Computer simulations of the wetting properties of neon on heterogeneous surfaces

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We use the grand canonical Monte Carlo method to study the nature of wetting transitions on a variety of heterogeneous surfaces. The model system we explore, Ne adsorption on Mg, is one for which a prewetting transition was found in our previous simulations. We find that the first order transition present on the flat surface is absent from the rough surface. Nevertheless, the resulting isotherms are, in some cases, so close to being discontinuous that the distinction would be difficult to discern in most experiments. [S1063-651X(99)07004-X]

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I. INTRODUCTION

The last decade has seen a great increase in the study of wetting transitions. Particular attention has been drawn to the case of simple gases on alkali metal surfaces, for which the first experimental examples of the prewetting (first order transition) phenomenon have been seen [1–8]. The subject has attracted even wider interest with the recent addition of Hg transitions to the list of adsorption systems exhibiting these phenomena [9,10]. Theoretical interest in this problem is extensive and diverse; important open questions include which systems are likely to display the transitions [11–15], their sensitivity to the adsorption potential [16,17], the nature and dimensionality of long-range forces [18], the possibility of higher order transitions [19], and the influence on the transition of surface irregularity [20–25].

In a previous paper [26], henceforth called I, we explored several of these questions. Specifically, we used the grand canonical Monte Carlo method of statistical mechanics to compute the nature of wetting transitions of Ne on weakly adsorbing surfaces. That work found that alkali metals attract Ne so weakly that nonwetting behavior was predicted for all temperatures below 42 K, i.e., 95% of the Ne bulk critical temperature. This result is consistent with experimental data of Hess, Sabatini, and Chan; using a quartz microbalance technique, they found a wetting transition near 43.4 K on Rb, and evidence of a drying transition on a Cs surface [27].

In I, we found that the case of Ne adsorption on Mg is quite different from that on the alkali metals; the reason is that the Ne adsorption potential on Mg is approximately four times as attractive as that experienced on Cs, and twice as attractive as that on Li [28]. We found prewetting transition behavior on Mg in the regime $22 < T < 30$ K. This is manifested as a coverage discontinuity at a pressure which depends sensitively on both T and the adsorption potential. In paper I, we also explored the effect on the transition of a (periodic) corrugation of the adsorption potential by constructing a simple cubic model of Mg, with properties chosen

to correspond qualitatively to real Mg (e.g., lattice constant $a = 4.01$ Å). We found that the principal effect of this corrugation was a small shift in the prewetting transition characteristics, as expected from a qualitative argument which attributes the shift to the atoms' extra attraction due to the periodic part of the potential.

This paper extends the Ne/Mg study to the case of heterogeneous surfaces. Such surfaces here are constructed by either adding Mg atoms to or subtracting them from the semi-infinite simple cubic lattice employed in I. We find a qualitative change in the adsorption behavior: the prewetting transition disappears, as expected from the general theory of adsorption on irregular surfaces. In the case of small heterogeneity, we find that the adsorption can exhibit a very rapid rise as a function of P; this ''quasitransition'' might not be distinguishable from a true (first order) transition in a laboratory experiment. In other cases, the rapid rise is replaced by a fairly gentle increase of coverage with P. As P approaches saturated vapor pressure, the coverage dependence may correspond to either complete wetting (divergent film growth) or nonwetting behavior, depending on the kind of heterogeneity. Thus we find that surface irregularity can change a wetting system into a nonwetting system. This can be rationalized from a crude thermodynamic argument based on the interfacial free energy cost of an irregular film.

This paper presents our geometry and computational method in Sec. II, and our results in Sec. III. We discuss our conclusions and open questions in Sec. IV. We emphasize that our results may well depend on the specific model, which is not completely general.

II. GEOMETRY AND METHOD

Our calculational technique was discussed extensively in I, to which we refer the interested reader. Briefly, we perform gcmc simulations of Ne adsorption on a model surface. The Ne atoms are confined to a space bounded on one side by the surface and on the other side by a region ($z > L = 78$ Å) of infinite potential energy. The Mg surface is periodically replicated as discussed below. It gives a semi-infinite domain of Mg atoms which reside on sites of a simple cubic lattice. Each Mg atom interacts with the Ne atoms with a Lennard-Jones (LJ) pair potential with param-

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eters $\epsilon_{gs}=15$ K and $\sigma_{gs}=5.01$ Å . These values were chosen in I to approximate the theoretical potential of Ref. [28], appropriate to the case of a Ne atom above a flat Mg surface. Finally, the Ne-Ne interaction is also taken to have a LJ form, with parameters 33.9 K and 2.78 Å . These assumed functional forms, as well as the assumption of classical statistical mechanics, should be of at least qualitative accuracy and are conventional in this field. We do not aspire to quantitative accuracy in the potential, because (to our knowledge) no one really knows the characteristics of the physisorption potential in the case of a rough metallic surface [29].

