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Structure and Dynamics of a Submonolayer Film Adsorbed on Solid Surfaces*

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The equilibrium configuration of a submonolayer film adsorbed on a solid surface is analyzed via a model classical Hamiltonian. In this model, the adsorbed atoms or molecules are represented by point particles interacting through connecting springs and the substrate is simulated by a two-dimensional periodic potential. The resulting structure of the film is found to be either commensurate or incommensurate with the periodic potential, depending on the force constant of the springs, the amplitude of the periodic potential, and the degree of mismatch between the length of the unstretched springs and the lattice parameter of the underlying periodic potential. Next, the lattice-vibration spectrum of the film is studied. It is found that when the film structure is incommensurate, the excitation spectrum starts from zero energy. In the commensurate structure the phonon spectrum always starts at a finite frequency. It is noted that this difference between commensurate and incommensurate behavior has an important influence on the thermodynamic properties of the film. Qualitative comparison with experimental data is made.

I. INTRODUCTION

A submonolayer film adsorbed on a solid surface is a system with complexity rivaling that of a three-dimensional solid: The atoms or molecules in the film can exist in various phases (and undergo phase transitions); and they interact in a complicated manner with the substrate underneath. Recently, the system of He^3 or He^4 submonolayers adsorbed on solid surfaces has received considerable experimental and theoretical consideration.[1] Dash and coworkers have performed a series of experiments with He submonolayers adsorbed on a copper sponge, and found that at low temperatures the contribution of the adsorbed layer to the specific heat has a T^2 dependence. This peculiar behavior seems to indicate that the film behaves like a two-dimensional solid. However, if we neglect the substrate completely, the concentration of He atoms and vapor pressure under those experimental conditions indicates that it is very unlikely for the adsorbed atoms to condense into a solid phase. Taking the substrate into account, condensation into complete registry seems possible, but then the specific heat would have an exponential behavior at low temperature. This apparent paradox remains unexplained at the present time. However, the latter alternative motivates one to ask the following: When the atoms or molecules exist in a solid phase[2] on the surface, does their configuration bear any simple relation with the lattice underneath, and how will their configuration influence thermodynamic properties? In this paper, we attempt to answer these questions for a system described by a model classical Hamiltonian. The equilibrium configuration (the ground state) is obtained by minimizing the system potential energy, i.e., the kinetic part of the energy is neglected. This is equivalent to neglecting zero-point vibrations. Because of the extreme light mass of helium ^{3} atom, this model may not be directly applicable to a system of He molecules adsorbed on surface: It would be more appropriate for an adsorbate of other rare gas species such as Ne and Ar.

II. HAMILTONIAN AND THE DIFFERENCE EQUATION

In actuality, for many physisorption systems, various central factors, such as the nature of the adsorbate-adsorbate and adsorbate-substrate interactions, are little known. It seems worthwhile, therefore, to investigate idealized models of the system to arrive at a qualitative understanding of the interplay of various factors in determining the equilibrium configuration and excitation spectrum.

We adopt here a "rigid substrate" model. In this model, the substrate is replaced by a sinusoidal potential. The adsorbed molecules are restricted to lie in the x-y plane, and their short-range interaction is approximated by elastic forces between nearest neighbors. Assuming the molecules can be ordered in a square array, the Hamiltonian of the system then takes the form

$$\begin{aligned} H &= T+\varphi\,, \\ T &= \tfrac{1}{2}\sum_{l,m} M\dot{\vec{\mathrm{r}}}^{2}(l,m)\,, \\ \varphi &= \frac{\alpha}{2}\sum_{l,m}\{[x(l+1,m)-x(l,m)-\mu]^2 \\ &\quad +[y(l,m+1)-y(l,m)-\mu]^2\} \\ &\quad +\frac{\beta}{2}\sum_{l,m}\{[x(l,m+1)-x(l,m)]^2 \\ &\quad +[y(l+1,m)-y(l,m)]^2\} \\ &\quad -W\sum_{l,m}\left(\cos\frac{2\pi}{a}x(l,m)+\cos\frac{2\pi}{a}y(l,m)\right). \end{aligned} \tag{2.1}$$

Here $\vec{\mathrm{r}}(l,m)=x(l,m)\vec{\mathrm{e}}_x+y(l,m)\vec{\mathrm{e}}_y$ is the position vector of the $(l$-$m)$th molecule, α and β are force constants, and M and μ are the mass and natural spacing of the adsorbed molecules, respectively. The ordering of the molecule is such that $x(l+1,m) > x(l,m)$ and $y(l,m+1) > y(l,m)$.

In this Hamiltonian, the terms proportional to β in the elastic energy represent a resistance to shearing stress. This term is essential for the two-dimensional character of the excitation spectrum. It is chosen to be of the simple form represented in (1) to allow the x and y components to remain uncoupled. To find the equilibrium configuration $\vec{\mathrm{r}}(l,m)$ of the system, we minimize the potential energy with respect to $\vec{\mathrm{r}}(l,m)$. This results in a set of difference equations

$$\begin{aligned} (\alpha\,\Delta_1^2+\beta\,\Delta_2^2)x(lm) &= 2\pi W/a\,\sin 2\pi/a\,x(l,m)\,, \\ (\beta\,\Delta_1^2+\alpha\,\Delta_2^2)y(l,m) &= 2\pi W/a\,\sin 2\pi/a\,y(l,m)\,, \end{aligned} \tag{2.2}$$

where $\Delta_1^2 x(l,m)\equiv x(l+1,m)-2x(l,m)+x(l-1,m)$ and $\Delta_2^2 x(l,m)\equiv x(l,m+1)-2x(l,m)+x(l,m-1)$. It is convenient to introduce the following dimensionless quantities:

$$\xi\equiv x/a,\quad \eta\equiv y/a,\quad b\equiv\mu/a,\quad U\equiv 4W/\alpha a^2\,.$$

In terms of these quantities, (2.1) and (2.2) take the form

$$\begin{aligned} H=\tfrac{1}{2}\alpha a^2\Bigg(&\sum_{lm}\frac{M}{\alpha}[\dot{\xi}^2(l,m)+\dot{\eta}^2(l,m)] \\ &+[\xi(l+1,m)-\xi(lm)-b]^2 \\ &+[\eta(l,m+1)-\eta(l,m)-b]^2 \\ &+\frac{\beta}{\alpha}[\xi(l,m+1)-\xi(l,m)]^2 \\ &+\frac{\beta}{\alpha}[\eta(l+1,m)-\eta(l,m)]^2 \\ &-\frac{U}{2}\cos 2\pi\eta(l,m)-\frac{U}{2}\cos 2\pi\xi(l,m)\Bigg) \end{aligned} \tag{2.3}$$

and

$$\begin{aligned} (\Delta_1^2+\beta/\alpha\,\Delta_2^2)\,\xi(l,m) &= \pi U/2\sin 2\pi\,\xi(l,m)\,, \\ (\Delta_2^2+\beta/\alpha\,\Delta_1^2)\,\eta(l,m) &= \pi U/2\sin 2\pi\,\eta(l,m)\,. \end{aligned} \tag{2.4}$$

We expect that two adsorbate systems whose natural spacings differ only by a multiple of the lattice parameter would show a close resemblance in the configurations. To facilitate the discussion of these systems under a single category, we introduce for any of the length z such as η, b, etc. (measured in units of a), the corresponding reduced quantity $\tilde{z}$ defined by the relation

$$\tilde{z}\equiv\mathrm{mod}(z;\,1)=z-p\,, \tag{2.5}$$

p being an integer chosen such that $\mathrm{mod}(z\,;\,1)\in[-\tfrac{1}{2},\tfrac{1}{2}]$. These reduced quantities allow an easy physical interpretation. For example, $\tilde{\xi}(l,m)$ and $\tilde{\eta}(l,m)$ are just the coordinates of the (l,m)th particle reduced to the first unit cell of the substrate periodic potential.

