
COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in the Physical Review. Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Comment on “Chemically frozen phase separation in an adsorbed layer”

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In a recent paper [Phys. Rev. E **52**, R4616 (1995)], J. Verdasca, P. Borckmans, and G. Dewel predict that an interplay between adsorption, desorption, and surface diffusion may result in the formation of “frozen” islands in the case of attractive adsorbate-adsorbate interactions. The model employed, however, is not realistic because the authors neglect the influence of adsorbate-adsorbate interactions on the desorption rate. Involving the latter effect in the analysis suppresses the formation of frozen patterns. [S1063-651X(97)10903-5]

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Critical phenomena occurring in adsorbed overlayers at conditions far from equilibrium are of high current interest [1]. To simulate such phenomena, one inevitably needs to employ a series of assumptions and simplifications which should, of course, reflect the main properties of a system under consideration. The recent paper by Verdasca, Borckmans, and Dewel [2], treating the island formation in the course of the $2A \rightarrow A_2$ reaction, does not seem to satisfy the latter requirement.

Physically, the island formation is connected with attractive adsorbate-adsorbate interactions ($\epsilon < 0$). The process occurs at temperatures below the critical temperature, $T < T_c$. To describe the time evolution of adsorbate coverage in this case, the authors [1] employ the following equation:

$$\frac{\partial \theta}{\partial t} = k_a P(1 - \theta) - k_d \theta^2 + M \nabla^2 \frac{\delta F}{\delta \theta}, \quad (1)$$

where the first and second terms correspond to A adsorption (P is pressure) and A_2 desorption, respectively, and the third term, constructed phenomenologically by using the standard Landau-Ginzburg expression for the free energy and taking into account conservation of particles, originates from surface diffusion (this term is the same as in the well-known Cahn-Hilliard equation).

Assuming the adsorption and desorption rate constants, k_a and k_d , to be independent of coverage, Verdasca, Borckmans, and Dewel [2] have shown that Eq. (1) predicts the formation of frozen islands. In reality, however, the attractive adsorbate-adsorbate interactions should affect the rate of

desorption [3], and this effect is expected to be even stronger than that on the rate of diffusion because the former process involves two particles. To illustrate the latter statement, we need equations for desorption kinetics with lateral interaction. The phenomenological Landau-Ginzburg approach is not oriented toward describing desorption. This approach, however, is well known to be equivalent to the mean-field approximation (MFA) [in particular, it predicts the same critical exponents as MFA]. Thus, we *may* complement the Landau-Ginzburg approach for treating the phase transition by standard MFA equations for describing desorption (this combination is common in the theory of phase transitions) in order to show the type of effects that are ignored in Ref. [2]. In general, simulating the rate processes on solid surfaces, we should distinguish the adsorbate-adsorbate interactions in the ground and activated states [3] (the terms “ground” and “activated” correspond to those in transition state theory). For desorption, the latter interactions are usually negligible [3]. In this case, the MFA expression for the rate constant of associative desorption is as follows [3] (for simplicity, we take into account only the nearest-neighbor interactions ϵ_1 and in addition set $k_B = 1$):

$$k_d = \exp[2(z-1)\epsilon_1 \theta / T] k_d^0, \quad (2)$$

where k_d^0 is the desorption rate constant at low coverages, and z is the number of nearest-neighbor sites.

The important point is that in the spinodal region the mean-field desorption rate [Eq. (2) with $\epsilon_1 < 0$ at $T < T_c = z|\epsilon_1|/4$] *decreases* with increasing coverage *faster* than the adsorption rate. Thus, for $k_a P(1 - \theta) = k_d \theta^2$, the derivative

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$$h = -d[k_a P(1 - \theta) - k_d \theta^2]/d\theta \quad (3)$$

is *negative*. Analyzing then the linear dynamics correspond-

ing to Eq. (1) (in analogy with Ref. [2]), one realizes that the perturbations with small wave numbers are not stable. The latter indicates that the formation of frozen islands is hardly possible.

[1] R. Imbihl and G. Ertl, *Chem. Rev.* **95**, 697 (1995).

[2] J. Verdasca, P. Borckmans, and G. Dewel, *Phys. Rev. E* **52**, R4616 (1995).

[3] V. P. Zhdanov, *Elementary Physicochemical Processes on Solid Surfaces* (Plenum, New York, 1991).