The initially flat surface consists of (x/y periodically replicated) square cells of dimension 28.07 Å , each containing 49 surface atoms. The algorithm used for creating our rough surfaces involves a surface profile function produced in momentum space (and then Fourier transformed). The procedure begins with a random, Gaussian-distributed profile function. Then one applies a correlation filter to remove high wave vector components. The filter is a Lorentzian function, with a width equal to the periodicity. Our rough surfaces are characterized in either of two ways. One involves a quantity called σ, defined as the root mean square deviation (from a mean value of zero) of the topmost atoms' values of z. The other is the specification of the rough geometry, i.e., the actual number and shapes of the various imperfections. We note that our ''rough'' surface is actually periodic, but this should not affect our conclusions excepting those phenomena (i.e., exactly at transition) which involve fluctuations with wavelengths larger than the cell size (i.e., 28.07 Å). The same limitation applies, of course, to all phenomena studied with simulations.

III. RESULTS

Our methods and results involve fully three-dimensional (3D) functions, such as the density and potential energy. For ease of depiction and interpretation, we present 2D graphs of different kinds. We define, in general, a 2D function $U(x,y)$ as the minimum, as a function of z, of the 3D potential $V(x,y,z)$ experienced by a Ne atom. An example appears in Fig. 1, which shows this function in the case of a simulation unit cell which possesses both a single added Mg atom and a single atomic ''pit,'' i.e., a hole created by the extraction of one surface layer Mg atom. Figure 2 shows the dependence on z of $V(x,y,z)$ above three different Mg atoms on this surface (an ordinary surface atom, an adatom, and an atom at the bottom of the pit). One is struck by the fact that the Mg adatom creates a very extended region of unfavorable potential for a Ne atom. This is a consequence of the large hard core length of the Ne-Mg pair potential. In contrast, one observes that the pit provides a very attractive region; however, this attractive region is very narrow and does not extend significantly above the neighboring surface atoms. We shall see, as a result, that the pit does not greatly enhance Ne adsorption in its vicinity. Note also in Fig. 1 that away from the imperfections the function $U(x,y)$ varies by a factor of about 20%, due to the atomic periodicity alone. This variation and its effect on wetting were discussed in I.

Most of the simulations in this paper have been carried out at a temperature $T=28$ K. This temperature is intermediate between the wetting temperature (22 K) and the prewetting
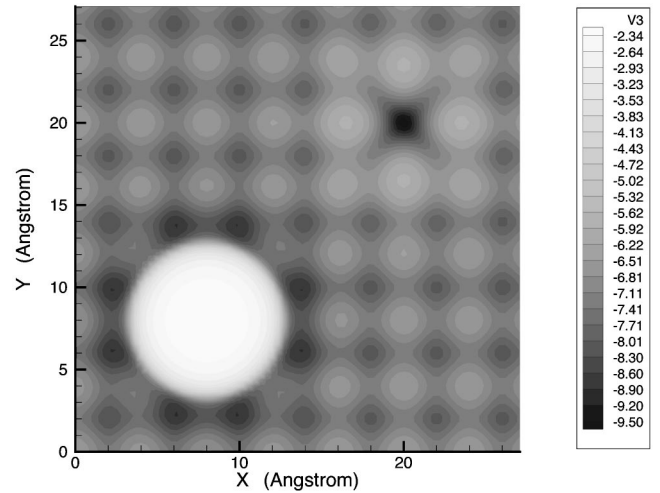

FIG. 1. Potential energy $U(x,y)$, defined in the text, as a function of lateral position on the surface for the case of one Mg adatom at $(x,y)=(8.02,8.02$ Å$)$ and one missing surface atom at $(20.05,20.05$ Å$)$ in each simulation cell, which contains 49 surface atoms. The scale at right is expressed in units of the well depth of the gas-Mg atom pair potential, which has the value 15 K.

