discordance with experimental facts.

Therefore, under some conditions, the mechanism analyzed and discussed in Ref. [2], using a particularly simple kinetics, may give rise to a stable structuration of the adlayer. Never had we, however, claimed it to be universal in its application.

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