Ground-state phase diagrams for physisorption systems in one dimension

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We examine the ground-state phase diagram for a one-dimensional physisorption system with nearest-neighbor Lennard-Jones interactions. We conclude that the phase diagram is qualitatively different from that of the Frenkel-Kontorowa model. In particular, we find that there are two basic regions, one in which phase changes take place in a first-order manner and a second region of second-order transitions. The sequence of appearance of the first-order transitions is analyzed and the position of the boundary layer separating the two regions is obtained. It is shown that within the boundary layer the phase diagram can become exceedingly complicated, with structure appearing on very small length scales.

The phase diagrams of physisorbed systems have been intensively studied for many years.[1] These systems represent an essential laboratory in which many types of two-dimensional phase transitions can be studied.[2] The early experimental work on the determination of phase diagrams relied on thermodynamic measurements of adsorption isotherms[3] and heat capacities.[4] More recent studies utilizing neutron,[5] x-ray[6] and electron-diffraction[7] techniques have proven to be particularly adept at probing atomic and molecular configurations, especially when used in a complementary mode.

Physisorption phase diagrams are now known for numerous combinations of adsorbates and substrates.[8] For nonspherical adsorbates, the influence of more complicated types of interactions (for example, quadrupolar in N_2) yield low-temperature orientationally ordered phases like the pinwheel and herringbone patterns.[7,9] In general, however, the low-temperature equilibrium configurations for the classical noble gases are simple, close-packed types of structures (the exception being Xe, which is reported as disordered on some substrates[8,10]).

A simple model of physisorption was introduced by Frenkel and Kontorowa[11] (FK) which consists of a set of harmonically bonded atoms residing in a cosine external potential. The model was solved in the continuum limit by Frank and van der Merwe[12] who were able to associate the commensurate-incommensurate transition with an instability with respect to domain-wall (soliton) formation. The ground state was studied in detail by Ying,[13] who concluded that there were first-order transitions in this model. This conclusion was corrected by Aubry, who showed rigorously[14–17] that the transitions in the FK model are continuous in the sense that there are no coexisting phases. The ground state has been subsequently studied by many authors.[18–20] Aubry, in particular, showed that the ground-state equation of motion is equivalent to the much studied standard map.[21] Thus, an enormous body of information is available concerning the FK ground state.

In this paper, we wish to study the ground state of a more realistic physisorption model by replacing the harmonic bond of the FK model by a Lennard-Jones type of interaction. The consequences of this change on the ground-state phase diagram are profound. We shall argue that the FK ground-state phase diagram is qualitatively different from a realistic physisorption ground-state phase diagram.

The key to this difference is the presence of a nonconvex well in a realistic interaction as compared with the convex FK harmonic bond. Aubry's theorem, with regards to the absence of first-order transitions, fails in the presence of a nonconvex potential. Indeed, we shall show that regions of first-order transitions dominate large areas of the phase diagram.

Consider a one-dimensional system of atoms described by a Hamiltonian of the form

$$H=\sum_i [V(u_i)+W(u_i-u_{i-1})] , \tag{1}$$

where the external field is a periodic function $V(u)=V(1+u)$, and the nearest-neighbor interaction W is bounded from below and attains its unique minimum when $u_i-u_{i-1}=\gamma$. In Eq. (1), the variable $u\varepsilon[-\infty,+\infty]$. In the model that we consider here, we make the choices

$$V(u)=\tfrac{1}{2}f(\gamma)V_0[1-\cos(2\pi u)] , \tag{2}$$

$$W(y)=f(\gamma)\left[(\frac{\gamma}{y})^{12}-2(\frac{\gamma}{y})^{6}+1\right] . \tag{3}$$

We have $W''(\gamma)=72f(\gamma)/\gamma^2$ and, thus, by choosing $f(\gamma)=\text{const}\times\gamma^2$, we eliminate the undesirable γ dependence of the curvature at the bottom of the well.[22] For definiteness, we use $f(\gamma)=\gamma^2$.