critical temperature (30.6 K) computed for the (nonperiodic, flat) Mg surface in I [30]. Figure 3 displays the isotherms computed for Ne on several different Mg surfaces. For reference, we note that a nominal monolayer coverage is about 60 Ne atoms per periodic surface cell, derived by as-
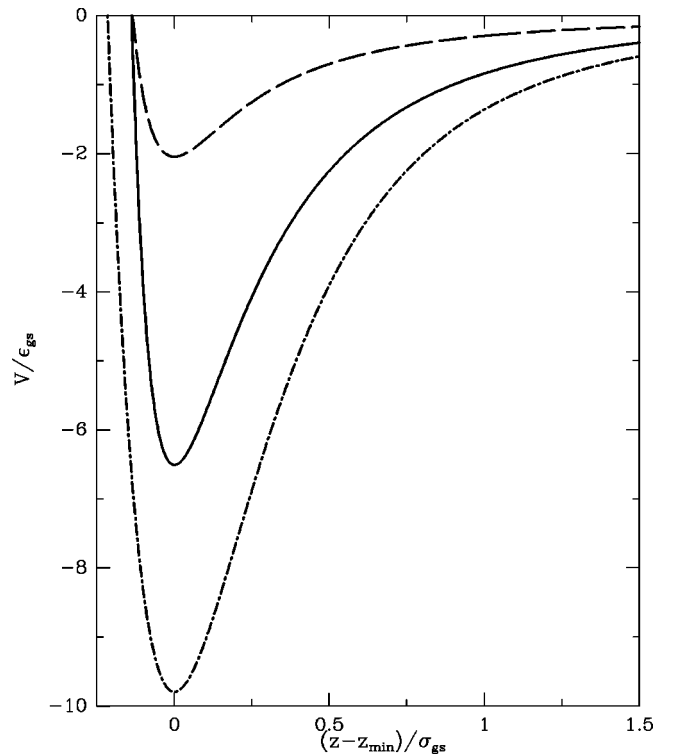

FIG. 2. Potential energy $V(x,y,z)$ as a function of normal distance z above three surface atoms' sites: above the adatom (dashes), above the pit (dash-dotted), and above a surface atom in the unperturbed surface (full curve). The curves are shifted so that their minima coincide. The values of z_{min} are 9.50, 3.6, and 5.16 Å, respectively.
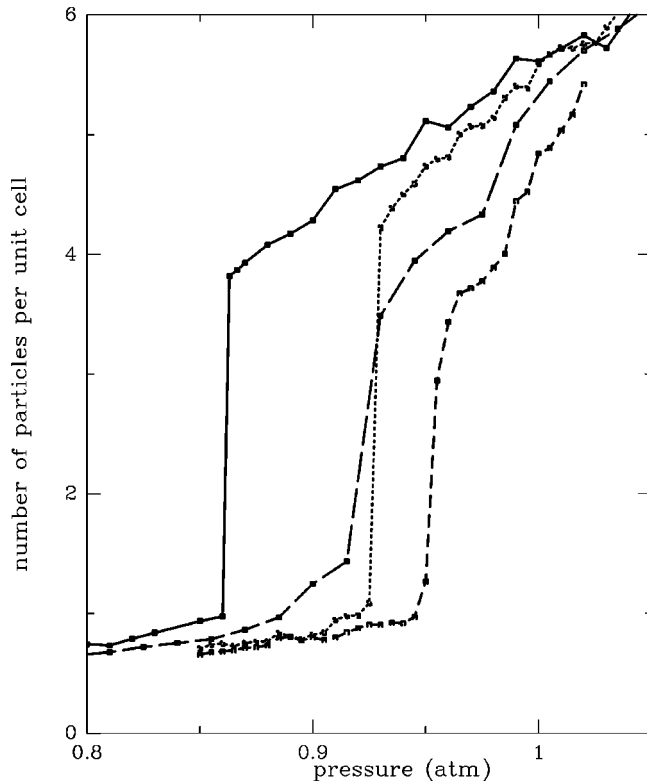
FIG. 3. Adsorption isotherms on a flat Mg surface (full curve), a surface with a single missing adatom per unit cell (short dash), a surface with one adatom (long dash), and a surface with an adatom and a missing surface atom (medium dash). The area of the Mg unit cell is 16.08 $Å^2$.

FIG. 4. 2D density of adsorbed Ne on the surface of Fig. 1, at $P=0.945$ atm and $N=47.4$ particles (0.96 particles per Mg unit cell), just below the rapid rise of adsorption. The density scale at right is expressed in units of inverse $Å^2$.

