Wall Tension and Heterogeneous Substrate

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The wall tension of a heterogeneous wall is considered within a semi-infinite planar Ising model. Using Monte Carlo simulation techniques, we have obtained the microscopic validity of Cassie's law describing the wall tension of a heterogeneous substrate as the average of the wall tensions corresponding to the pure components. [S0031-9007(96)00343-2]

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Wetting phenomena are very important in many technical processes. It is quite remarkable that many predictions or interpretations still refer to the well-known Young's equation established two centuries ago. Consider a liquid B, in coexistence with its vapor phase A, put on top of a solid wall W. The different tensions characterizing the three pairs of media are denoted τ_{AW}, τ_{BW}, and τ_{AB}. Young's equation relates the contact angle θ of a sessile drop of B on the top of W

$$\tau_{AB}\cos\theta = \tau_{AW} - \tau_{BW} \equiv \Delta\tau\,. \tag{1}$$

Numerous studies have been devoted to that equation. The microscopic validity of Eq. (1) has in particular been established in [1,2]. Let us here stress that this equation holds for perfectly pure and flat substrates W, which of course never appear in nature.

The generalization of this equation to take into account heterogeneous substrates has been started by Cassie [3] and by Wenzel [4] to treat the case of rough substrates. A first attempt to reconsider the effect of roughness has been studied in detail in [5]. That is the reason why we here concentrate on the effect of chemical heterogeneities. Consider thus a substrate constituted of two species W_1 and W_2. Two approaches may be developed: The first one concerns the behavior of the contact angle of this sessile drop, and the second one is related to the wall tension $\Delta\tau$. Let us start with the first case. By putting a drop of liquid on top of a heterogeneous substrate, we can observe the appearance of two angles θ_a and θ_r, respectively, advancing and receding angles. The difference between θ_a and θ_r is a dynamical effect which leads to the so-called hysteresis of contact angles [6,7].

The equilibrium properties of such a system are instead contained in the wall tension $\Delta\tau$ that we will study here. For simplicity, let us restrict ourselves to a $d = 2$ system. Assume also that the species W_1 and W_2 appear on top of the wall with a concentration f_1 and f_2 ($f_1 + f_2 = 1$). Let us denote $\Delta\tau_1$ and $\Delta\tau_2$ the pure wall tensions associated with W_1 and W_2, respectively. Cassie's law gives the prediction that

$$\Delta\tau_{12} = f_1\Delta\tau_1 + f_2\Delta\tau_2\,, \tag{2}$$

where $\Delta\tau_{12}$ is the wall tension of the heterogeneous substrate 1-2. This equation simply states that the wall tension has to be related to the average of the pure component quantities. However, for microscopic heterogeneities, the validity of Eq. (2) is certainly questionable. Starting from van der Waals theories and electrostatic considerations, Israelachvili and Gee [8] suggest instead averaging the wall tension to average the polarizabilities, dipole moments, or surface charges. This leads to a new equation of the form

$$\Delta\tau_{12} = [f_1(\tau_{AB} + \Delta\tau_1)^2 + f_2(\tau_{AB} + \Delta\tau_2)^2]^{1/2} - \tau_{AB}\,.$$

This equation should then replace Cassie's whenever the heterogeneities on the top of the substrate are of microscopic scale. It is far from obvious how to establish the validity of that equation from an experimental point of view since this requires very detailed knowledge of the properties of the substrate surface. Nevertheless, we can analyze that problem within appropriate microscopic simulations. That is precisely the aim of this Letter.

Using Monte Carlo simulation techniques we will indeed obtain the microscopic validity of Cassie's law. Let us now introduce the model that we will consider here. The two-dimensional Ising model is defined on the lattice $Z \times Z$. To each lattice point (i_1, i_2) we associate a spin variable σ_i which may take two values $+1$ and -1 according to the presence of a molecule at i ($+1$ if the site i is occupied by a molecule and -1 if the site i is vacant). The interaction energy of these spins is described by the Hamiltonian