The ground-state configurations can be obtained by solving the Griffiths-Chou[23–25] (GC) minimax eigenvalue equation:

$$V(u)+\min_{u'}\{W(u'-u)+S(u')\}=\varepsilon+S(u) , \tag{4}$$

here ε is the eigenvalue and $S(u)$ is the (right-hand) eigenfunction. GC showed that ε is the energy per particle for a given configuration. The configuration can be labeled by its winding number ω where $\omega=d/p$ mod(1)

and the integers d and p are defined by $u_{n+p}=d+u_n$. The configuration is determined uniquely from $S(u)$ and the energy. The winding number is defined for d and p relatively prime; however, for unambiguous labeling of the phases, we shall relax that restriction, as will be made clear below.

In Fig. 1, we show the ground-state phase diagram for the sine-Lennard-Jones (sLJ) system of Eqs. (2) and (3). The FK phase diagram is shown in the inset of Fig. 1.

The FK phase diagram has a line of mirror symmetry at $\gamma=0.5$. The major features are the tongues corresponding to the low periodic structures $\omega=\frac{0}{1}, \frac{1}{2}, \frac{1}{3}$, and $\frac{1}{4}$. At every value of V_0 there is a finite region of the phase diagram associated with every rational value of ω. The transitions between regions are continuous in the manner described by Aubry.[26]

The sLJ phase diagram differs qualitatively. Clearly there is no symmetry, as a function of γ, in the sLJ phase diagram. There is, however, a general pattern within each unit interval of γ. There exists a value of V_0 above which all transitions are first order. There exist bow-shaped regions at small V_0 centered about $\gamma=0.5,1,5,\ldots$ for which all transitions appear to be second order. There are boundary regions connecting the first- and second-order transition regions where the phase boundaries can be exceedingly complicated.

We shall concentrate on the region $0\leq\gamma<1$. The pattern in the appearance of phases for the first-order part of the phase diagram ($V_0\gtrsim 2$) is $\omega=\frac{1}{1}, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \ldots$ as γ is decreased from 1 to 0. This pattern can be understood in terms of the change in curvature of the interaction due to the presence of the van der Waals tail. Each phase with $\omega=1/p$ corresponds to a grouping of p atoms spaced by γ and each p group is centered at the minimum of adjacent wells in the external potential. This sort of configuration cannot appear in a system like the FK model where large separations relative to γ are as penalized energetically as small separations relative to γ.

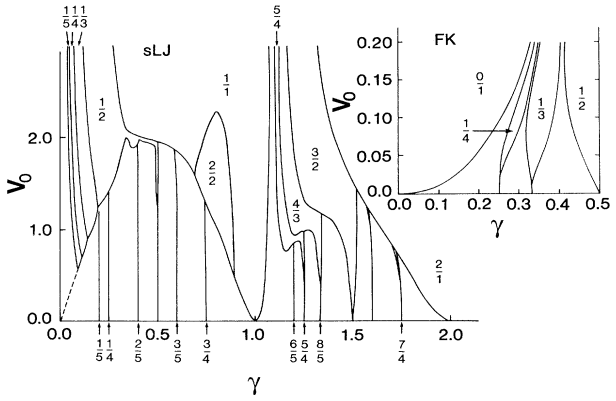

FIG. 1. The phase diagram for the sine-Lennard-Jones system of Eqs. (3) and (4). In the region $0<\gamma<1$, for $V_0\gtrsim 2$, the sequence of transition $\frac{1}{1}, \frac{1}{2}, \frac{1}{3}, \ldots$ is first order. For small V_0 the transitions are second order with almost vertical phase lines. As a consequence of the nonconvex shape of the Lennard-Jones potential, nonminimal periodic configurations can appear, such as the $\omega=\frac{2}{2}$ phase here and the $\omega=n/2n$ region shown in Fig. 2. In the inset we show the phase diagram of the Frenkel-Kontorowa model for comparison.