A model Hamiltonian similar to that described by Eq. (1) has been analyzed by Frank and Van Der Merwe[4] in their theory of two-dimensional dislocations (Ref. 4 will be hereafter referred to as FV). These authors approximated the resultant difference equation by the corresponding differential equation and obtained a closed form for the solution of $x(l,m)$, regarding l,m as continuous variables. The result obtained by FV is qualitatively successful in explaining various dislocation phenomena. However, the validity of the differential equation solution is limited to a small region where the phases $\tilde{x}(l,m)$, $\tilde{y}(l,m)$ are slowly varying functions of l and m. Moreover, within such an approximation, one cannot determine whether the final spacing of the molecules in the monolayer bears any simple fractional relation to the period of the periodic potential. This question of "commensurability" of the structure has important consequences for the excitation spectrum of the film, as we shall see in later sections. For these reasons, we propose to study the Hamiltonian in (2.3) retaining the discrete nature of the configuration $\vec{\mathrm{r}}^{\,0}(l,m)$. This will allow us to look into the finer details of the configuration $\vec{\mathrm{r}}^{\,0}(l,m)$, and a generalization of the concept of "pseudomorphism" (adsorbate being in registry with the substrate). In the region where the phase of the solution is slowly varying, we obtain good agreement with the result obtained by FV.

III. BOUNDARY CONDITIONS

It is easy to see from the form of the Hamiltonian that because of the assumed form for the shearing stress, the configuration in the lowest-energy state has the property

$$\xi(l,m)=\xi(l)\ ,\quad \eta(l,m)=\eta(m)\ , \tag{3.1}$$

and the problem of determining the structure is reduced to two one-dimensional problems. We shall discuss below only the solution for $\xi(l)$. The solution for $\eta(m)$ follows in an identical way. Equation (1.4) now becomes a set of two second-order nonlinear difference equations. We still need to specify the boundary conditions. For a submonolayer film, the appropriate boundary condition is to allow the substrate potential to extend over an infinite area. For the molecules on the boundary, we could, of couse, use the open end boundary condition by specifying that the tension in the spring joining the boundary particle to the next one be set to zero. Mathematically, this proves to be inconvenient. We know from the theory of lattice dynamics that if N^2 is the total number of molecules in the film, the influence of boundary conditions on the bulk properties goes down as $1/N$.[5] Hence, in the limit $N\to\infty$, i.e., for a film covering a larger surface area, we can safely replace the actual system by a film of infinite extent. The general form for the solution $\xi(l)$ may now be written as

$$\xi(l)=lc+d+\delta(l)\ . \tag{3.2}$$

Here c is the mean spacing of the molecules in the equilibrium state (in units of a) and can be quite different from the natural spacing b. d is chosen such that the term $\delta(l)$, which describes deviation from a rigid lattice, satisfies the property

$$\langle\delta(l)\rangle=0\ , \tag{3.3}$$

where $\langle\cdots\rangle\equiv\lim_{N\to\infty}(1/N)\sum_{m=1}^{N}(\cdots)$, since the nonvanishing average of $\delta(l)$ can be adsorbed in the initial phase d. The function $\delta(l)$ can be Fourier analyzed as

$$\delta(l)=\sum_{q_s} t(s)\,\sin 2\pi(q_s\,l+e_s)\ ,\quad q_s\in(0,\pi)\ . \tag{3.4}$$

We can now give a simple classification of the types of solution $r(l,m)$.

a. Commensurate. This is a structure for which the phase angle of the molecules in the external potential is periodic, i.e.,

$$\tilde{\xi}(l)=\tilde{\xi}(l+p)\quad\text{for all } l,m\ ,$$

$$\tilde{\eta}(m)=\tilde{\eta}(m+p)\quad\text{for all } l,m\ , \tag{3.5}$$

p being an integer.

We define the smallest value of p for which (4.4) can be satisfied as the *order* of the commensurate structure. It is easy to see that the mean spacing c and the Fourier coefficients q_s must then assume the form p_1/p, p_1 being an arbitrary integer. According to our definition, commensurate structure of a given order p includes a whole class of structures whose mean spacings differ from each other by a multiple of the lattice parameter a. For example, a film which is in perfect registry with the substrate and another film having a (2×1) structure are both classifed as first-order commensurate structure. We note that a commensurate structure of order p is composed of superlattices with each unit cell containing p^2 molecules.

b. Incommensurate. If any of the quantities c and q_s is irrational, the structure is nonrepeating. We call such a situation noncommensurate.

It is clear from the above definition that the incommensurate structure is just the limiting case of commensurate structure when its order approaches infinity. However, as we shall see in Sec. IV, the difference between the total energy of the commensurate and incommensurate state decreases as the order p increases. Hence, when the order is much larger than unity, the question of "commensurability" is somewhat academic. For practical purposes, a convenient way of description is to introduce a cutoff $\bar{p}$ in the order of the commensurate structure, beyond which we make no distinction between the two classes of structure. Before we go on to calculate the energy of the various structures, we should point out that the present definition of commensurate and incommensurate structure bears close relation with the various concepts such as "coincident structure" and "registry"[6] which have appeared in the literature of surface physics.

IV. GROUND-STATE ENERGY OF COMMENSURATE STRUCTURES

In this section, we restrict our discussion to commensurate structures with order $p\leq3$. We treat each commensurate structure separately according to its order.

a. First order ($p=1$). When $p=1$, $\delta(l)$ is identically zero and $x(m)$ assumes the simple form

$$\xi(l)=p_0 l+d_1\ ,\quad \eta(m)=p_0 m+d_2\ . \tag{4.1}$$

Substitution of (4.1) into the expression for potential energy gives

$$E_1\equiv 2\varphi_1/N^2\alpha a^2=b^2-\tfrac{1}{2}U[\cos 2\pi d_1+\cos 2\pi d_2]\ . \tag{4.2}$$

For E_1 to be a minimum, p_0, d_1, and d_2 should obviously be chosen to satisfy the following:

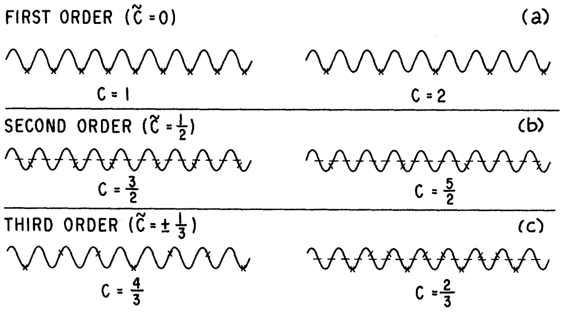

FIG. 1. Schematic diagram of commensurate structures of order 1–3. × denotes position of an adatum in the external periodic potential. For each order, we have illustrated two structures whose mean spacings differ only by a multiple of the wavelength of the periodic potential.

$$p_0=b-\tilde{b}\ , \tag{4.3}$$

$$d_1=d_2=0\ . \tag{4.4}$$

The potential energy is then

$$E_1=\tilde{b}^{\,2}-U\ . \tag{4.5}$$

The physical picture of this state is exceedingly simple. It is shown schematically in Fig. 1(a). Every molecule is located in a minimum of the potential well and equally spaced.

b. Second order ($p=2$). The general form of $\xi(l)$ for $p=2$ is

$$\xi(l)=cl+d+t\sin(l\pi+2\pi e)\ , \tag{4.6}$$

with $\tilde{c}=\frac{1}{2}$.

