Kinetics of soliton line formation in incommensurate structures

M. S. Veshchunov

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A mechanism is proposed by which soliton lines can form in a two dimensional crystal near the point where it undergoes transition to an incommensurate phase as the degree of incommensurability changes. This mechanism is connected with the appearance of dislocation pairs in the lattice of soliton lines under the action of an external stress, and their subsequent increase in length up to the point where pairs can annihilate one another. We estimate the characteristic time for such a process, and compare this mechanism with other possible mechanisms. It is predicted that applying a periodic external stress should make possible experimental study of the process of soliton line formation.

Recently, there has been increased interest in two-dimensional crystalline systems, as a result of enhanced experimental capabilities; in particular, there is new interest in adsorbates on sufficiently perfect crystal surfaces.

In many cases, when atomic monolayers of noble gases are adsorbed on graphite substrates, one observes crystalline phases which are incommensurate with the substrates[1]; similar effects are seen when alkali metals are adsorbed on refractory metal substrates.[2]

In order to investigate theoretically the transition to such an incommensurate phase, very simple one-dimensional[3] and two-dimensional[4] models have been proposed for the layers adsorbed on a substrate with a periodic "relief" potential. To describe a real substrate, models have been proposed which take into account the finite elasticity of the substrate,[5–8] along with the disorder of the substrate due to point defects.[9,10] In Ref. 11, the author studied the transition to the incommensurate phase on a substrate with line defects (steps or dislocations) which disorder the relief potential in one direction. Not long ago, a similar study was completed by Lyuksyutov[12] who used a similar method (reduction of the two-dimensional statistical problem to a one-dimensional quantum problem with disorder).

It must be pointed out that the majority of papers which study the transition to the incommensurate phase concern themselves with properties of the ground state of the incommensurate phase, or with statistical properties at finite temperatures. However, the question of kinetic properties of the transition to this phase is equally interesting, in particular the kinetics of soliton line generation. The present work is dedicated to addressing this question.

Analysis of the experimental data and theoretical models has led to the conclusion that during the transition to the incommensurate phase soliton lines appear in the lattice of atoms which are commensurate with the substrate. In the case where the incommensurability appears only in one direction, these lines run parallel. In this case, in constructing a model of the phase transition, it is sufficient to investigate the shift of atoms only in the direction in which the incommensurateness appears.

The simplest Hamiltonian which describes such a model has the form

$$H = \int dx\,dy \left\{ \frac{1}{2}\lambda_1 \left(\frac{\partial u}{\partial x}\right)^2 + \frac{1}{2}\lambda_2 \left(\frac{\partial u}{\partial y}\right)^2 + v \cos\left[\frac{2\pi}{c}(na+u_n)\right]\right\}, \quad (1)$$

where $u(x,y)$ is the shift in atomic positions, $x = na$, where a and c are close to the adatom and substrate periods in the direction of incommensurability x (we remark that our results are easily generalized to the case of arbitrary commensurability ratio $a/c = m/n$); λ_1, λ_2 are elastic constants of the adsorbed layer; and v is the amplitude of the substrate "relief" potential.

An analysis of the ground state of the Hamiltonian (1) shows that when the incommensurability parameter $\delta = (a - c)/c$ reaches a certain critical value δ_c, a periodic array of soliton lines arises with period $l \propto (\delta - \delta_c)^{-1/2}$,[4] where $l \to \infty$ as $\delta \to \delta_c$.

In experiments with noble gas atoms on a graphite substrate, the period of the adatom lattice is determined by the pressure (or chemical potential) of the gas which is in thermodynamic equilibrium with the layer. The average distance between soliton lines is observed to change as a function of the gas pressure.[1,13] In connection with this result, the question arises of how new soliton lines are formed, i.e., their generation rate, as we move away from the critical incommensurability.

The simplest mechanism for changing the concentration of soliton lines as the external pressure varies invokes the appearance of new solitons at the sample boundaries or at defects, and the redistribution of solitons in the film far from these boundaries so as to establish a new equilibrium structure. Such a mechanism is in turn contingent on soliton diffusion over distances comparable to the film size, and apparently is not always the most effective way to establish rapidly the new equilibrium state of the system.

We want to propose another mechanism whereby new soliton lines can appear, and compare it to the one above. To do this, let us study the two-dimensional lattice of soliton lines. Because the soliton superstructure has a continuous translation group relative to the substrate, we can treat it as a new two-dimensional lattice on a smooth substrate.[14,15] We can describe such a lattice with the help of the Hamiltonian

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$$H=\frac{1}{2}\int d^2r[K_x(\partial_x u)^2+K_y(\partial_y u)^2], \tag{2}$$

where the constants K_x and K_y are connected with the elastic constants of the adatom lattice through the relations[15]

$$K_x\propto T^2/\Gamma a^2 l, \qquad K_y\propto \Gamma l/a^2, \qquad \Gamma\sim(\lambda_1 v)^{1/2}a; \tag{3}$$

so that they satisfy the identity

$$a^2(K_xK_y)^{1/2}/T=\pi. \tag{3'}$$

Below its melting temperature, such a lattice always contains coupled pairs of dislocations with opposing Bürgers vectors (these pairs dissociate into single dislocations at the melting point). When the pressure of the gas changes, a tensile (or compressive) elastic stress appears in the adatom lattice, and consequently in the soliton lattice. On the one hand, this stress changes the equilibrium concentration of dislocation pairs; on the other hand, it tends to increase the distance between those dislocations which make up the pairs. At the moment when the distance between pairs of dislocations has increased enough so that they can annihilate and dislocate other pairs, a new soliton line appears in the lattice.