It is straightforward to compute the first-order phase boundaries within the simple model described above. The boundary between phases $\omega=1/2m$ and $\omega=1/(2m-1)$ is given, in the limit $2m\gamma\ll 1$, by

$$V_0=\frac{1}{\pi^2\gamma^2\left[m(2m-1)(4m-1)/6\right]}\ . \tag{5}$$

The boundary between the $\omega=1/2m$ and $\omega=1/(2m+1)$ phases can be obtained by letting $m\rightarrow m+\frac{1}{2}$ in Eq. (5). This result is in excellent agreement with the numerical work. The phase boundaries are thus curves of the form $V_0=\text{const}/\gamma^2$. The γ^2 dependence is a general result, independent of the particular functional form of $W(y)$, and it is due only to the quadratic minima in $V(u)$. [This result does depend on $W(y)$ having the same generic shapes as Eq. (3): unique minimum and a long-ranged attractive tail with zero asymptotic slope.] From (5), we can show that the width of a $2m$ periodic configuration at fixed V_0 as $m\rightarrow\infty$ is given by

$$\Delta\gamma=\frac{1}{\pi}\left(\tfrac{3}{4}\right)^{3/2}\left[\frac{1}{V_0^{1/2}m^{5/2}}\right]\ . \tag{6}$$

The vertical phase boundaries in the second-order region indicate that the configurations within this region can be modeled as $\omega=\gamma$. The energy per particle for an $\omega=\gamma$ phase is given by $E_\gamma=\frac{1}{2}V_0f(\gamma)$. The energy per particle for the $\omega=\frac{1}{1}$ phase is given by

$$E_{1/1}=f(\gamma)(\gamma^{12}-2\gamma^6+1)\ .$$

Thus, the phase boundary between the $\omega=\gamma$ phases and the $\omega=\frac{1}{1}$ phase is given by

$$V_0=2(\gamma^{12}-2\gamma^6+1)\ . \tag{7}$$

This remarkable result shows that the shape of this phase boundary is a reflection of the underlying microscopic interparticle potential. This is evident from Fig. 1.

The shape of the interfacial region between the $\omega=\gamma$ phases and the $\omega=1/2m$ phases can be shown to be given, in general, by

$$V_0=\frac{2\sin(\pi\gamma)}{\sin(2\pi m\gamma)}W[1-(2m-1)\gamma]\ , \tag{8}$$

and for $\omega=1/(2m-1)$ let $m\rightarrow m-\frac{1}{2}$ in Eq. (8). Now using (5) we can eliminate m in (8) in the large-m and small-γ limit to obtain

$$V_0=\frac{2\sin(\pi\gamma)}{\sin\left[\left(6\pi\gamma/V_0\right)^{1/3}\right]}[1+O(\gamma^6)]\ . \tag{9}$$

An approximate solution of (9) for $\gamma\ll 1$ is $V_0/\gamma\approx 2\pi$ (which works because $3^{1/3}\approx\pi/2$) and this is shown as the dashed line in Fig. 1.

The $\omega=\frac{2}{2}$ phase shown in Fig. 1 is another type of first-order sequence which can appear in this system. Configurations with *nonminimal periodicity* are forbidden

in FK-type systems by rigorous results due to Aubry. In the sLJ system, the nonconvex part of the interaction allows such a phase to be energetically favorable with respect to the $\omega=\frac{1}{1}$ by allowing the system to lower its energy by stretching one bond and shrinking the neighbor bond. The $\frac{2}{2}$-$\frac{1}{1}$ coexistence region in Fig. 1 is given by

$$V_0=24\gamma^6(7-13\gamma^6)/\pi^2 .$$

This produces a region with a maximum at $\gamma=(\frac{7}{26})^{1/6}\approx 0.803\,56$ and $V_0=\frac{6}{13}(7/\pi)^2\approx 2.2914$.

The boundary layer between the regions of second- and first-order transitions can be rather complicated. In Fig. 2, we blow up the phase diagram in the vicinity of $V_0=2$ and $\gamma=0.4$. This interesting structure is a connection between the $\omega=\frac{1}{2}$ phase in the first-order region and the $\omega=\frac{1}{2}$ phase in the second-order region. It consists of a series of regions of configurations of the type $\omega=n/2n$, for n an integer, connected by first-order transitions. The region is formed because of the ability of the system to lower its energy by stretching and shrinking nearest-neighbor bonds. Thus, the $\omega=\frac{1}{2}$ configuration has atoms at $\{x,1-x\}$ and the $\omega=\frac{2}{4}$ configuration has atoms at $\{x,1-x,1+y,2-y\}$ with $x+y=\gamma$. Thus, the $\omega=\frac{2}{4}$ system has approximately three bond lengths of γ and one unit bond length. This pattern is maintained for the higher periodic configurations. Thus, we may describe the appearance of these $\omega=n/2n$ states by $(2n-1)\gamma_{2n}+1=n$ or