Since ξ and η directions are completely symmetric, we have also

$$\eta(m)=cm+d+t\sin(m\pi+2\pi e)\ . \tag{4.7}$$

Substitution of (4.6) and (4.7) into the potential energy gives

$$E_2\equiv 2\varphi_2/N^2\alpha a^2=(b-c)^2+4t^2\sin^2 2\pi e + U\sin 2\pi d\ \sin(2\pi t\sin 2\pi e). \tag{4.8}$$

The correct choice of the quantities c, d, e, and t are based on the consideration that they should render the potential energy a minimum. We leave the details of the determination of their values to the Appendix and only list the results below:

$$c=b-\tilde{b}+\tfrac{1}{2}\operatorname{sgn}(\tilde{b})\ ,$$

$$\text{where } \operatorname{sgn}\tilde{b}\equiv|\tilde{b}|/\tilde{b}\ , \tag{4.9}$$

$$d=\tfrac{1}{4},\quad e=-\tfrac{1}{4}\ ,$$

and t is given by the solution of the transcendental equation

$$t=\pi U/4\cos 2\pi t,\quad t\in[0,\tfrac{1}{4}]\ . \tag{4.10}$$

c. Third order ($p=3$). The general form of $\xi(l)$ for $p=3$ is

$$\xi(l)=cl+d+t\sin 2\pi(cl+e)\ , \tag{4.11}$$

with $\tilde{c}=\pm\frac{1}{3}$, and a similar expression holds for $\eta(m)$. In terms of (4.11), the expression for potential energy is now

$$E_3\equiv 2\varphi_3/N^2\alpha a^2=(b-c)^2+\tfrac{3}{2}t^2 - U\langle\cos 2\pi[cl+d+t\sin 2\pi(cl+e)]\rangle\ . \tag{4.12}$$

The procedure by which values of c, d, e, and t are determined is again described in the Appendix. The result is

$$c=b-\tilde{b}+\tfrac{1}{3}\operatorname{sgn}(\tilde{b})\ ,\quad d=0,\quad e=\tfrac{1}{2}\ ; \tag{4.13}$$

t is given by the solution of the transcendental equation

$$t=\pi U/3[J_1(2\pi t)+\cos 2\pi t]\ ,\quad t\in[0,t_0]\ , \tag{4.14}$$

where t_0 correspond to the first zero of $J_1(2\pi t)+\cos 2\pi t$. Various commensurate structures of order 1–3 are illustrated schematically in Fig. 1.

V. GROUND-STATE ENERGY OF INCOMMENSURATE STRUCTURES $(p\to\infty)$

Commensurate structures of small order can be treated exactly as seen in the previous paragraphs. However, when the order of the structure approaches infinity, such an exact solution is no longer feasible. For an incommensurate structure, $\xi(l)$ is now represented by the full series

$$\xi(l)=cl+d+\textstyle\sum_s t(s)\sin 2\pi(q_s+e_s)\ , \tag{5.1}$$

where c and q_s are irrational numbers. For the energy to be an extremum, $\xi(l)$ must be a solution of the difference equation (2.5):

$$\Delta_1^2\xi(l)=\pi U/2\sin 2\pi\xi(l)\ . \tag{5.2}$$

We introduce the Green's function $G(l,l')$ defined by the equation

$$\Delta_1^2 G(l,l')=\delta_{l,l'}\ . \tag{5.3}$$

Then the general solution of $\xi(l)$ may be written as

$$\xi(l)=cl+d+\sum_{l'}G(l,l')\pi U/2\sin 2\pi\xi(l')\ . \tag{5.4}$$

The Green's function $G(l,l')$ is easily found as

$$G(l,l')=\int_{-1/2}^{+1/2}dk[e^{ik(l-l')2\pi}](4\sin^2 k\pi)^{-1}\ . \tag{5.5}$$

Substitution of (5.5) into (5.4) and using the method of iteration yields the following expansion for $\xi(l)$:

$$\xi(l)=lc+d+\sum_{s=1}^{\infty}t(s)\sin 2\pi s(cl+d)\ , \tag{5.6}$$

the amplitude $t(s)$ being proportional to $(U)^s/\sin sc\pi$. We note that even when $U\ll 1$, the amplitude $t(s)$ can

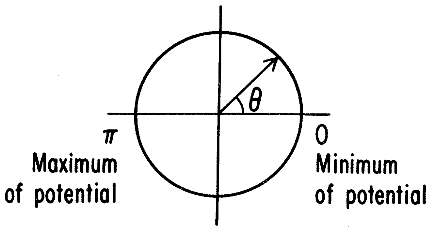

FIG. 2. Position of the phase of the lth adatom $\theta = 2\pi(cl+d)$ relative to the extremal points of the periodic potential.

be of considerable magnitude for some large values of s, say, s_0 ($s_0 \gg 1$) for which $s_0 c$ is close to integer value. This actually indicates an instability towards a commensurate structure of order s_0. As we have emphasized previously, we will neglect the difference between this kind of commensurate structure of large order and a true incommensurate structure. It is seen that in the limit $U \ll 1$, the $s=1$ term in the Fourier series of $\delta(l)$ contributes most to the ground-state energy. This conclusion should hold true even for large values of U from a consideration of phase coherence. Figure 2 is a schematic diagram showing the position of the phase $2\pi(cl+d)$ with respect to the minimum and maximum of the potential; it is not difficult to see that in the Fourier series $\sum_{s=1}^{\infty} t(s) \sin 2\pi s(cl+d)$, only the term with $s=1$ is in the right direction of minimizing the energy for all values of l. Other Fourier components are incoherent. Hence, the equilibrium configuration in this case can be reasonably approximated by retaining only the $s=1$ term in the Fourier series of $\delta(l)$. It is noteworthy that in the second- and third-order commensurate state this choice of Fourier component and phases give the exact answer. The quantities c and d here can be determined by variational method. The details are left in the Appendix. The result is

$$c = b - \pi t^2 \sin \pi c \,,$$
$$E_\infty \equiv 2\varphi_\infty / N^2 \alpha a^2 \qquad (5.7)$$
$$= 2t^2 \sin^2 c\pi + t^4 \pi^2 \sin^2 2\pi c - U J_1(2\pi t) \,,$$

where t is given by the smallest positive solution of the transcendental equation

$$t = \pi U / 2 \sin^2 c\pi \, J_1'(2\pi t) \,. \qquad (5.8)$$

Equation (5.8) can be solved graphically for t as a function of c and U, substitution of the solution into (5.7) gives the corresponding value for b and leads to a functional dependence of t and c on b and U. The energy E_∞ then can also be expressed as a function of b and U. We wish to point out here a very important fact: The potential energy of the incommensurate structure E_∞ is independent of the initial phase d. This conclusion is obviously independent of the approximation used for $\xi(l)$. It leads to a fundamental difference between the excitation spectrum of incommensurate and commensurate structures.