suming a 2D density equal to the $\frac{2}{3}$ power of the density of the 3D liquid. One of the isotherms in Fig. 3 is that obtained in paper I with the ''perfect'' flat surface of Mg; one observes there a vertical prewetting transition at $P=0.862$ atm. This corresponds to a coverage jump by a factor of 4, as discussed in I. The closest isotherm rise to this arises in the case of a small pit (created by removing one surface atom). This appears to be discontinuous near $P=0.93$ atm. We have not yet employed sufficient computational resources to examine this functional dependence in detail; the difficulty lies in the divergent fluctuations in coverage when isotherms become so very steep. A nonanalytic dependence of N on P cannot be ruled out at this time. A third curve in Fig. 3 corresponds to the case of a single adatom. Here, too, we find a rapid variation of coverage with P, occurring at somewhat higher $P=0.92$ atm. Finally, one observes another isotherm, corresponding to both an adatom and a pit, i.e., the geometry corresponding to Fig. 1. The rise here is even more rapid than in the single adatom case, which is perhaps curious because the surface is less homogeneous. Similarly surprising, at first glance, is that the rise occurs at even higher $P=0.952$ atm than for the other two heterogeneous cases. Very naively, one might have expected the isotherm for the case of an adatom and a pit to be intermediate between those in the cases of a single impurity, i.e., adatom or pit. That expectation is a consequence of a ''superposition'' supposition, which would be valid if the regions of imperfection were remote from each other, so their effects did not interfere. The rather different reality reflects
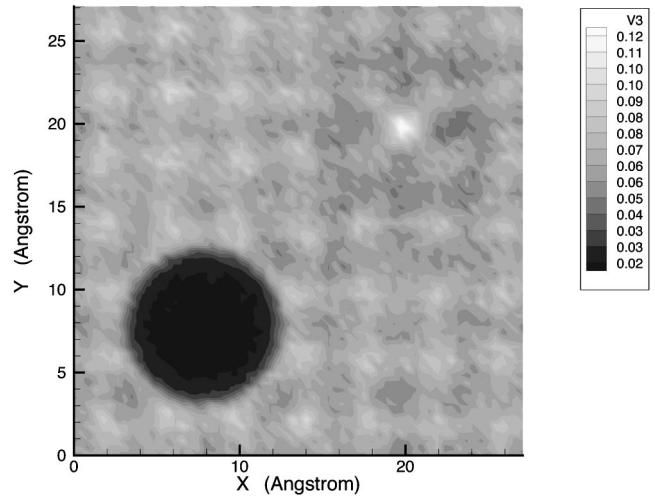
the collective behavior of the wetting transition; the net adsorption is not a superposition of adsorption from distinct regions of the surface. Specifically, the case of both an adatom and a pit is the least attractive overall of the four cases considered, so that the adsorption rise occurs at the highest pressure of all. When this quasitransition ultimately occurs, the thick film (present above the transition) experiences the remote heterogeneity weakly, so that for P higher than the quasitransition value, the net coverage is almost independent of the heterogeneity. This argument rationalizes the increased abruptness of the adatom plus pit isotherm relative to that for the adatom alone.

We define a 2D density in the usual way, by integrating the 3D density of the film over the z coordinate at fixed (x,y). Figures 4–6 display the evolution of this 2D density at the quasitransition in the case of a simulation unit cell which possesses both an adatom and a pit. One sees that the adatom inhibits Ne adsorption near it, even when the (average) net coverage is several layers. Note that the region at
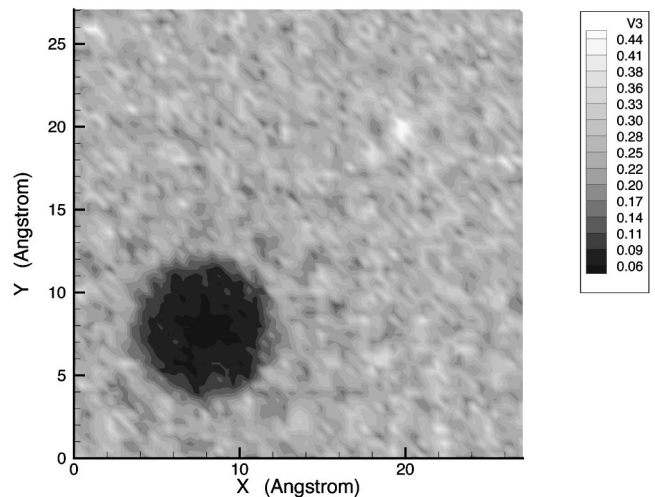

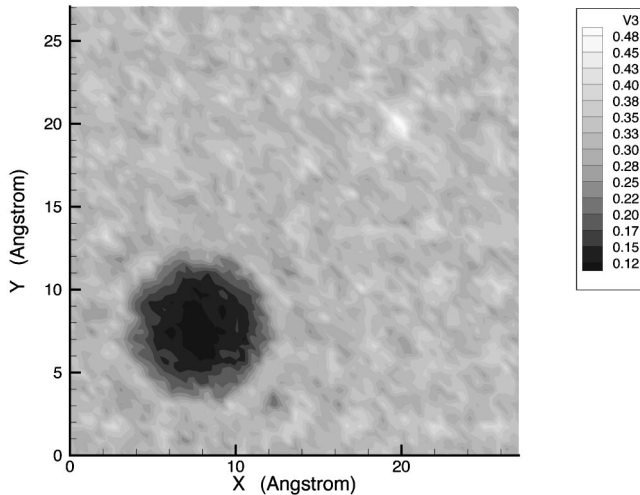FIG. 5. Same as Fig. 4, except at $P=0.965$ atm and $N=180$ (3.67 particles per unit cell).