$$\gamma_{2n}=(n-1)/(2n-1) ,$$

where γ_{2n} is the value of γ at which the system makes a transition from a state with period $2n-2$ to a state with period $2n$. This relation predicts the occurrence of the transitions with remarkable accuracy (e.g., $n=2\rightarrow\gamma_4=0.333$, $n=3\rightarrow\gamma_6=0.400$, etc). We can also approximately compute the width of the regions as a function of n. Let $\Delta_n\equiv\gamma_{n+1}-\gamma_n$, then $\Delta_n=1/[(2n)^2-1]$ or

$$\lim_{n\rightarrow\infty}\Delta_n\approx\frac{1}{(2n)^2} .$$

We note that $\gamma_\infty=\frac{1}{2}$; however, at $\gamma\sim 0.49$, this sequence of states meets the $\omega=\frac{1}{2}$ tongue. Thus, there is a maximum periodic state in this sequence which can be estimated from the coexistence line at

$$\gamma\approx 0.49\rightarrow 2n_{\max}\approx 500 .$$

Thus, $\gamma=0.49$ is not an accumulation line of $n/2n$ phases. It should also be noted that there are triple points located at the top and bottom of each coexistence line. The energy per particle for an $\omega=n/2n$ system can be easily written using this model:

$$E_{n/2n}=\frac{1}{2n}f(\gamma)\left[2n\left[\frac{V_0}{2}\right]+\gamma^{12}-2\gamma^6+1\right] .$$

Since $\gamma<\frac{1}{2}$, this approximate energy is nearly degenerate with the $\omega=\gamma$ configurations and thus, from Eq. (7), we expect that the boundary region of the phase diagram around $V_0\approx 2$ will be complex.

There is considerable additional structure in this region which appears at small length scales. In Fig. 3, we show a portion of the boundary of the $\omega=\frac{3}{6}$ configuration. There are islands of phases sitting within the $\omega=\frac{3}{6}$ region, there is a region where the $\omega=\frac{6}{13}$, $\frac{5}{13}$, and $\frac{5}{12}$ are mixed together on a length scale much smaller than Fig. 3, and there is (to numerical accuracy) a quadruple point signaling coexistence of the $\omega=\frac{3}{6}$, $\frac{2}{6}$, $\frac{6}{13}$, and $\frac{5}{13}$ phases. There are also numerous triple points.

The region $1,\leq\gamma<2$ shown in Fig. 1 is similar in structure to the region with $0\leq\gamma<1$. There is a large-V_0 first-order transition region and a small-V_0 second-order transition region separated by a boundary layer which can be complicated. The boundary with the $\omega=\frac{2}{1}$ phase has the same interesting shape as the $\omega=\frac{1}{1}$ boundary because of a scaling relationship in Eq. (7), $\gamma\rightarrow\gamma/n$ for an

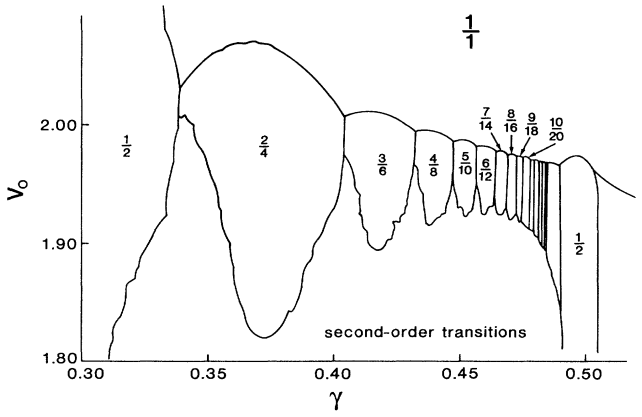

FIG. 2. A blowup of the connection between the $\omega=\frac{1}{2}$, first-order region and the $\omega=\frac{1}{2}$ second-order region. The sequence of phases with $\omega=n/2n$ can be modeled as groups of $2n-1$ atoms separated by spacing γ and one pair separated by unit spacing. The boundary between the region of second-order transitions and the $\omega=n/2n$ phases can be complex.