VI. PHASE DIAGRAM

In Sec. V, we have obtained expressions for the potential energy per molecule E_1, E_2, E_3, E_∞, etc., as a function of two basic parameters in the problem: U, the ratio of strength of potential to the elastic energy, and $\tilde{b}$, which is a measure of mismatch of the film and the substrate. In Figs. 3(a) and 3(b), we display the variation of E_1, E_2, E_3, and E_∞ with $|\tilde{b}|$ for two fixed values of $\sqrt{U}$, namely, $\sqrt{U} = 0.32$ and $\sqrt{U} = 0.64$ (E_1, etc., are all even func-

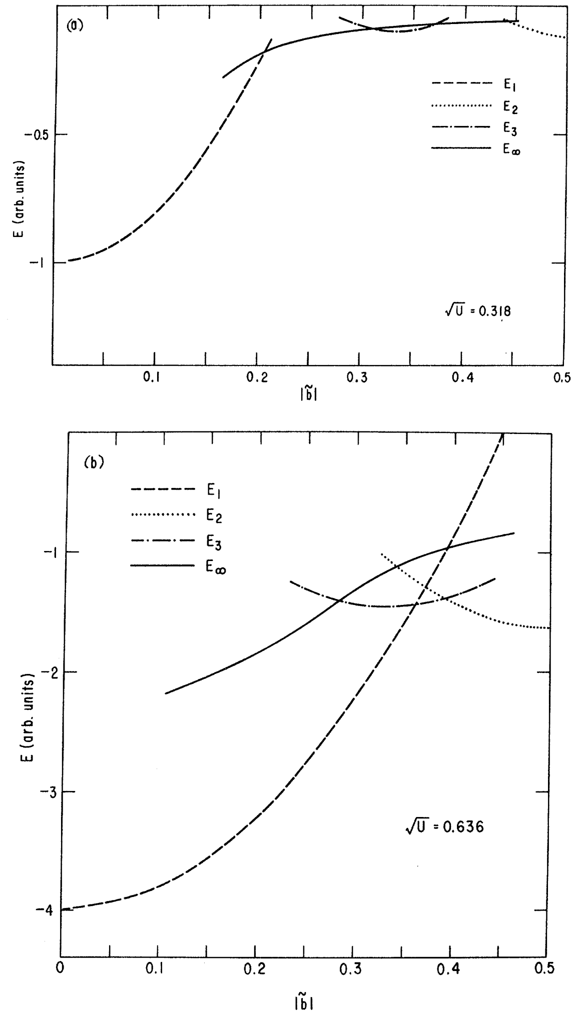

FIG. 3. Potential energy per adatom as a function of mismatch of the spacing ($\tilde{b}$) for two different values of U. E_1, E_2, E_3, E_∞, etc., are the potential energy of the first order, second order, third order, and incommensurate structure, respectively.

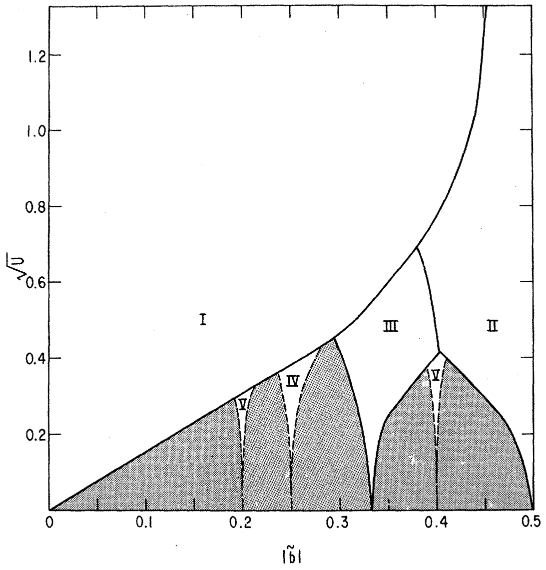

FIG. 4. Phase diagram: I—first order, II—second order, III—third order, IV—fourth order, V—fifth order; shaded region: incommensurate structures and commensurate structures of order >5.

tions of $\tilde{b}$). For $\sqrt{U}=0.32$, commensurate structure of order 1–3 has lower energy for values of $\tilde{b}$ near 0, $\frac{1}{3}$, and $\frac{1}{2}$. Other values of $\tilde{b}$ favor an incommensurate structure. Since we have not computed the energy functions for higher-order commensurate structure, we cannot exclude the possibility of higher-order commensurate structure in this region. When $\sqrt{U}=0.64$ the lowest-energy structure is of order 1–3, and as the value of $|\tilde{b}|$ varies, successive transitions occur in the sequence first order, third order, second order. We can now construct a phase diagram showing the region in $(\sqrt{U},\ |\tilde{b}|)$ space where various structure has the lowest energy. This is shown in Fig. 4. We note the following facts:

(i) For values of $\sqrt{U}<\frac{1}{2}$, the boundary between the first-order commensurate structure and the incommensurate one in $(\sqrt{U}, \tilde{b})$ space is a very nearly straight line corresponding to the condition

$$\sqrt{U}/\tilde{b}=1.54\ . \tag{6.1}$$

Or in terms of the unscaled units

$$(W/a)^{1/2}(\lambda-pa)^{-1}=0.77\ . \tag{6.2}$$

This is in good agreement with the value of critical misfit given by FV for the special case $p=1$. The agreement with the differential equation approach here is not surprising, since the boundary of these two structures lies in the region $|\tilde{b}|<1$, for which the phase of the solution is slowly varying. In Fig. 5, we have plotted $\tilde{c}$ against $\tilde{b}$ for the incommensurate structures at $\sqrt{U}=0.225$. According to the phase diagram, transition between the two structures should occur at $\tilde{b}=0.145$, at which point $\tilde{c}$ jumps from 0 to 0.032. The transition is therefore *first order* in the usual terminology of phase transition. (The reader is cautioned not to confuse between first-order phase transition and a first-order commensurate structure.)

(ii) The range of $\tilde{b}$ (for a fixed U) for which a commensurate structure exists decreases with increasing order of the structure.

It is now obvious how higher-order commensurate structures enter this phase diagram. For example, we have illustrated schematically on the phase diagram where the fourth- and fifth-order structure should appear. The fourth-order structure should occur in a narrow strip around $\tilde{b}=\frac{1}{4}$ and the fifth-order structure around $\tilde{b}=\frac{1}{5}$ and $\tilde{b}=\frac{2}{5}$. As the order increases, the width of each strip decreases. Strictly speaking, a true incommensurate structure only exists in the limit $U\to 0$, i.e., an infinitely weak periodic potential. For values of U between 0.2 and 0.4, we conjecture that the structure of the film would be commensurate of order $p<10$. For $U\geq 0.4$, it can be seen from the phase diagram that the structure is definitely commensurate with order between 1 and 3.