FIG. 6. Same as Fig. 4, except at $P=1$ atm and $N=237$ (4.83 particles per unit cell).

lateral distance 6 Å from the adatom has, instead, a slightly enhanced density due to the attractive potential (barely visible in Fig. 1) at the intersection of the adatom and the rest of the surface. Finally the pit very slightly increases the adsorption in its vicinity (at all coverages). This can be understood in terms of the attractive potential near the pit in Fig. 1. Because this region of added attraction is so small, the net contribution is only a few percent of a monolayer coverage, i.e., a few Ne atoms per unit cell of the simulation.

Figure 7 shows the evolution of the adsorption behavior as the surface becomes progressively rougher. This general behavior is straightforward to interpret. Increasing irregularity forces the quasitransition value of P higher because the film growth is depressed by the irregularity. Note that the quasitransition in the cases of σ equal to 0.2 and 0.3 Å is nearly discontinuous. The reason for this is that the thick film, above the transition, is insensitive to the heterogeneity below. Hence the dominant effect of the latter is to postpone the jump to ever higher P. Ultimately, at $\sigma = 0.4$ Å, the behavior becomes nonwetting. The cost of depositing a film becomes too great for wetting to occur when the surface is so rough.

Figure 8 displays results indicating the sensitivity of the adsorption to the presence of holes of various size on the surface. Since a small hole (i.e., a single atom) postpones the quasitransition jump, it is not surprising that a large hole postpones it even more. In the case of a very wide and deep hole, however, the behavior is quite different. The hole then is so large as to provide a very attractive environment for Ne, inducing adsorption even at quite low P because of the favorable coordination within the corners of the large hole. Ultimately, at sufficiently high P, the adsorption becomes similar to that on a flat surface in all cases shown.

Figure 9 indicates the adsorption's dependence on the size of islands of adatoms. As discussed above, the single atom yields a steeply rising isotherm at pressure above the flat surface's transition value. A 2×2 adatom cluster produces a more drastic effect: the isotherm is rather smooth, eventually rising to agree with that of the flat surface.

Finally we look at the effect of temperature on the prewetting behavior by simulating the adsorption at lower tempera-
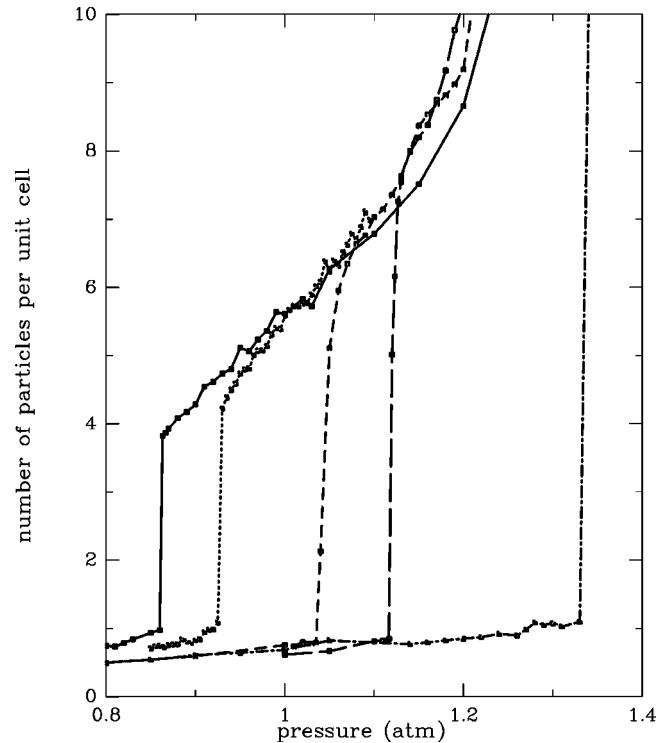

FIG. 7. Adsorption isotherms on a flat surface (full curve) and on rough surfaces with σ value as follows: one missing surface atom (0.08, small dash), six randomly distributed missing atoms (0.2, medium dash), ten random missing atoms (0.3, large dash), and 11 random missing atoms plus six adatoms (0.4, dash-dotted line). The last of these shows a rapid increase in coverage only at saturated vapor pressure, meaning it is a nonwetting surface.

tures. Here we focus on the simplest of the heterogeneous surfaces: the Mg surface with one additional Mg atom added on, and the one with a Mg atom removed. We simulated at temperature intervals of 0.5 K from $T=25$ to 28 K and the results are shown in Figs. 10 and 11. At the lowest and highest temperatures, the result for the flat surface is also shown. As the temperature decreases, the prewetting behavior on the two heterogeneous surfaces becomes more similar, so that by 25 K the isotherms are indistinguishable in shape, different only in the transition pressure. Also, the prewetting transition on the heterogeneous surfaces lies closer to the pressure for the transition on the flat surface at the lower temperature. Presumably, at some even lower temperature the results for all three surfaces would be indistinguishable. This is an interesting result since the effect of heterogeneity on adsorption properties is usually greater at lower temperatures.