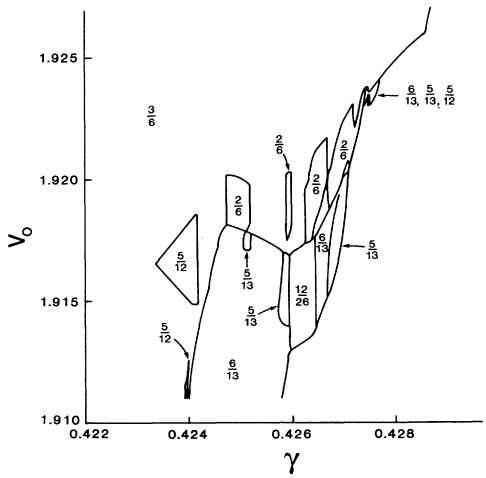

FIG. 3. A blowup of part of the border of the $\omega=\frac{3}{6}$ phase in Fig. 2 showing the extremely complex array of configurations at this length scale.

$\omega = n/1$ phase. In this region of γ, connections between the first- and second-order regions, like that of Fig. 2, appear for $\omega = \frac{3}{2}$, $\frac{4}{3}$, $\frac{5}{4}$, and $\frac{6}{5}$. Some of the smooth-looking boundaries (like those of the $\omega = \frac{5}{4}$ and $\frac{6}{5}$ phases) show much additional structure when viewed on a smaller length scale than Fig. 1.

In this note we have discussed the ground-state phase diagram for a realistic one-dimensional physisorption model consisting of a chain of particles interacting with nearest-neighbor Lennard-Jones forces and placed in an external cosine potential. We have shown that this system has a qualitatively different ground state than the canonical FK model. The Lennard-Jones potential is nonconvex, permitting first-order transitions to appear. The physical basis for this behavior is that the asymmetry of the potential in the neighborhood of the point of inflexion permits the system to lower its energy in some ranges of V_0 by shrinking and stretching neighboring bond lengths.

There may be some interesting experimental consequences. As noted above, the reported ground-state configurations of the classical noble gases tend to be close packed and simple. We can predict that, if an adatom-substrate combination can be found such that the adatom-adatom equilibrium spacing is half of the periodicity of the substrate and that the system is strongly bound in the sense that the corrugation height is twice the adatom-adatom well depth, then the ground state will occur in a region of the phase diagram where its structure may be exceedingly complicated. There has been some interest in chemisorbed quasi-one-dimensional systems.[27–30]

There has been a great deal of recent effort in examining the phase diagrams of systems interacting with nonconvex $W(y)$. Yokoi, Tang, and Chou[31] examined the chiral XY model. They found an extremely rich structure that included superdegenerate points, multiphase points, an accumulation point of triple points, and winding numbers with nonminimal periodicities. Marchand, Hood, and Caillé calculated phase diagrams for model nonconvex $W(y)$'s with a convex (parabolic) $V(x)$. They found first-order phase transitions, superdegenerate points, winding numbers with nonminimal periodicity, and a possible quasicontinuous transition.[32] Marianer and Bishop[33] examined the statics and some dynamics for a nonconvex W, Sasaki and Floria,[34] using a more complicated version of the perturbed sinusoidal V of Griffiths and Chou,[23] found the occurrence of asymmetric periodic structures, first-order phase transition, and other features. Miller examined the ground state of a chain on a discretized triangular lattice and found bands of superdegenerate points, nonminimally periodic structures, and evidence that taking the continuum limit is not simple.[35] We believe that the phase diagram of Fig. 1 represents the generic type that applies to general physisorbed-type systems.

[1] J. G. Dash, *Films on Solid Surfaces* (Academic New York, 1975).