VII. EXCITATION SPECTRUM OF THE MONOLAYER

To study the excitation spectrum, we return to the Hamiltonian H in (1.3). Suppose each molecule is displaced from its equilibrium position by a small amount, i.e.,

$$\begin{aligned}\xi(l,m)&=\xi^0(l)+u(l,m)\ ,\\ \eta(l,m)&=\eta^0(m)+v(l,m)\ .\end{aligned} \tag{7.1}$$

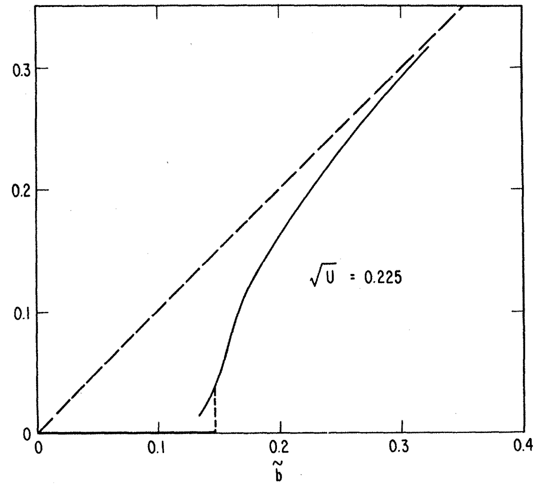

FIG. 5. The mean spacing of the incommensurate structure $\tilde{c}$ as a function of the mismatch $\tilde{b}$. The transition from an incommensurate structure to a first-order structure occurs with a discontinous jump of $\tilde{c}$.

Substituting (6. 1) into expression (2. 3) and noting that

$$\left.\frac{\partial\varphi}{\partial x}\right|_{\xi^0(l)}=0,\quad \left.\frac{\partial\varphi}{\partial y}\right|_{\eta^0(l)}=0\ , \tag{7. 2}$$

we obtain, to second order in u and v, the following expansion:

$$\frac{(H-\varphi^0)}{\alpha a^2}=\tfrac{1}{2}\sum_{l,m}\frac{M}{\alpha}\,[\mathring{u}^2(l,m)+\dot{v}^2(l,m)]$$

$$+\sum_{l,m;l',m'}D^{(1)}_{lm;l'm'}\,u(l,m)u(l'm')$$

$$+\sum_{l,m;l',m'}D^{(2)}_{lm;l'm'}\,v(l,m)v(l',m')$$

$$+\frac{\pi^2U}{2}\sum_{l,m}\cos[2\pi\xi^0(l)]u^2(l,m)$$

$$+\frac{\pi^2U}{2}\sum_{l,m}\cos[2\pi\eta^0(m)]v^2(l,m)\ . \tag{7. 3}$$

Here, the dynamical matrix is given as

$$D^{(1)}_{lm;l'm'}=[\delta_{ll'}\delta_{mm'}(1+\beta/\alpha)$$

$$-\tfrac{1}{2}\delta_{l,l'\pm1}\delta_{mm'}-(\beta/2\alpha)\delta_{ll'}\delta_{m,m'\pm1}]\ , \tag{7. 4}$$

$$D^{(2)}_{lm;l'm'}=[\delta_{ll'}\delta_{mm'}(1+\beta/\alpha)$$

$$-\tfrac{1}{2}\delta_{m,m'\pm1}\delta_{l,l'}-(\beta/2\alpha)\delta_{l,l'\pm1}\delta_{m,m'}]\ .$$

Since the displacements u, v are completely uncoupled in this model, we shall discuss below only those normal modes for which u is finite and $v=0$. The other independent normal modes can be simply obtained by replacing u by v. For the sake of convenience, we assume the film contains N^2 molecules and eventually allow $N^2\to\infty$. We introduce now the standard plane wave expansion

$$u(lm)=(1/N)\textstyle\sum_{\vec q}\varphi(\vec q)e^{i2\pi q_x l}e^{i2\pi q_y m}\ , \tag{7. 5}$$

$\varphi(q)$ satisfying the reality condition

$$\varphi(\vec q)=\varphi^*(-\vec q) \tag{7. 6}$$

In terms of these normal coordinates, the expression for the energy is now

$$\frac{2(E-\varphi)}{Ma^2}=\sum_q\mathring{\varphi}^*(\vec q)\ \varphi^*(\vec q)$$

$$+\sum_{\vec q}\omega_0^2(\vec q)\varphi(\vec q)\varphi^*(\vec q)$$

$$+\sum_{\vec q,\vec q'}F(\vec q,\vec q')\varphi(\vec q)\varphi(\vec q')\ , \tag{7. 7}$$

where

$$\omega_0^2(\vec q)=(2\alpha/M)[1-\cos2\pi q_x]+(2\beta/M)[1-\cos2\pi q_y] \tag{7. 8}$$

and

$$F(\vec q,\vec q')=(\pi^2U\alpha/2M)\langle\cos2\pi[\xi^0(l)]e^{i2\pi(q_x-q_x')}\rangle\,\delta_{q_y,q_y'}\ . \tag{7. 9}$$

For the first-order commensurate structure which is in registry with the potential, $F(q_x,q_x')\equiv\delta_{\vec q,\vec q'}\times\pi^2U\alpha/2M$. The normal-mode frequencies are simply given by

$$\omega^2(\vec q)=(2\alpha/M)[(1-\cos2\pi q_x)$$

$$+(\beta/\alpha)(1-\cos2\pi q_y)+\pi^2U/2]\ ,$$

i. e., the frequency spectrum starts at a finite value $\pi(U\alpha/M)^{1/2}$.

In the second-order commensurate structure, the solution $\xi^0(l)$ is given by

$$\xi^0(l)=\pm l/2+\tfrac{1}{4}-(-1)^l\,t(U)\ ;$$

substituting this into (6. 9) gives

$$F(q,q')=(\pi^2U\alpha/M)\langle\sin2\pi t(U)\,e^{i2\pi(q_x-q_x')l}\rangle\,\delta_{q_y q_y'}$$

$$=(\pi^2U\alpha/M)\sin2\pi t(U)\,\delta_{\vec q,\vec q'}\ . \tag{7. 10}$$

The frequency of the normal modes is in this case given by

$$\omega^2(\vec q)=(2\alpha/M)[(1-\cos2\pi q_x)+\beta/\alpha(1-\cos2\pi q_y)$$

$$+(\pi^2U/2)\sin2\pi t]\ . \tag{7. 11}$$

Again, $\omega(\vec q)$ starts at a finite value $\pi[(U\alpha/M)\sin2\pi t]^{1/2}$ which is lower than the first-order gap $\pi(U\alpha/M)^{1/2}$, except in the limit $t\to0$ which corresponds to the asymptotic region on the phase diagram near $\bar\delta=\tfrac{1}{2}$.

The excitation spectrum of higher-order commensurate structure can be determined in exactly the same manner as in the study of phonon spectrum of crystalline lattice with a basis. The normal modes will be divided into several branches. One general characteristic of commensurate structure is that there *exists no mode with zero frequency value.* This is due to the fact that the ground state of a commensurate structure is nondegenerate—there are no other states of equal energy which can be reached by an infinitesimal symmetry operation. We also note that the gap will decrease with increasing order of the structure.