$$H(\sigma) = -J\sum_{\langle ij\rangle}\sigma_i\sigma_j\,, \tag{3}$$

where $J > 0$ is the coupling between nearest-neighbor $\langle ij\rangle$ spins. Let $\Sigma = [-L, L] \times [-L, L]$ be a finite square in $Z \times Z$ and let us fix the value of the spins outside Σ to be $\sigma_i = +1$ for $i \notin \Sigma$. We restrict the sum in Eq. (3) over all nearest-neighbor pairs $\langle ij\rangle$ which have a nonempty intersection with Σ. The sum in Eq. (3) is therefore well defined and will be denoted H^+. Let $\mathcal{Z}^+$ be the partition function associated with this Hamiltonian, defined for the inverse temperature β as

$$\mathcal{Z}^+ = \sum_{\sigma\in\Sigma}\exp[-\beta H^+(\sigma)]\,.$$

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The partition function $\mathcal{Z}^-$ with $-$ boundary conditions $\sigma_i = -1$, for $i \notin \Sigma$, can be defined in a similar way.

In order to introduce a wall in the system, we consider the model on a semi-infinite lattice $Z \times Z^+$. To particularize the wall on which the sessile drop will be put, we add to the Hamiltonian a boundary magnetic field h, describing the properties of the wall. Let $\Lambda = [-L, L] \times [0, 2L]$ be a finite square in $Z \times Z$ and $W = \{(i_1, 0); i_1 \in [-L, L]\}$ be the wall. Let us fix the value of the spins outside Λ to be $\sigma_i = +1$ for $i \notin \Lambda$. The interaction energy for this choice of boundary conditions is described by the Hamiltonian

$$H^{+w}(\sigma) = -J \sum_{\langle ij \rangle \in \Lambda} \sigma_i \sigma_j - J \sum_{i \in \partial\Lambda \setminus W} \sigma_i - h \sum_{k \in W} \sigma_k ,$$

where $\partial\Lambda$ is the border of the box Λ. In a similar way we can define the Hamiltonian H^{-w} for boundary conditions $\sigma_i = -1$ for $i \notin \Lambda$. Using these two kinds of boundary conditions, the wall tension $\Delta\tau$ can be defined as

$$\beta \Delta\tau = \lim_{L \to \infty} -\frac{1}{2L + 1} \ln \frac{\mathcal{Z}^{+w}(\Lambda)}{\mathcal{Z}^{-w}(\Lambda)}, \tag{4}$$

where $\mathcal{Z}^{+w}$ and $\mathcal{Z}^{-w}$ are the partition functions associated with these Hamiltonians H^{+w} and H^{-w}, respectively. This can be explicitly calculated and the analytical formula can be found in [10]. A summary of the known rigorous result is given in [11]. Since by symmetry

$$\sum_{\sigma \in \Lambda} \exp[-\beta H^{-w}(-\sigma)] = \sum_{\sigma \in \Lambda} \exp[-\beta H^{+w}(\sigma)],$$

we easily get

$$\begin{aligned} \frac{\mathcal{Z}^{-w}(\Lambda)}{\mathcal{Z}^{+w}(\Lambda)} &= \frac{\sum_{\sigma \in \Lambda} \exp[-\beta H^{-\omega}(\sigma)]}{\sum_{\sigma \in \Lambda} \exp[-\beta H^{+\omega}(\sigma)]} \\ &= \frac{\sum_{\sigma \in \Lambda} \exp[-\beta H^{+w}(\sigma)] \exp(-2\beta h \sum_{k \in W} \sigma_k)}{\sum_{\sigma \in \Lambda} \exp[-\beta H^{+w}(\sigma)]} \\ &= \left\langle \exp\left(-2\beta h \sum_{i \in W} \sigma_i \right) \right\rangle_\mu , \end{aligned} \tag{5}$$

where the average $\langle \cdot \rangle_\mu$ has to be taken with respect to the measure

$$\mu(\{\sigma\}) = \frac{\exp[-\beta H^{+w}(\sigma)]}{\mathcal{Z}^{+w}} .$$

After this change of reference measure, the limit in Eq. (4) can be written as

$$\beta \Delta\tau = \lim_{L \to \infty} \frac{1}{2L + 1} \ln \left\langle \exp\left(-2\beta h \sum_{i \in W} \sigma_i \right) \right\rangle_\mu .$$

This equilibrium average can now be estimated by different techniques. Using cluster expansion [1] for our Ising model, one can show that in the limit $\beta \to \infty$, Cassie's law holds. For higher temperatures, we use Monte Carlo techniques based on Metropolis dynamics [12]. We perform our simulations in a box of 64×64 spins with a coupling constant $J = 1$. Beginning from a random initial configuration of spins the system evolves according to the Metropolis dynamics towards the equilibrium. As shown in Fig. 1, after 10 000 Monte Carlo steps (MCS) our system already presents a plateau. Calculating $\Delta\tau$ in that time region we obtain a good agreement with the analytical results, which confirms that the system is close equilibrium.

