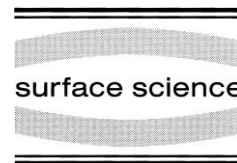




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Fluctuation effects at solid–liquid interfaces

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Abstract

Based on a generalized lattice gas theory and a Brownian dynamics simulation, we show that the fluctuations of the mean square displacements of a crystalline substrate coupled to the fluctuations of the adsorbate coverage may induce critical behavior for both subsystems. It is shown that an increase of the Lindemann parameter L_0 for the substrate drives the adsorbate to condensate. An increase of the coverage fluctuations induces a local melting of the substrate lattice, as this follows from an increase of the coverage-dependent Lindemann parameter L . © 1999 Published by Elsevier Science B.V. All rights reserved.

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Modification of an adsorbent under the influence of an adsorbate is the subject closely connected to such important phenomena as roughening [1–3], crystal growth [4], reconstruction [5–7], interfacial melting [8], etc. It is shown that thin (one to five monolayers) adsorbed films may induce in-plane stress and lead to structural rearrangements of the substrates. For solid–liquid interfaces the liquid has an additional entropic impact from its bulk, and also the interparticle interactions which differ (in a range or symmetry) from those induced by the substrate. This restricts the conditions at which an ordered film may be formed and represents a key difference from the

thin film phenomena. In particular, it is demonstrated [9,10] that the substrate displacements, being coupled to the interactions induced by the adsorbate, give rise to qualitatively new structures for both subsystems.

In this Letter we discuss the effects coming from the fluctuations of the mean square displacements and the occupation numbers. The surface is modelled as a two-dimensional square lattice (of spacing d) of adsorbing sites located on the top of the substrate atoms. The sites have the dispersive degrees of freedom due to the elastic properties of the substrate (phononic excitations or the anharmonicity effects). This is mediated by the substrate pair potential $U(\mathbf{R}_i, \mathbf{R}_j)$, where \mathbf{R}_i is a two-dimensional vector specifying the location of the site. We assume that the motion of the substrate in the direction perpendicular to the surface is forbidden. In the absence of the adsorbate the solid atoms vibrate around the equilibrium positions \mathbf{R}_i^0 in such a way that $\mathbf{u}_i = \mathbf{R}_i - \mathbf{R}_i^0$ is zero.

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The surface is exposed to a liquid with a given pair potential. The adsorbing potential is introduced as that of the sticky site model [11,12]. This model is chosen because, in addition to its mathematical simplicity, it allows us to describe a strong pinning of the adsorbate to the substrate positions. Owing to this specific potential the partition function can be reduced to that of the lattice gas with an additional integration over the substrate positions.

$$\Xi = \frac{1}{S^{N_s}} \int (d\mathbf{R}_i) e^{-\beta/2 \sum_{i,j} U(\mathbf{R}_i, \mathbf{R}_j)} \times \prod_{t_i} e^{-\beta/2 \sum_{i,j} W(\mathbf{R}_i, \mathbf{R}_j)^{t_i t_j}} e^{\beta \sum_i \mu_i t_i} \quad (1)$$

The ‘chemical potential’ is μ_i and $W(\mathbf{R}_i, \mathbf{R}_j)$ is the mean force potential for the adsorbate. The surface area is S and N_s is the number of adsorbing sites. Each pair of the solid sites interacts through the U potential plus an extra W contribution from a pair of adsorbed particles. The presence of this additional interaction is determined by the set of occupation numbers $t_i=0, 1$. To proceed further we extract the contribution corresponding to the reference state, i.e. the state with the sites located at the equilibrium positions $U(\mathbf{R}_i, \mathbf{R}_j) = U(\mathbf{R}_i^0, \mathbf{R}_j^0) + U(\mathbf{u}_i, \mathbf{u}_j)$, $W(\mathbf{R}_i, \mathbf{R}_j) = W(\mathbf{R}_i^0, \mathbf{R}_j^0) + W(\mathbf{u}_i, \mathbf{u}_j)$. After this rearrangement we have

$$\Xi = \prod_{t_i} e^{-\beta \sum_{i,j} W(\mathbf{R}_i^0, \mathbf{R}_j^0)^{t_i t_j}} e^{\beta \sum_i \mu_i t_i} \times \int (d\mathbf{u}_i) e^{-\beta \sum_{i,j} U(\mathbf{u}_i, \mathbf{u}_j)} e^{-\beta \sum_{i,j} W(\mathbf{u}_i, \mathbf{u}_j)^{t_i t_j}} \quad (2)$$