In order to describe this process quantitatively, we will first investigate the growth of a specific soliton line. Near the transition point, when the soliton line concentration is small and the interaction between different dislocation pairs can be neglected, the result can be generalized for any lattice solitons.

Let us assume that as a result of changing the pressure (or chemical potential) of the gas, a tensile stress $\sigma_{xx}=\lambda_1\partial u/\partial x$ along the x axis appears in the layer. Consequently in the soliton lattice a stress $\tilde{\sigma}_{xx}=K_x\partial u/\partial x=K_x\sigma_{xx}/\lambda_1$ develops. Then a force acts on the dislocation in the soliton lattice with minimum Bürger's vector:

$$F_y=\tilde{\sigma}_{xx}a=(K_x/\lambda_1)a\sigma_{xx}. \tag{4}$$

The tensile energy between dislocations in a single pair of length y equals

$$E=\frac{(K_xK_y)^{1/2}}{2\pi}a^2\ln\frac{|y|}{a}=\frac{T}{2}\ln\frac{|y|}{a}, \tag{5}$$

since the dislocation is under tension with a force $\Phi=T/2y$. The thermodynamic potential of formation of the nuclei of a dislocation pair roughly equals the inter-atomic elastic interaction in the added layer:

$$2F_c\sim\lambda_1 a^2. \tag{6}$$

Thus, the concentration of dislocation pairs of length y in an "induced" equilibrium, is

$$c_p{}^0(y)=\frac{1}{a^2}\exp\left[-\frac{F(y)}{T}\right], \tag{7}$$

$$F(y)=2F_c-\tilde{\sigma}_{xx}ay+\frac{T}{2}\ln\frac{y}{a}. \tag{8}$$

At some vertical spacing (i.e., pair size) y^*, the mutual tension between dislocations of a pair is counterbalanced by the external force; then $F(y^*)$ is a maximum. Dislocations separated by a space larger than y^* tend to spread farther apart, while at the same time dislocations with $y<y^*$ tend to annihilate. We can compare this situation with the existence of a critical dimension for nuclei in the classical theory of nucleation[16] (we also note that this problem is analogous to the problem of the motion of paired kinks for slip dislocations[17]).

As a result of this comparison, we can at once determine the rate of nucleation of dislocation pairs per unit length along the soliton line:

$$J=2D_d c_p{}^0(y^*)/2y', \tag{9}$$

where y' is determined by the equation

$$-\frac{1}{2}y'^2\left[\frac{\partial^2F}{\partial y^2}\right]_{y=y^*}=T, \tag{10}$$

and D_d is the diffusion constant for individual dislocations. For "supercritical" pairs ($y\gg y^*$), we can write down approximate expressions for the rate of drift of the dislocations under the action of the force $F=F_y-\Phi\approx F_y$:

$$v_{\text{dr}}=(D_d/T)\tilde{\sigma}_{xx}a. \tag{11}$$

Then if $\mathscr{L}$ is the average distance along a soliton line between dislocation pairs up to where they annihilate with dislocations from another pair, and τ is the average lifetime of a pair, we have

$$J\mathscr{L}\tau\sim 1, \qquad v_{\text{dr}}\tau\sim\mathscr{L},$$

where

$$\tau\sim(v_{\text{dr}}J)^{-1/2}. \tag{12}$$

This quantity at once also determines the nucleation time for a new soliton line:

$$\tau_1\sim\left[\frac{\lambda_1(\lambda_1 v)^{1/2}al}{T\sigma_{xx}}\right]^{3/2}\frac{a^2}{D_d}\exp\frac{F_c}{T}. \tag{13}$$

This relation was obtained by assuming that the external stress σ_{xx} is practically unchanged within the growth time of a new soliton line; if it is used to determine the time it takes a soliton line to appear in an arbitrary lattice, we should keep in mind that relation (13) becomes more precise the larger the applied stress is and the closer δ is to δ_c. In this case, the result of applying this stress can lead to a massive increase in the number of soliton lines, so that the appearance of the first line occurs in practice at constant stress. Relation (13) is only qualitatively useful for determining the time at which the new equilibrium state appears.

For a full description of the process it is necessary to take into account the fact that the stress in the lattice falls as new dislocation pairs appear and their lengths increase. Including this stage of the process is equivalent to including the coalescence stage in the theory of nucleation; our case admits of an analogous treatment.