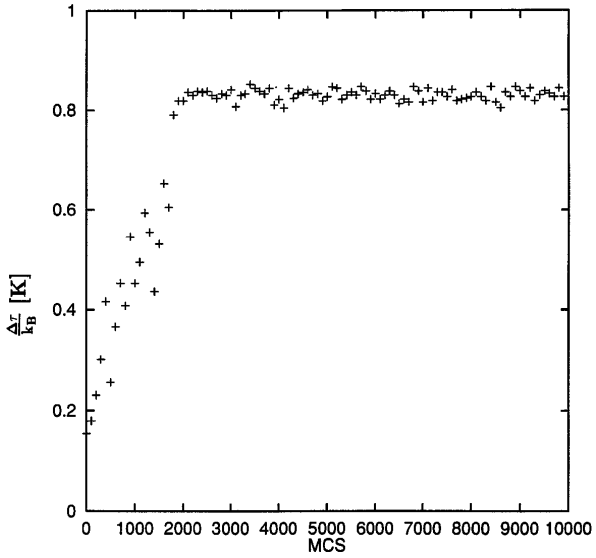

FIG. 1. Relaxation of $\Delta\tau$ calculated during one simulation for a purely homogeneous substrate with $h = 0.45$ and $Tk_B = 1.40$. Each point represents an average over 100 MCS.

For a given temperature $Tk_B = 1.4$, our numerical simulations for a homogeneous wall are plotted in Fig. 2

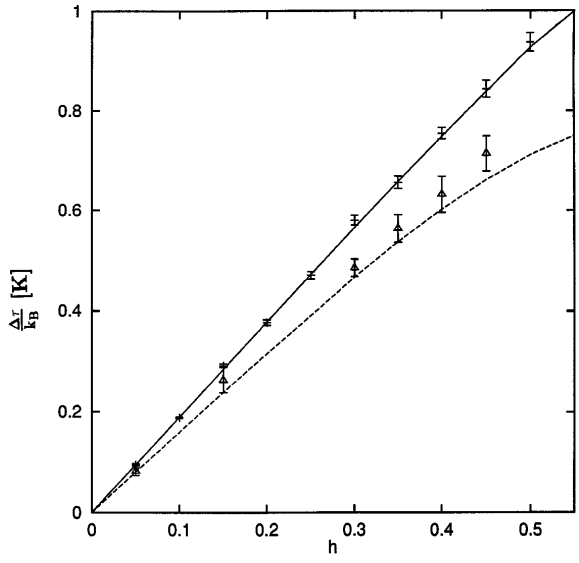

FIG. 2. The analytical results for $\Delta\tau$ corresponding to a homogeneous substrate and two temperatures, $Tk_B = 1.4$ (solid line) and $Tk_B = 1.8$ (dashed line); the simulation results are obtained as the average over 50 independent runs and are presented with their standard deviation error bars.