The free energy is

$$F = F_S^0 + F_L^0 - 1/\beta \ln \left[\prod_{t_i} \int (d\mathbf{u}_i) e^{-\beta \sum_{i,j} U(\mathbf{u}_i, \mathbf{u}_j)} e^{-\beta \sum_{i,j} W(\mathbf{u}_i, \mathbf{u}_j)^{t_i t_j}} - 1 \right] \quad (3)$$

Here F_L^0 is the adsorbate free energy for the rigid substrate case, F_S^0 is the free energy of the clean substrate and $\beta=1/kT$ is the Boltzmann factor. Two cumulant averages \dots_c correspond to the averaging over the displacement variables (for clean substrate) and over the occupation numbers (for rigid substrate). It is clear that these are permutable, so we use the same notations for both.

To clarify the meaning of this result we assume

the harmonic representation for the potentials $W(\mathbf{u}_i, \mathbf{u}_j) = \Delta_{ij}(\mathbf{u}_i - \mathbf{u}_j)^2$, $U(\mathbf{u}_i, \mathbf{u}_j) = D_{ij}(\mathbf{u}_i - \mathbf{u}_j)^2$. Here D_{ij} is the elastic matrix for the substrate and

$$\Delta_{ij} = 1/2 \left[\frac{\partial^2 W(\mathbf{R}_i, \mathbf{R}_j)}{\partial \mathbf{R}_i \partial \mathbf{R}_j} \right]_{\mathbf{R}_i^0, \mathbf{R}_j^0}$$

is a quasi-elastic matrix for the adsorbate. In general, the expansion for $W(\mathbf{u}_i, \mathbf{u}_j)$ may contain a linear term, which is dropped assuming that the equilibrium position of the lattice is close to an extremum of the mean force potential.

Expanding the exponentials in Eq. (3) we obtain

$$F = F_S^0 + F_L^0 + 1/2 \sum_{i,j} \Delta_{ij} (\mathbf{u}_i - \mathbf{u}_j)^2 \dots_0 \times [\dots_0 t_i t_j - \dots_0 t_i \dots_0 t_j] + \dots \quad (4)$$

Here \dots_0 stands for the averages calculated with the reference potentials. Since $\mathbf{u}_i \dots_0 = 0$, the value of $\mathbf{u}_i^2 \dots_0$ gives the mean square fluctuation of the displacements for the clean substrate. In general, this expansion contains higher-order terms which should be summed to give a self-consistent result for the free energy. It is seen that the coupling term is just a product of the correlation functions for separated subsystems. The pair correlation function for the clean substrate $G(\mathbf{R}_i^0 - \mathbf{R}_j^0) = 1/2 (\mathbf{u}_i - \mathbf{u}_j)^2 \dots_0$ may exhibit singularity when the substrate is close to the melting or displacive transition. The pair correlation function $\chi(\mathbf{R}_i^0 - \mathbf{R}_j^0) = \dots_0 t_i t_j - \dots_0 t_i \dots_0 t_j$ corresponds to the adsorbate provided that the lattice is rigid. This contribution is peculiar when the adsorbate approaches the order–disorder or the condensation transition. The coupling of these two regimes may lead to the non-trivial behavior which is studied in this Letter.

The simplest case of the coupling is the one involving the diagonal parts of both correlation functions. Thus, for the substrate we have the mean square fluctuation of the displacements $1/2 (\mathbf{u}_i - \mathbf{u}_j)^2 \dots_0 = \mathbf{u}_i^2 \dots_0 - \mathbf{u}_i \dots_0 \mathbf{u}_i \dots_0 = \mathbf{u}_i^2 \dots_0$. The diagonal part of $\chi(\mathbf{R}_i^0 - \mathbf{R}_j^0)$ reduces to the single site susceptibility $\chi_i(\Theta) = (\dots_0 t_i - 1/2)^2 \dots_0 - (\dots_0 t_i - 1/2)^2 \dots_0$ which measures the fluctuations of the coverage.

Instead of summation of the cumulant expansion [Eq. (4)] we analyze two limiting cases. In the case when the fluctuations of the displacements

dominate, we can determine their influence on the adsorption isotherm. The approximate free energy consists of a clean substrate term F_s^0 and that corresponding to the adsorbate with the interaction renormalized by the substrate. Assuming the mean field form for the latter term, we minimize the free energy with respect to the coverage $\theta_i = \langle t_i \rangle$. If only q nearest neighbors are taken into account, then we have $\theta = \theta_i$, $\Delta_i = \Delta_{ij}$. This yields the following equation for the adsorption isotherm:

$$\theta = \frac{\lambda^* e^{-q(W + EL_0^2)\theta}}{1 + \lambda^* e^{-q(W + EL_0^2)\theta}} \quad (5)$$