[2] See, for example, *Phase Transitions in Surface Films,* Vol. 51 of *NATO Advanced Study Institute,* edited by J. G. Dash and J. Ruvalds (Plenum, New York, 1980).

[3] A. Thomy and X. Duval, J. Chim. Phys. **66**, 1966 (1969); **67**, 1101 (1970).

[4] M. Bretz *et al.*, Phys. Rev. A **8**, 1589 (1973).

[5] See, for example, H. Taub in *Vibrational Spectroscopies for Adsorbed Species,* ACS Symposium Series No. 137, edited by A. T. Bell and M. L. Hair (ACS, New York, 1980), and references cited therein.

[6] D. E. Moncton *et al.*, Phys. Rev. Lett. **46**, 1533 (1981).

[7] See, for example, S. C. Fain, Jr., Ber. Bunsenges. Phys. Chem. **90**, 211 (1986), and references cited therein.

[8] For a partial compilation see H. Ohtani *et al.*, Surf. Sci. **23**, 155 (1986).

[9] H. Taub, in *The Time Domain in Surface and Structural Dynamics,* Vol. 228 of *NATO Advanced Study Institute,* edited by G. J. Long and F. Grandjean (Plenum, New York, 1987).

[10] See the discussion of Xe/Ag(111) in L. W. Bruch and J. M. Phillips, Surf. Sci. **91**, 1 (1980), and references cited therein.

[11] Y. I. Frenkel and T. Kontorowa, Zh. Eksp. Teor. Fiz **8**, 1340 (1938).

[12] F. C. Frank and J. H. van der Merwe, Proc. R. Soc. London, Ser. A **198**, 205 (1949); **198**, 216 (1949).

[13] S. C. Ying, Phys. Rev. B **3**, 4160 (1971).

[14] S. Aubry, J. Phys. (Paris) **44**, 147 (1983).

[15] M. Peyard and S. Aubry, J. Phys. C **16**, 1593 (1983).

[16] S. Aubry and P. Y. LeDaeron, Physica D **8**, 381 (1983).

[17] S. Aubry, Physica D **7**, 240 (1983).

[18] G. Theodorou and T. M. Rice, Phys. Rev. B **18**, 2840 (1978).

[19] A. D. Novaco, Phys. Rev. B **22**, 1645 (1980).

[20] S. R. Sharma, B. Bergersen, and B. Joos, Phys. Rev. B **29**, 6335 (1984).

[21] See, for example, B. V. Chirikov, Phys. Rep. **52**, 263 (1979); J. M. Greene, J. Math. Phys. **20**, 1183 (1979); S. J. Shenker and L. P. Kadanoff, J. Stat. Phys. **27**, 631 (1982); J. N. Mather, Topology **21**, 457 (1982).

[22] J. M. Phillips (private communication).

[23] R. B. Griffiths and W. Chou, Phys. Rev. Lett. **56**, 1929 (1986).

[24] W. Chou and R. B. Griffiths, Phys. Rev. B **34**, 6129 (1986).

[25] J. E. Byrne and M. D. Miller, Phys. Rev. B **39**, 374 (1989).

[26] S. Aubry, in *Solitons and Condensed Matter Physics,* edited by A. Bishop and T. Schneider (Springer, Berlin, 1978).

[27] G. Ertl and J. Küppers, Surf. Sci. **21**, 61 (1970).

[28] H. A. Englehardt and D. Menzel, Surf. Sci. **57**, 591 (1976).

[29] K. Christmann and J. E. Demuth, J. Chem. Phys. **76**, 6308 (1982).

[30] K. De'Bell, Phys. Lett. A **126**, 197 (1987).

[31] C. S. O. Yokoi *et al.*, Phys. Rev. B **37**, 2173 (1988).

[32] M. Marchand *et al.*, Phys. Rev. Lett. **58**, 1660 (1987); Phys. Rev. B **37**, 1898 (1988).

[33] S. Marianer and A. R. Bishop, Phys. Rev. B **37**, 9893 (1988).

[34] K. Sasaki and L. M. Floria, J. Phys. **1**, 2179 (1989).

[35] M. D. Miller, Phys. Rev. B **41**, 11 396 (1990).