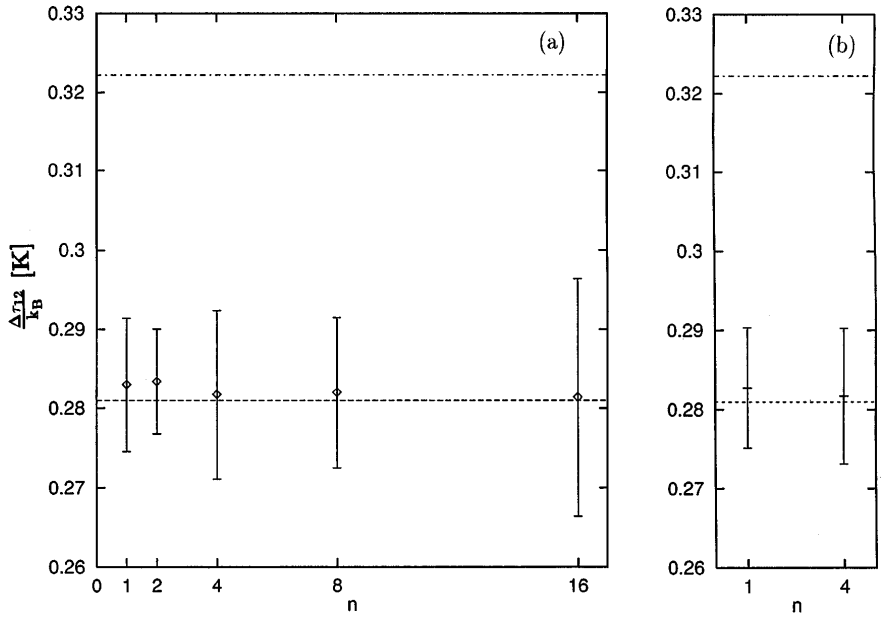

FIG. 3. $\Delta\tau_{12}$ as a function of the patches size n for a given concentration $f_2 = 0.25$. In (a), the patches of impurities of size n are regularly distributed, the data points are obtained as the average over 50 independent runs and are presented with an error bar corresponding to three standard deviations. In (b), the patches of impurities of size n are randomly distributed, the data points are the average of wall tension over 100 independent random substrates. The dashed line is Cassie's law prediction while the dash-dotted line has to be associated with Israelachv

and compared to the analytical result. The time averages and their associated statistical fluctuations are computed between 9000 and 10 000 MCS. The difference is less than 3% away from the exact result. To take into account the importance of the finite size effects, we have also considered a system of 300×300 sites for $Tk_B = 1.4$. The corresponding results are almost identical to the 64×64 ones.

Let us now introduce our two species 1 and 2 within the wall. This can easily be done by considering two values for the coupling h: h_1 with the concentration f_1 and h_2 with the concentration f_2 ($f_1 + f_2 = 1$). These couplings refer to the attraction energy between the substrate and the molecule of liquid. The strategy that we have chosen here is to first consider a given substrate with $f_1 L$ sites with coupling h_1 and $f_2 L$ sites with h_2. For this frozen disorder, we have studied $\beta\Delta\tau_{12}$ which is equal [cf. Eq. (5)] to the limit

$$\beta\Delta\tau_{12} = \lim_{L\to\infty} \ln \frac{1}{L} \left\langle \exp\left(-2\beta \sum_{i\in W} h_i \sigma_i \right) \right\rangle_\nu ,$$

where now the average $\langle\cdot\rangle_\nu$ has to be taken with respect to the Gibbs measure

$$\nu(\{\sigma\}) = \frac{1}{Z_h^{+w}} \exp\left[J\beta \left(\sum_{\langle ij\rangle\in\Lambda} \sigma_i\sigma_j + \sum_{i\in\partial\Lambda\setminus W} \sigma_i \right) + \beta \sum_{k\in W} h_k \sigma_k \right],$$

where $h_i = h_1$ or h_2, depending on the position i, and Z_h^{+w} is the partition function defined as

$$Z_h^{+w} = \sum_{\sigma\in\Lambda} \exp\left[J\beta \left(\sum_{\langle ij\rangle\in\Lambda} \sigma_i\sigma_j + \sum_{i\in\partial\Lambda\setminus W} \sigma_i \right) + \beta \sum_{k\in W} h_k \sigma_k \right].$$