The treatment of the incommensurate case is more difficult. We shall consider here only the case $U\ll1$, i. e., the weak-potential region, where perturbative theory with U as the expansion parameter is possible. As the phase diagram indicates, this is exactly the region where incommensurate structure is most likely to exist.

Referring back to the solution for the incommensurate structure in Sec. IV, we have

$$\xi^0(l) = cl + d - t\sin 2\pi(cl+d) \tag{7.12}$$

and

$$t = (\pi U/2\sin^2 c\pi)\, J_1'(2\pi t) \ . \tag{7.13}$$

We introduce now the following definition:

$$\lambda \equiv \pi^2 U/2\sin^2 c\pi \ . \tag{7.14}$$

For $\lambda \ll 1$, the solution for t can be obtained in closed form by expanding $J_1(t)$ on the rhs of (6.15) in powers of λ. To first order in λ

$$\begin{aligned} &t = \lambda/2 + O(\lambda^2)\ , \\ &\xi^0(l) = cl + d - (\lambda/2)\sin 2\pi(cl+d) + O(\lambda^2)\ . \end{aligned} \tag{7.15}$$

Substitution of (6.7) into (6.9) gives for the incommensurate structure

$$\begin{aligned} F(q,q') = \frac{\pi^2 U\alpha}{M}\langle \cos 2\pi[cl+d-(\lambda/2)\sin 2\pi(cl+d)]\, e^{i2\pi(q_x-q_x')l}\rangle \delta_{q_y q_y'} &= \lambda(\alpha/M)\sin^2 c\pi[\delta_{q_x, q_x'-c}\, e^{i2\pi d} + \delta_{q_x, q_x'+c}\, e^{i2\pi d}]\,\delta_{q_y, q_y'} \\ &+ \lambda^2(\alpha/2M)\sin^2 c\pi[\delta_{q_x, q_x'} - \tfrac{1}{2}\delta_{q_x, q_x'-2c}\, e^{i2\pi d} - \tfrac{1}{2}\delta_{q_x, q_{x+2c}'}\, e^{i2\pi d}]\,\delta_{q_y, q_y'} + \cdots \ . \end{aligned} \tag{7.16}$$

Following the standard procedures in the theory of lattice dynamics,[5] it can be easily shown that the frequency spectrum can be obtained as the solution of the following infinite secular equation:

$$\begin{vmatrix} \ddots & V & 0 & & & & \\ & -\omega^2+\omega_1^2(\vec{q}-2\vec{c}) & V & 0 & & & \\ & V^* & -\omega^2+\omega_1^2(\vec{q}-\vec{c}) & V & 0 & & \\ & 0 & V^* & -\omega^2+\omega_1^2(\vec{q}) & V & 0 & \\ & & 0 & V^* & -\omega^2+\omega_1^2(\vec{q}+\vec{c}) & V & \\ & & & 0 & V^* & -\omega^2+\omega_1^2(\vec{q}+2\vec{c}) & \\ & & & & 0 & V^* & \\ & & & & & & \ddots \end{vmatrix} = 0, \tag{7.17}$$

Where

$$\vec{q}-\vec{c} \equiv (q_x - c,\ q_y),\ (\vec{q}+\vec{c}) \equiv (q_x + c, q_y)\ ,$$

$$\begin{aligned} &V \equiv (\lambda\alpha/M)(\sin^2 c\pi)e^{i2\pi d} + O(\lambda^2)\ , \\ &\omega_1^2(\vec{q}) = (2\alpha/M)(1-\cos 2\alpha q_x) \\ &\qquad + (2\beta/M)(1-\cos 2\pi q_y) \\ &\qquad + (\alpha/2M)\lambda^2\sin^2 c\pi + O(\lambda^4)\ . \end{aligned} \tag{7.18}$$

To determine $\omega(q)$ to second order in λ^2, it is sufficient to diagonalize a 3×3 block, namely,

$$\begin{vmatrix} -\omega^2+\omega_1^2(\vec{q}-\vec{c}) & V & 0 \\ V^* & -\omega^2+\omega_1^2(\vec{q}) & V \\ 0 & V & -\omega^2+\omega_1^2(\vec{q}+\vec{c}) \end{vmatrix} = 0. \tag{7.19}$$

The three branches of solution of (6.21) are shown schematically in Fig. 6.

For values of q_x near $c/2$ and $-c/2$, $\omega_1(q) \approx \omega_1(q+c)$ and a gap appears in the phonon spectrum. Near the value $q = c/2$, $\omega(\vec{q})$ is approximately determined as

$$\begin{aligned} \omega^2 = \tfrac{1}{2}\ &\omega_1^2(\vec{q}) + \omega_1^2(\vec{q}-\vec{c}) \\ &\pm \tfrac{1}{2}\{[\omega^2(\vec{q}) - \omega_1^2(\vec{q}-\vec{c})] + 4|V|^2\}^{1/2}. \end{aligned} \tag{7.20}$$

Near $q = 0$, the frequency of the lower branch can be determined by the usual perturbation theory

$$\begin{aligned} \omega^2(\vec{q}) &= \omega_1^2(\vec{q}) + |V^2|\{[\omega_1^2(\vec{q}) - \omega_1^2(\vec{q}+\vec{c})]^{-1} + [\omega_1^2(\vec{q}) - \omega_1^2(\vec{q}-\vec{c})]^{-1}\} \\ &= \frac{2\alpha}{M}(1-\cos 2\pi q_x) + \frac{2\beta}{M}(1-\cos 2\pi q_y) + \frac{\alpha}{2M}\lambda^2\sin^2 c\pi \left\{\frac{(\sin^2\pi\tilde{c})(\sin^2\pi q_x) - \sin^2 2\pi q_x}{\sin^2 c\pi - \sin^2 2\pi q_x}\right\} + O(\lambda^4)\ . \end{aligned} \tag{7.21}$$

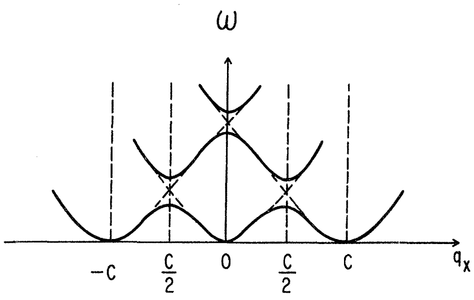

FIG. 6. Phonon spectrum of an incommensurate structure.

Hence, we arrived at the important conclusion that to order λ^4 at last

$$\omega(q=0)=\text{const}\times|q| \quad \text{for} \quad |q|\ll 1 \ . \tag{7.22}$$

The displacement corresponding to the $q=0$ mode is

$$U(l)\propto[1+(\lambda/2)\cos 2\pi(cl+d)] \ . \tag{7.23}$$

This we recognize immediately as the displacement of a molecule when the phase d is changed to $d+\delta d$ (to first order in λ). The existence of a zero-frequency mode is a direct consequence of the fact that the *incommensurate structure is degenerate*. Under an infinitesimal operation which shifts the phase d of every molecule by the same amount we arrive at the same structure. The existence of a zero-frequency mode is therefore expected to hold true beyond perturbative theory.