For the two heterogeneous surfaces, at all temperatures the prewetting transition occurs at nearly the same pressure. However, as the temperature decreases, the transition on the surface with a single adatom goes from continuous to discontinuous, which means the nominal prewetting critical temperature T_{PW}^c is shifted to a lower value by the addition of the adatom heterogeneity. The prewetting transition on the surface with a missing atom retains its nearly first order (vertical) character at all temperatures studied. Therefore, in the temperature range studied here, there is no change in T_{PW}^c caused by the removal of the Mg adatom from the surface.
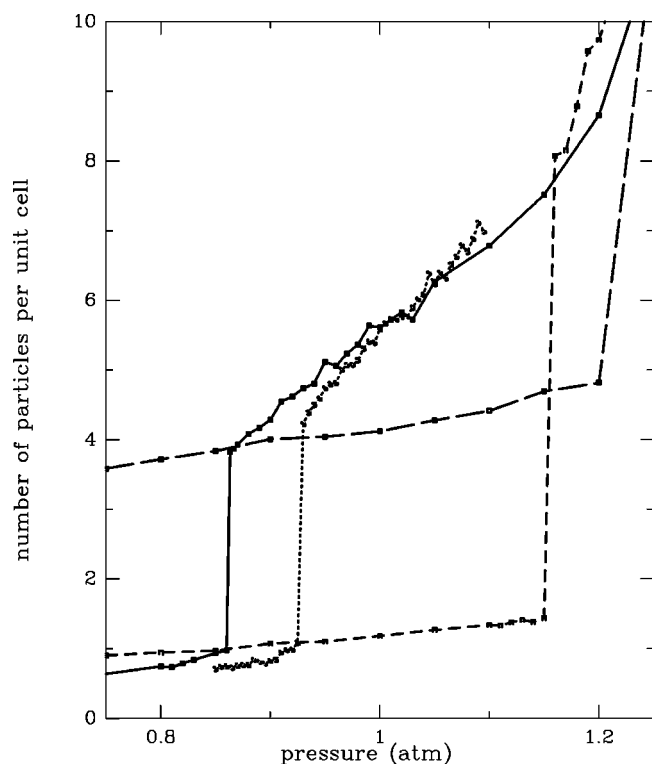
FIG. 8. Adsorption isotherms in the case of a flat surface (full circles), a single missing surface atom (small dash), a cubic hole of depth 8.02 Å (medium dash), and a cubic hole of depth 16.04 Å (large dash).
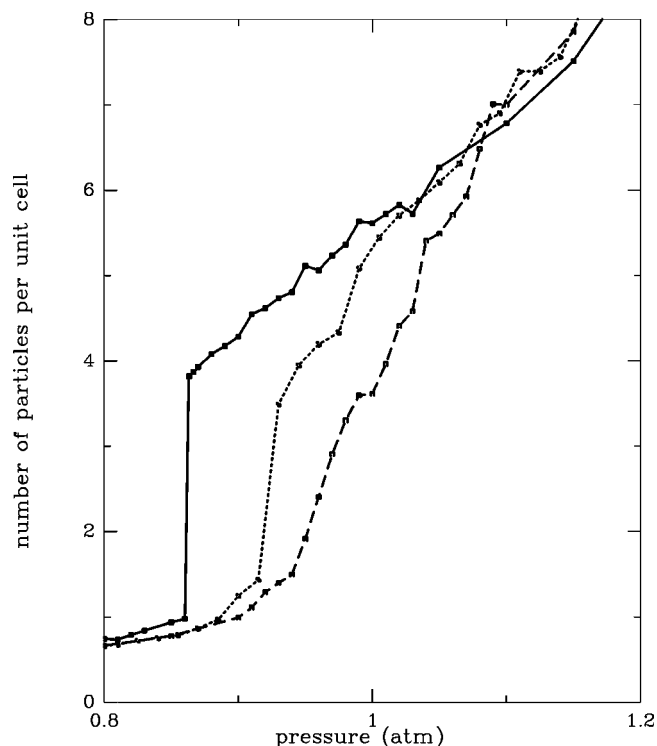