where $E = \beta \Delta d^2$ is the dimensionless elastic energy of the adsorbate, $L_0^2 = \mathbf{u}_0^2 / d^2$ is the squared Lindemann parameter for the clean substrate, $W = \beta W(d)$ is the lateral interaction for the adsorbate at the equilibrium positions and $\lambda^* = \exp(\beta \mu)$ is the stickiness parameter. It is seen that the effective interaction between the adsorbates has an additional contribution coming from the mean square displacements of the substrate. The sign of this term is determined by the coupling constant Δ . For negative Δ the interaction is attractive and an increase of L_0 may lead the adsorbate to condense (even at $W = 0$). This is illustrated in Fig. 1, where the coverage is plotted as a function of $\ln \lambda^*$.

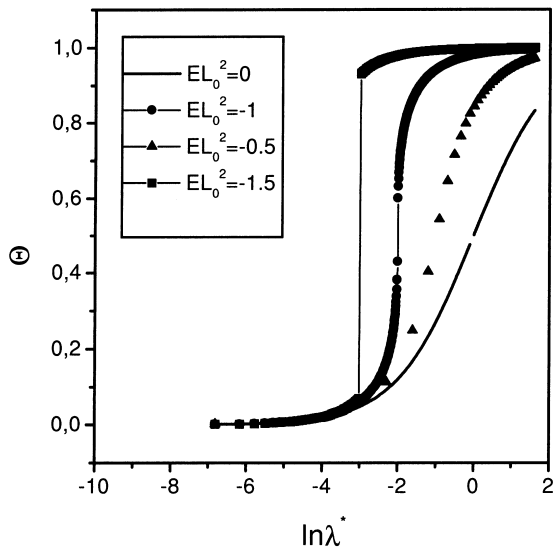


Fig. 1. The coverage θ as a function of $\ln \lambda^*$ at different EL_0^2 .

Now we analyze another limiting case, i.e. when the fluctuations of the occupation numbers dominate. The free energy may be represented as F_L^0 plus the substrate contribution with the elastic matrix D_{ij} renormalized by the adsorbate term. This allows us to determine the mean squared displacement in the presence of coverage. Using the flat spectrum approximation [13] for the normal mode frequency, we find the coverage-dependent Lindemann parameter

$$L^2 = \frac{L_0^2}{1 + \chi(\theta)\Delta/D} \quad (6)$$

This quantity is displayed in Fig. 2. It is seen that for negative Δ an increase of the coverage fluctuations [$\chi(\theta) = \theta(1 - \theta)$ for Langmuirian F_L^0] leads to an increase of the Lindemann parameter, which is a quantitative measure of the melting. Based on this we conclude that the coverage fluctuations may induce the melting of the substrate. For two-dimensional systems, however, this criterion should be accepted with some caution. In the absence of long-range order [14] the value of L_0^2 diverges logarithmically with the system size. Nevertheless, for finite distances this qualitative estimation is justified [1].

To recover the structure appearing due to this

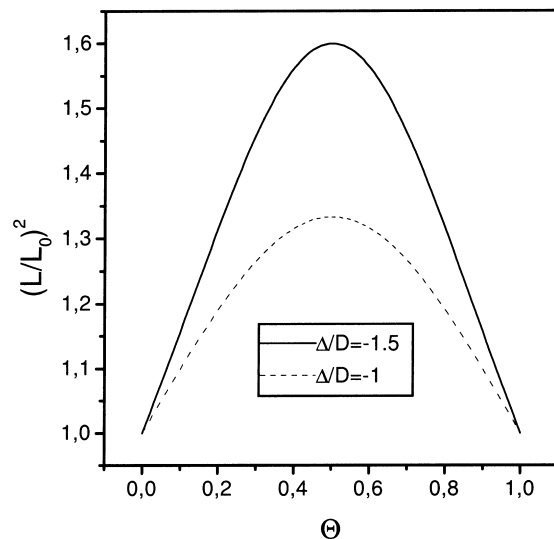


Fig. 2. The ratio of the Lindemann parameters $(L/L_0)^2$ as a function of coverage at different Δ/D .