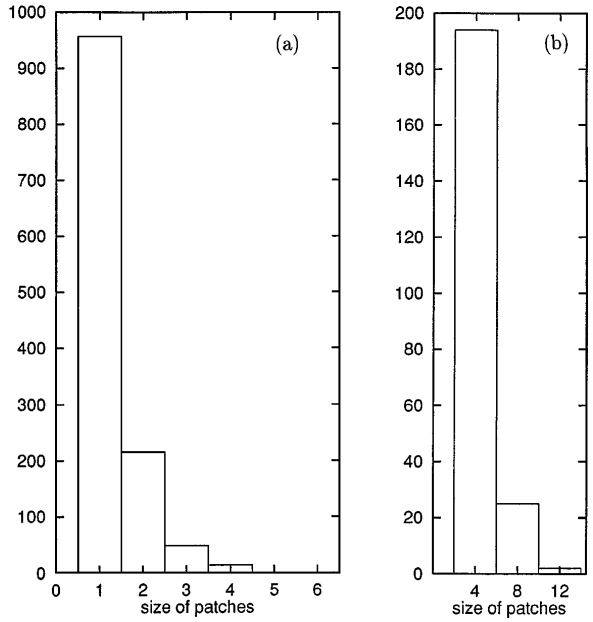

FIG. 4. The histogram of the distribution of the size of patches for random distribution of the fixed number of single sites in (a) and fixed number of groups of four sites in (b).

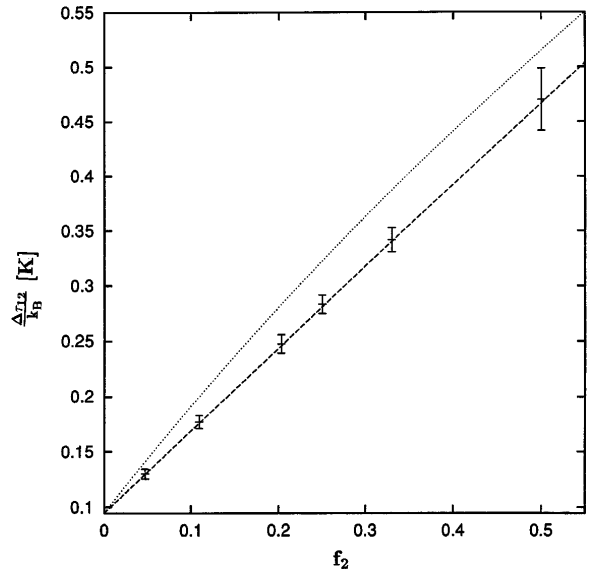

FIG. 5. $\Delta\tau_{12}$ as a function of the concentration f_2 of the regularly distributed sites with coupling constants $h_1 = 0.05$ and $h_2 = 0.45$. Data points correspond to the average over 50 independent runs; the error bars correspond to three standard deviations. The dashed line shows Cassie's prediction while the dotted line gives the Israelachvili-Gee law where $\Delta\tau_{AB}$ has been computed in Ref. [9].

Using ergodicity and detailed balance conditions, the asymptotic time behavior of that quantity can be identified to the equilibrium average $\Delta\tau_{12}$. This technique allows thus a detailed analysis of $\Delta\tau_{12}$ as a function of the concentration of sites with coupling constants h_1 and h_2. Our simulation has shown that the quantity $\Delta\tau_{12}$ does not depend on the details of the geometry. For fixed concentration $f_2 = 0.25$ we give in Fig. 3 $\Delta\tau_{12}$ as a function of the size n of regular patches of n sites covering the substrate. For the same concentration $f_2 = 0.25$, we also give in Fig. 3 the wall tension $\Delta\tau_{12}$ for a random distribution of the sites of heterogeneities. This $\Delta\tau_{12}$ is in fact the average over 100 independent random substrates with fixed $f_2 = 0.25$. To characterize the associated distribution of substrates, we give in Fig. 4 the histogram of the size of the patches of the heterogeneities. By 1, we measure isolated heterogeneities, by $2, 3, 4, \ldots$ patches of consecutive impurities. This independence of $\Delta\tau_{12}$ with respect to the substrate geometry, in terms of patches and of random distribution of heterogeneities, allows thus a detailed analysis of $\Delta\tau_{12}$ as a function of the concentration of sites with coupling h_1. The results for the given temperature $Tk_B = 1.40$ are given in Fig. 5. These results clearly indicate the validity of Cassie's law.

In conclusion, we have shown how ideal experiments performed on computers can be helpful in getting a microscopic understanding of the rich variety of phenomena appearing in the vicinity of surfaces. There is no doubt that our validity of Cassie's law via Monte Carlo techniques will usefully be complemented by other techniques, such as molecular dynamics.

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