VIII. APPLICATION OF THE MODEL

Before discussing the connection of our result with the experimental work, we need to have a reasonable estimate of the two important parameters W and $\tilde{b}$ occurring in the model. We can estimate the unscaled values of W and μ by assuming a Lennard-Jones-type interaction among the nearest neighbors of the adsorbates:

$$v(\vec{r})=-4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6] \ . \tag{8.1}$$

The length of the spring constant is approximated by the separating of two molecules for which the potential energy $V(\vec{r})$ is a minimum, i.e.,

$$\mu=\sigma(2)^{1/6} \ . \tag{8.2}$$

The force constant α corresponds to the second derivative of the potential at the minimum, namely,

$$\alpha=\frac{\partial^2 V}{\partial\mu^2}=57.1\,\frac{\epsilon}{\sigma^2} \ . \tag{8.3}$$

The amplitude of the periodic potential W can be obtained by performing a lattice sum with the position of the adsorbed molecule as variable. This has been done for specific physisorption systems.[7,8] We consider here two illustrative systems.

a. Ne *on* Xe. Taking the values of Lennard-Jones parameters for Ne[9] as

$$\sigma_{\text{Ne-Ne}}=2.749\ \text{Å}, \quad \epsilon=35.6\ (°\text{K}),$$

$$a\ (\text{Xe lattice const})=4.31\ \text{Å}\ ,$$

and the following value of W^{10} from Ref. 8, $W=60$ °K, we obtain the following value for $\sqrt{U}$ and $\tilde{b}$:

$$\begin{aligned} U^{1/2}&=(4W/\alpha a^2)^{1/2}=0.218\ , \\ \tilde{b}&=0.31\ . \end{aligned} \tag{8.4}$$

b. Ar *on* Xe. For Ar, $\sigma_{\text{Ar-Ar}}=3.4$ Å, $\epsilon=124$ °K[10], $W=140$ °K, yielding the values for $U^{1/2}$ and $\tilde{b}$

$$U^{1/2}=0.223, \quad \tilde{b}=-0.15\ . \tag{8.5}$$

The phase diagram indicates that with these choices of parameters, Ne on Xe is in the shaded region. According to our previous discussions, at a value of $\sqrt{U}=0.218$, it is mostly likely in a commensurate of order 3–10. The system of Ar on Xe is in the first-order structure, but lies very close to the phase boundary between first-order structure and incommensurate structure. This result offers a qualitative explanation as to why the observed heat of adsorption of Ne on Xe is smaller than the calculated value[8] based on a model of complete registry. For the system of Ar on Xe, which we have shown to be in a first-order structure, the observed value of heat of adsorption does agree fairly well with the theoretical value.

Recent experiments by Dash[11] and co-workers on the specific heat of Ne and Ar submonolayers adsorbed on a copper sponge indicates an $\exp(-A/T)$ dependence at low temperatures. However, the coefficient A is much smaller than the estimate based on a completely registered model. This suggests strongly that the system under study is in a commensurate structure of small order so that the coefficient A is finite but small.

Bassett[12] has studied the deposition of silver and copper on both amorphous carbon and graphite, and of silver on molybdenite. He observed a remarkably high degree of mobility for the translation and rotation of an entire island of overgrowth. This is not difficult to understand within our model of incommensurate structure. The change in the value of the phase from d to $d+\delta d$ corresponds to the motion of an entire island with no energy change. In a more realistic two-dimensional model with rotationally invariant Hamiltonian, we would also expect the layer of film to have a rotational mode at zero frequency. This idea of incommensurate structure is also the basis underlying the theory offered by Reiss[13] in explaining this phenomena. As we have stated at the beginning of this work, if He monolayers adsorbed on an argon-coated surface do form a solid film, then the T^2 specific heat observed by Dash *et al.* can be easily understood by assuming the structure of the film to be incommensurate.

Finally, we discuss briefly how a more realistic Hamiltonian would modify the conclusion reached in this paper. Frank and Van Der Merwe[14] have considered the influence of second harmonic term in the potential and the results remain the same qualitatively, unless the second harmonic term is so large as to produce a new minimum. Within our model, it is easy to see that higher harmonics in the periodic potential play about the same role as higher powers of the first harmonic and hence, would not change the qualitative picture. Recently, Van Der Merwe[15] has also considered a more complicated model which allows for misfits along two interfacial directions. Again, the result is similar to the one-dimensional case.

IX. CONCLUSION

In this paper, we have analyzed the structure of a submonolayer film based on a very idealized model. The structures of the film are classified into two categories—commensurate and incommensurate. The incommensurate structure is defined very naturally as the limiting case of the commensurate structure when the order approaches infinity. It is also demonstrated how the excitation spectrum of the two classes differ from each other. Although the model is too crude to attach much quantitative significance to it, we believe that the characterizations of the structure and excitation spectrum will carry into a more realistic model. These general features could prove very helpful in the theory of epitaxy and surface transport.

Finally, this model serves as a pedagogical system which exhibits a series of first-order phase transitions. This is very similar to the sequence of excitonic instabilities in narrow-gap semiconductors predicted by Kohn.[16]

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APPENDIX

Derivation of E_2, E_3, and E_∞

1. *Second-Order Commensurate State*

According to

$$E_2 = (b-c)^2 + 4t^2 \sin^2 e + U(\sin 2\pi d)\sin(2\pi t \sin 2\pi e)\ , \tag{A1}$$

minimization of E_2 with respect to d, e, and t, respectively, yields the equations

$$\cos 2\pi d \sin(2\pi t \sin 2\pi e) = 0\ , \tag{A2}$$

$$\cos 2\pi e\,[8t + 2\pi U \sin(2\pi d)\sin(2\pi t \sin 2\pi e)] = 0\ , \tag{A3}$$

$$\sin 2\pi e\,[8t \sin 2\pi e + 2\pi U \sin 2\pi d \cos(2\pi t \sin 2\pi e)] = 0\ . \tag{A4}$$

The only choice of d, e, and t which is consistent with these equations while allowing the energy to be a minimum is

$$d = 1/4, \quad e = -1/4\ , \tag{A5}$$

t being then given by the solution of (A4) in the first quarter, i.e.,

$$t = \tfrac{1}{4}\pi U \cos 2\pi t\ , \quad t \in [0, \tfrac{1}{4}]\ . \tag{A6}$$

The choice of c is determined by the condition that $(b-c)^2$ should be a minimum subject to the requirement that $\tilde{c} = \pm\frac{1}{2}$. It is easily seen by inspection that c should be chosen as

$$\tilde{c} = (\operatorname{sgn}\tilde{b})\tfrac{1}{2}\ , \quad c = b - \tilde{b} + (\operatorname{sgn}\tilde{b})\tfrac{1}{2}\ . \tag{A7}$$

Substitution of (A5) and (A6) into (A1) gives

$$E_2 = (\tilde{b} - \tfrac{1}{2}\operatorname{sgn}\tilde{b})^2 + 4t^2(U) - (1/\pi)\,[\pi^2 U^2 - 16t^2(U)]^{1/2}\ , \tag{A8}$$

$t(U)$ being the solution of (A6).