transition, we perform a Brownian dynamics (BD) simulation which allows us to go beyond the small distortions up to a complete rearrangement of the surface. A similar approach has been developed recently [15–24] in the framework of the generalized Frenkel–Kontorova model. We consider two interacting subsystems of $N_j = 1 \times 10^3$ particles (where $j = 1, 2$ for the substrate and for the adsorbate atoms respectively). The case of $N_2/N_1 = 1$ is reported here. One of them is confined to the minima of the external periodic potential $V_0(\mathbf{R})$, which is used to model the square crystalline surface. In general, the substrate atoms can move from these minima being affected by the adsorbate. Another subsystem describes the adsorbate, which is attracted to the substrate (moving) atoms and does not interact directly with the potential $V_0(\mathbf{R})$. For simplicity we set both atomic masses $m_j = 1$. The initial positions for the substrate atoms were taken as being placed in the minima of substrate potential. Random distributions of atomic coordinates and velocities were used as the initial configurations for adsorbate particles. It was checked that the qualitative features of the final distribution (and, essential for this study, quantitative ones) do not depend on the specific initial configuration. The equation of motion for the atomic coordinates \mathbf{R}_{ji} is

$$\begin{aligned} \dot{\mathbf{R}}_{ji} + \eta \dot{\mathbf{R}}_{ji} + \frac{1}{R_{ji}} V_0(\mathbf{R}_{ji}) \delta_{j1} \\ + \frac{1}{R_{ji} \quad kl} V(\mathbf{R}_{ji} - \mathbf{R}_{kl}) = \delta F(\mathbf{R}_{ji}; t) \end{aligned} \quad (7)$$

where $1 \leq i \leq N_j$. To model a thermal bath we apply the Gaussian random force $\delta F(\mathbf{R}_{ji}; t)$

$$\begin{aligned} \delta F(\mathbf{R}_{ji}; t), \delta F(\mathbf{R}_{j'i'}; t) \\ = 2\eta T \delta_{jj'} \delta(\mathbf{R}_{ji} - \mathbf{R}_{j'i'}) \delta(t-t') \end{aligned} \quad (8)$$

to all atoms. The coefficient $\eta = 1$ corresponds to the external viscous damping due to energy exchange between the adsorbate and the substrate. It defines the system temperature T . We calculated the average square of velocity to control the temperature fixed $T = 1$. The interaction potential is chosen to be $V(|\mathbf{R}_{jj'}|) = V_{jj'} \exp(-|\mathbf{R}_{jj'}|^2/a_{jj'})$. The interaction is repulsive within a subsystem

($V_{jj} > 0$) and is attractive for different subsystems ($V_{12} < 0$) with a short-range repulsive core contribution $V_{21} > 0$. Numerical solution of Eq. (7), supplemented by the periodic boundary conditions, enables us to calculate the density distributions $\rho_j(\mathbf{R}) = \sum_i \delta(\mathbf{R} - \mathbf{R}_{ij})$ and, after the averaging, the two-body correlation functions $G_{j,j'}(\mathbf{R}, \mathbf{R}') = \rho_j(\mathbf{R}) \rho_{j'}(\mathbf{R}')$, which are the quantitative measures of the configurations observed.

The global behavior of the system is reflected by the gray-scale map, which is obtained as follows. Starting with an appropriate initial configuration, we wait a transient time t_{tr} until the system reaches a steady state. Then, for discrete time moments $t_k = t_{tr} + k\delta t$ we calculate the numbers of both kinds of atoms within small two-dimensional cells $\{x_{ji}, x_{ji} + \delta x_{ji}\} \times \{y_{ji}, y_{ji} + \delta y_{ji}\}$. These counts are accumulated during an averaging time t_{av} . Based on this we determine the stationary distribution function $\rho_j(\{x, y\})$, which gives the probability of finding a particle of j th type in a small $\delta x_{ji} \times \delta y_{ji}$ cell around a pair of coordinates (x_{ji}, y_{ji}) . The function obtained should be normalized to unity. The characteristic times of the procedure described should be chosen numerically to result in negligibly small further corrections to both densities $\rho_j(\{x, y\})$ at fixed temperature $T = 1$ and $\eta = 1$. Numerical simulation gives the following values for these parameters: $t_{tr} = 20$, $t_{av} = 50$, $\delta t = 0.02$. The phase space used for the calculation was discretized with $\delta x = 0.01$ and $\delta y = 0.01$.

To test this technique we calculated the distribution function for the system of non-interacting substrate atoms perturbed by the random source (temperature) only. The density map ($\rho_j(\{x, y\})$) as a function of $\{x, y\}$ contains a regular set of maxima with the width monotonously depending on the noise intensity. This structure survives up to reasonably high temperatures. The thermal energy should be lower than the magnitude V_0 of the external potential. Above this energy the ‘percolation’ of the particles between different potential valleys appears. This corresponds to the melting of the substrate. The snapshots exhibit the formation of various topological defects (dislocations, vacancies, etc.).