FIG. 9. Adsorption isotherms in the case of a flat surface (full curve), a single adatom (dots), and a 2×2 quartet of adatoms (dashes).
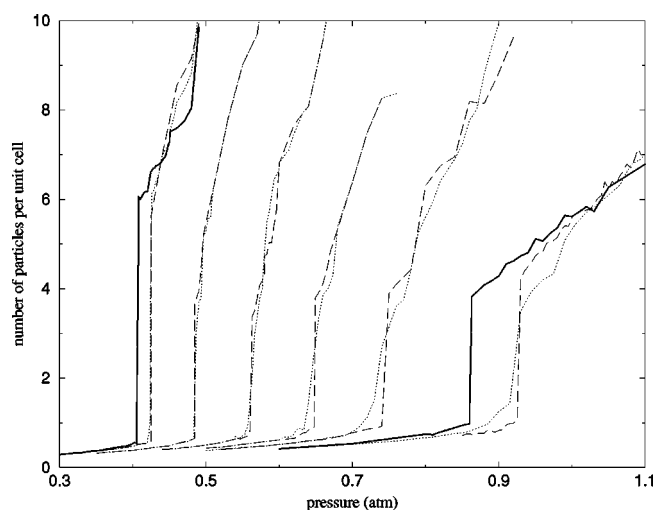

FIG. 10. Adsorption isotherms at different temperatures are shown for the surface with a single missing adatom per unit cell (long dashed lines), and for the surface with one additional adatom per unit cell (dotted lines). The isotherms, from left to right, are for temperatures $T = 25$, 25.5, 26, 26.5, 27, and 28 K. Isotherms for the flat Mg surface are shown for the highest and lowest temperatures (solid lines).

IV. SUMMARY AND CONCLUSIONS

This paper has explored the effect of heterogeneity on the wetting transition. To the best of our knowledge, ours is the first such study for a system which is both realistic and relevant to current or forthcoming experiments. The case of Ne is one which has exhibited wetting transitions on alkali metal surfaces. Unfortunately, these transitions are not amenable to our simulation method because they occur so close to the critical temperature. This has led us to explore the case of Mg, for which the wetting transition is predicted to occur at $\approx 60\%$ of the bulk Ne critical temperature (44.4 K).
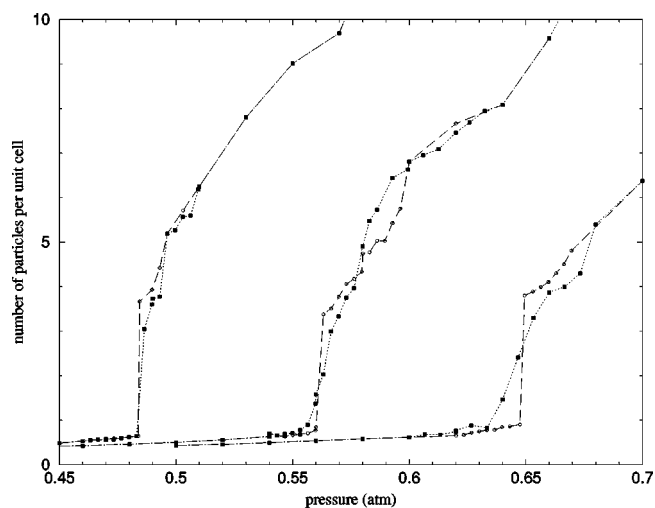

FIG. 11. Same as Fig. 10, but data points are shown with open circles, for the surface with a single missing adatom (long dashed lines), and squares for the surface with one additional adatom (dotted lines). Only the isotherms at $T = 25.5$, 26, and 26.5 K are plotted. Continuous growth is seen at all of these temperatures for the extra adatom surface, while on the other surface a first order phase transition is indicated.

Our most intriguing result is that the shape of the adsorption isotherm is relatively insensitive to small heterogeneity; a 2% (of surface atoms) imperfection frequency leads to an isotherm in one case (single missing atom) which has a nearly first order prewetting transition but with a transition pressure that is nearly 5% greater than that of the flat surface. For the ''inverse'' situation (where a surface atom is added to the flat surface) the ''transition'' is no longer first order, although a steep rise in coverage occurs at the same pressure. When the temperature decreases, this coverage rise becomes more vertical, and eventually exhibits first order character. This is an indication that this small surface imperfection brought about a decrease in the prewetting critical temperature. Our expectation is that when the heterogeneity creates a perturbation in the surface field which is on the order of the correlation length or larger, the wetting will no longer be accompanied by a first order transition. Since correlation lengths decrease as temperature decreases, the order of the transition shifts from continuous to first order for surfaces with sufficiently small perturbations.

As the surfaces become more irregular, the transition is no longer first order (though it may look rather vertical), but the quasitransition pressure continues to shift to higher pressures as the degree of heterogeneity increase (as seen in Fig. 7). In contrast, some forms of heterogeneity, e.g., bumps, lead to the kind of smooth and continuous behavior which might have been expected generically; see Fig. 9. Such behavior manifests no remnant of a transition.