2. *Third-Order Commensurate State*

According to (3.14), we have

$$E_3 = (b-c)^2 + \tfrac{3}{2}t^2 - U\,\langle \cos 2\pi[cl + d + t \sin 2\pi(cl+e)]\rangle\ . \tag{A9}$$

We differentiate E_3 with respect to d, e, and t, respectively, and make use of the mathematical identities[17]

$$\cos 2\pi(t \sin x) = J_0(t) + 2\sum_{s=1}^{\infty} J_{2s}(2\pi t)\cos 2sx\ ,$$

$$\sin 2\pi(t \sin x) = 2\sum_{s=0}^{\infty} J_{2s+1}(2\pi t)\sin(2s+1)x\ . \tag{A10}$$

This leads to the following conditions for E_3 to be an extremum:

$$3t+\pi U J_0(2\pi t)\left[\cos 2\pi(d-e)-\cos 2\pi(2cl+d+e)\right]$$

$$+\pi U\textstyle\sum_s J_{2s}(2\pi t)\left\{\begin{array}{l}\cos 2\pi[-2cl+d-(2s+1)e]-\cos 2\pi[(2-2s)cl+d-(2s-1)e]\\ +\cos 2\pi[2cl+d+(2s-1)e]-\cos 2\pi[(2+2s)cl+d+(2s+1)e]\end{array}\right\}$$

$$+\pi U\textstyle\sum_s J_{2s+1}(2\pi t)\left\{\begin{array}{l}\cos 2\pi[(2s-1)cl+(2s-1)e-d]-\cos 2\pi[(2s+1)cl+(2s+1)e-d]\\ +\cos 2\pi[(2s+1)cl+d+(2s-1)e]-\cos 2\pi[(2s+3)cl+d+(2s+1)e]\end{array}\right\}=0\;, \quad \text{(A11)}$$

$$J_0(2\pi t)\left[\sin 2\pi(d-e)+\sin 2\pi(2cl+d+e)\right]$$

$$+\textstyle\sum_s J_{2s}(2\pi t)\left\{\begin{array}{l}\sin[-2cl+d-(2s+1)e]+\sin[(2-2s)cl+d-(2s-1)e]\\ +\sin[2cl+d+(2s-1)e]+\sin[(2+2s)cl+d+(2s+1)e]\end{array}\right\}$$

$$+\textstyle\sum_s J_{2s+1}(2\pi t)\left\{\begin{array}{l}\sin[(2s-1)cl+(2s-1)e-d]+\sin[(2s+1)cl+(2s+1)e-d]\\ +\sin[(2s+1)cl+d+(2s-1)e]+\sin[(2s+3)cl+d+(2s+1)e]\end{array}\right\}=0\;, \quad \text{(A12)}$$

$$J_0(2\pi t)\sin 2\pi(cl+d)$$

$$+\textstyle\sum_s J_{2s}(2\pi t)\ \{\sin[(1-2s)cl+d-2se]+\sin[(1+2s)cl+d+2se]\}$$

$$+\textstyle\sum_s J_{2s+1}(2\pi t)\ \{\sin[2scl+2se-d]+\sin[(2s+2)cl+d+2se]\}\ =0\;. \quad \text{(A13)}$$

The apparent complexity of these equations can be reduced by noting the following mathematical properties:

$$\langle \sin(l\tfrac{2}{3}\pi s)\rangle \equiv 0\;, \qquad \text{(A14)}$$

$$\langle \cos(l\tfrac{2}{3}\pi s)\rangle = \delta_{s,3k}\;, \qquad \text{(A15)}$$

and

$$\textstyle\sum_s a_s J_s(t)=0 \ \text{ for all } t \Rightarrow a_s=0 \ \text{ for all } s\;. \quad \text{(A16)}$$

Since (A12) and (A13) must hold for arbitrary value of t, (A14), (A15, and (A16) lead to the following choice for d and e:

$$d=0 \ \text{ or } \ \tfrac{1}{2}\;, \quad e=0 \ \text{ or } \ \tfrac{1}{2}\;. \qquad \text{(A17)}$$

The value of E_3 for various combinations of d and e are

(a) $d=0$, $e=0$;

$$E=(b-c)^2+\tfrac{3}{2}t^2-(U/2)[1-J_0(2\pi t)-\sin(2\pi t)]\;;$$

(b) $d=\frac{1}{2}$, $e=\frac{1}{2}$,

$$E=(b-c)^2+\tfrac{3}{2}t^2-(U/2)[-1+J_0(2\pi t)-\sin(2\pi t)]\;;$$

(c) $d=0$, $e=\frac{1}{2}$,

$$E=(b-c)^2+\tfrac{3}{2}t^2-(U/2)[1-J_0(2\pi t)+\sin(2\pi t)]\;;$$

(d) $d=\frac{1}{2}$, $e=0$;

$$E=(b-c)^2+\tfrac{3}{2}t^2-(U/2)[J_0(2\pi t)-1+\sin(2\pi t)]\;.$$

When $t>0$, the third choice would obviously be the one that minimizes the energy. Hence, finally, we have

$$x(l)=cl-t(U)\sin 2\pi cl\;, \qquad \text{(A18)}$$

$$E_3=(b-c)^2+\tfrac{3}{2}t^2(U)-(U/2)[1-J_0(2\pi t)+\sin(2\pi t)]\;, \qquad \text{(A19)}$$

with t being given the solution of

$$t=(\pi U/3)[J_1(2\pi t)+\cos(2\pi t)], \quad t\in[0,\ t_0]\;, \qquad \text{(A20)}$$

where t_0 is the first zero of $J_1(2\pi t)+\cos(2\pi t)$, and c is determined by the same consideration as in the second-order commensurate state, i.e., by Eq. (A7).

3. *Incommensurate State*

Substituting (3.30) into the expression for the potential energy gives

$$E_\infty = (b-c)^2 + 2t^2 \sin^2 c\pi - U\langle \cos 2\pi[cl + d + t\sin(cl+d)]\rangle \ . \quad \text{(A21)}$$

With the help of (A10), this can be simplified to

$$\begin{aligned} E_\infty &= (b-c)^2 + 2t^2 \sin^2 c\pi \\ &\quad - U\langle \cos 2\pi(cl+d)\{J_0(2\pi t)\cos 2\pi[2s(cl+d)]\}\rangle \\ &\quad - 2U{\textstyle\sum_s}\ J_{2s+1}(2\pi t)\,\langle \sin 2\pi(cl+d)\sin(2s+1)\,2\pi(cl+d)\rangle \\ &= (b-c)^2 + 2t^2\sin^2 c\pi - UJ_1(2\pi t), \qquad \text{(A22)} \end{aligned}$$

where we have made use of the fact that if c is irrational, then

$$\langle \sin 2\pi scl\rangle = 0\ , \quad \langle \cos 2\pi scl\rangle = \delta_{s,0}\ . \quad \text{(A23)}$$

Minimizing E_∞ with respect to t and c gives

$$t = (\pi U/2\sin^2 c\pi)\,J_1'(2\pi t)\ , \quad \text{(A24)}$$

$$c = b - \pi t^2 \sin 2\pi c\ . \quad \text{(A25)}$$

The expression for the potential energy can finally be written as

$$E_\infty = 2t^2\sin^2 c\pi + \tfrac{1}{4}t^4\sin^2 2\pi c - UJ_1(2\pi t)\ . \quad \text{(A26)}$$

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