This simple picture is essentially affected by the interaction induced by the adsorbed atoms. In the

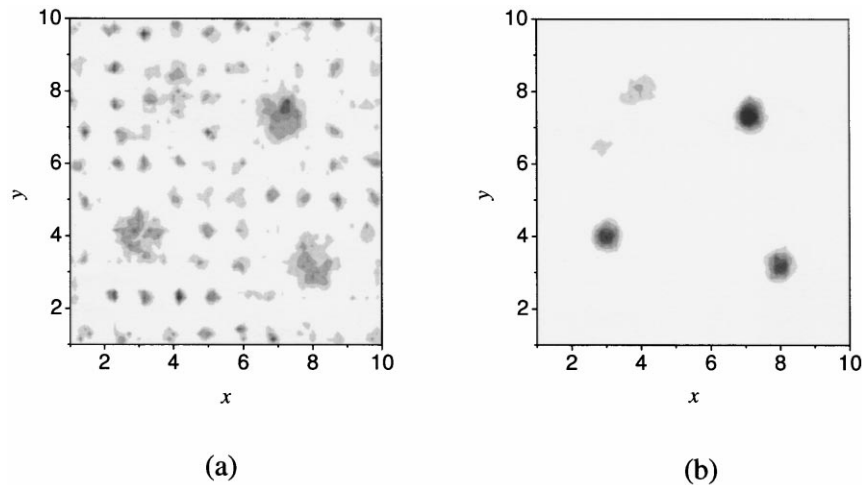


Fig. 3. Gray-scale map for continuous many-body density $\rho_f(\{x, y\}; t)$ for the substrate (a) and the adsorbate (b), calculated for $T=1$ and the following other model parameters: $V_{11}=2.5$, $V_{12}=-1.5$, $V_{21}=-V_{12}/2$, $V_{22}=V_{11}$, $a_{11}=1.25$, $a_{22}=0.05$, $a_{12}=0.5$, $a_{21}=0.00125$, and $\eta=1.0$.

context of the analytical study, we concentrate here on a set of interaction parameters that favors a strong attraction of the adsorbed particles to each surface atom. The adsorbate–adsorbate interaction results in some distortion of the crystal lattice around the adsorbate islands (the coverage fluctuations). If the magnitude of this distortion (the mean square displacements) is large enough, then new adsorbates are involved into this process, etc. This scenario agrees with the theoretical predictions concerning the coupling between the fluctuations of both subsystems. To investigate the many-body effects we suppose also that the mutual repulsion of liquid particles is not strong enough to prevent an attraction of many adsorbates to the vicinity of the same substrate atom. Then the fluctuation of the adsorbate density expands along the lattice and attracts the nearest atoms from the substrate. This process generates ‘liquid drops’ with an extremely high concentration of adsorbates and destroys completely the initial lattice around the drops. In this case we observe a nucleation of many adsorbed islands into a finite number of large clusters. Simultaneously, the substrate atoms are also mixed with these clusters. A typical distribution of density for such a state is shown in Fig. 3. This was obtained for the following model parameters: $V_{11}=2.5$, $V_{12}=-1.5$, $V_{21}=-V_{12}/2$,

$V_{22}=V_{11}$, $a_{11}=1.25$, $a_{22}=0.05$, $a_{12}=0.5$, $a_{21}=0.00125$, $\eta=1.0$ and $T=1.0$. The potential magnitudes and effective radii are measured in terms of V_0 and the undistorted lattice spacing respectively. For pictorial purposes, only a high-level slice for the adsorbate density is displayed (Fig. 3b). The same calculations were performed for widely distributed model parameters with the same mutual relations between different interactions. Qualitatively close gray-scale maps were obtained for all cases.

In summary, we have shown that a coupling of the fluctuations at solid–liquid interfaces may lead to new phenomena, such as interfacial melting and nucleation involving the substrate as well as the adsorbate. Interparticle interaction brought to the interface by the liquid molecules is one of the most essential driving forces for these effects. This distinguishes the processes described in this Letter from those observable in the presence of thin films, where the lateral interactions between the adsorbates are mainly induced by the substrate. This study suggests that the interface should be described as a finite range formation involving several crystalline and liquid layers. Nevertheless, a more refined theoretical investigation is required to provide a quantitative description of the effects estimated here. First of all this should concern the

treatment of topological defects [25] and their appearance due to the misfit A/D . Secondly, it is conceptually important to determine the crossover between substrate- and adsorbate-dominating regimes. This may result in a change of the universality class of the interfacial phenomena, since one goes from a strictly two-dimensional to a three-dimensional model of the interface. We hope to investigate these issues in a future study.

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