Our results are based on very simple models of the potential, surface geometry, and varieties of heterogeneity. Nevertheless, we suspect that a few provisional conclusions are valid. A general (and unfortunate) conclusion is that adsorption data are not easily ''inverted'' to learn about the nature or degree of heterogeneity. Indeed, we found several instances where heterogeneity yielded sharp, transitionlike behavior which might be misinterpreted as arising from a perfect, or near-perfect, surface. Finally, we have confirmed the expectation that heterogeneity could eliminate the first order wetting transition, at least in the present case.

Future theoretical and simulation work is needed to extend our study. One important question is whether the so-called ''quasitransition'' behavior is actually singular, reflecting a higher order transition. Another question pertains to the behavior of the isotherms very close to the wetting transition temperature. These problems, as well as pursuit of the critical regime, will take much more simulation time than we have employed here. It is clear that such a study will be very useful, as will be experimental study of the sensitivity of the isotherms to surface structure.

[1] P. Taborek and J. E. Rutledge, Phys. Rev. Lett. **68**, 2184 (1992).

[2] J. E. Rutledge and P. Taborek, Phys. Rev. Lett. **69**, 937 (1992).

[3] K. S. Ketola, S. Wang, and R. B. Hallock, Phys. Rev. Lett. **68**, 201 (1992).

[4] E. Cheng, G. Mistura, H. C. Lee, M. H. W. Chan, M. W. Cole, C. Carraro, W. F. Saam, and F. Toigo, Phys. Rev. Lett. **70**, 1854 (1993).

[5] P. Taborek and J. E. Rutledge, Phys. Rev. Lett. **71**, 263 (1993).

[6] G. Mistura, H. C. Lee, and M. H. W. Chan, J. Low Temp. Phys. **96**, 221 (1994).

[7] R. B. Hallock, J. Low Temp. Phys. **101**, 31 (1995).

[8] A. F. G. Wyatt, J. Klier, and P. Stefanyi, Phys. Rev. Lett. **74**, 1151 (1995).

[9] V. F. Kozhevnikov, D. I. Arnold, S. P. Naurzakov, and M. E. Fisher, Phys. Rev. Lett. **78**, 1735 (1997).

[10] F. Hensel and M. Yao, Eur. J. Solid State Inorg. Chem. **34**, 861 (1997).

[11] C. Ebner and W. F. Saam, Phys. Rev. Lett. **38**, 1486 (1977).

[12] J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).

[13] S. Sokołowski and J. Fischer, Phys. Rev. A **41**, 6866 (1990).

[14] M. J. P. Nijmeijer, C. Bruin, A. F. Bakker, and J. M. J. van Leeuwen, Mol. Phys. **72**, 927 (1991).

[15] Y. Fan and P. A. Monson, J. Chem. Phys. **99**, 6897 (1993).

[16] M. J. Bojan, M. W. Cole, J. K. Johnson, W. A. Steele, and Q. Wang, J. Low Temp. Phys. **110**, 653 (1998).

[17] M. W. Cole, Fluid Phase Equilibria **150-151**, 559 (1999).

[18] R. Lipowsky, Phys. Rev. B **32**, 1731 (1985).

[19] P. Tarazona and R. Evans, Mol. Phys. **48**, 799 (1983).

[20] K. Hui and A. N. Berker, Phys. Rev. Lett. **62**, 2507 (1989).

[21] M. Aizenman and J. Wehr, Phys. Rev. Lett. **62**, 2503 (1989).

[22] A. N. Berker, J. Appl. Phys. **70**, 5941 (1991).

[23] A. N. Berker, Physica A **194**, 72 (1993).

[24] C. Bruin, Physica A **251**, 81 (1998).

[25] R. Blossey, T. Kinoshita, X. Muller, and J. Dupont-Roc, J. Low Temp. Phys. **110**, 665 (1998).

[26] M. J. Bojan, G. Stan, S. Curtarolo, W. A. Steele, and M. W. Cole, Phys. Rev. E **59**, 864 (1999).

[27] G. B. Hess, M. J. Sabatini, and M. H. W. Chan, Phys. Rev. Lett. **78**, 1739 (1997).

[28] A. Chizmeshya, M. W. Cole, and E. Zaremba, J. Low Temp. Phys. **110**, 677 (1998).

[29] In the ''academic'' case of a surface consisting of weakly interacting atoms or molecules, of course, one may add their individual contributions for any arbitrary configuration.

[30] As discussed in Ref. [26], these temperatures underestimate by ≈20% what we believe to be the true wetting temperatures on a jellium version of Mg, because of a systematic difference between the theoretical potential of Ref. [28] and the pairwise sum potential used in our simulations. However, the effect of the corrugation is to lower the temperature by a roughly similar amount, so the statement in the text may be accurate by coincidence.