To do so, let us examine the way the stress in the layer behaves in proportion to the appearance and growth of dislocation pairs. We assume that a homogeneous stress $\sigma_{xx}=\sigma$ is applied in the layer. The work done by the force acting on each dislocation pair $|F_y| = \sigma a$ in increasing the length of the ith pair of dislocations to a length y_i equals $W = |F_y|\, y_i$. This quantity can be written in the form $W = \sigma_{xx} U_{xx_i}$ where $U_{xx_i} = \int d^2 r u_{xx_i}$. Then $U_{xx_i} = ay_i$ and after summing over all pairs of dislocations we obtain

$$U_{xx}=\sum_i\int d^2ru_{xx\,i}=\sum_i ay_i.$$

Consequently, the stress in the layer which is relieved by dislocation pairs equals $\Omega = \lambda_1 \Sigma_i a y_i$. Correspondingly, for the stress in the soliton lattice we have $\tilde\Omega = K_x \Sigma_i a y_i$. The resulting (or remanent) stress $\Delta(t)$ in the soliton lattice arising from the external stress σ_{xx} in the presence of dislocation pairs is connected with the critical dislocation pair $y^*(t)$ by the relation

$$\Delta(t)=T/2ay^*(t). \tag{14}$$

Thus,

$$\tilde\Omega(t)+\Delta(t)=\text{const}=\tilde\sigma_{xx}. \tag{15}$$

Introducing the distribution function $f(y,t)$ for dislocation pairs, we can express the quantity $\tilde\Omega(t)$ in the form

$$\tilde\Omega(t)=a\int yf(y,t)\,dy, \tag{16}$$

while the equation of continuity in the "configuration space" of lengths y is likewise

$$\frac{\partial f}{\partial t}+\frac{\partial}{\partial y}(fv_y)=0, \tag{17}$$

where $v_y = dy/dt$ can be expressed through the diffusion coefficient for dislocations (see 11):

$$\frac{dy}{dt}=2D_d\left[\Delta(t)a-\frac{T}{2y}\right]=-2TD_d\left(\frac{1}{y}-\frac{1}{y^*}\right). \tag{18}$$

The system of equations (14)–(18) is analogous to the system obtained by Lifshitz and Slezov for describing the coalescence of nuclei [see, e.g., Ref. (16)]. Its solution has the form

$$\bar y(t)=y^*(t)\propto t^{1/2}, \tag{19}$$

where $\bar y$ is the average dimension of a pair; this agrees completely with the results of dimensional analysis in the theory of nucleation in d-dimensional systems ($\sim t^{1/d}$).[18]

We remark that up to now we have used in our description the phenomenological parameter D_d, which can be related to a quantity D_g which is actually measured: the diffusion coefficient of the gas.

Let us investigate a growing soliton line which ends on a dislocation. The growth of this line, which proceeds due to drift of the dislocation, is fueled by the atoms in the gas phase which connect with it. The departure from equilibrium of the gas-film system is damped out, and equilibrium reestablished, as a result of the growth of new soliton lines, so that we can assume (approximately) that the thermodynamic potential of an atom linked to the soliton line is equal to the chemical potential in the gaseous medium far from the surface (this approximation gets better the closer we are to equilibrium). Having assigned the chemical potential of the gas far from the surface, we therby assign to the latter its equilibrium concentration c_0. Near the dislocation we have a quasistationary concentration distribution $c(r)$ for the gas. Then as a result of connecting a new atom to the soliton line we liberate some energy $T\ln[c(a)/c_0]$; consequently, there is a force acting on the dislocation

$$F=-\frac{T}{a}\ln\frac{c(a)}{c_0}. \tag{20}$$

This force counterbalances the force $\tilde\sigma_{xx}a$, acting on the dislocation as a result of the applied force. In this way, we get

$$\tilde\sigma_{xx}a=\frac{T}{a}\ln\frac{c(a)}{c_0}$$

so that near the dislocation

$$c(a)=c_0\exp(\tilde\sigma_{xx}a^2/T).$$

The steady-state condition can be converted into the condition that the divergence of the diffusion current of atoms from the gas to the dislocation be zero:

$$\nabla\mathbf{J}=-\nabla\left(\frac{D_rc}{T}\nabla T\ln\frac{c}{c_0}\right)=0. \tag{21}$$

Solving equation (21) with boundary conditions

$$\begin{aligned} &c(r)\to c(a)\quad \text{for}\quad r\to a,\\ &c(r)\to c_0\quad \text{for}\quad r\to\infty, \end{aligned} \tag{22}$$

we obtain

$$c-c_0=c_0\left[\exp\left(\frac{\tilde\sigma_{xx}a^2}{T}\right)-1\right]\frac{a}{r}. \tag{23}$$

The resulting atomic current far from the dislocation for $\tilde\sigma_{xx}a^2 \ll T$ equals

$$I=-2\pi r^2D_g\frac{\partial c}{\partial r}=2\pi D_gc_0\left[\exp\left(\frac{\tilde\sigma_{xx}a^2}{T}\right)-1\right]\approx 2\pi D_ga^2c_0\frac{\tilde\sigma_{xx}}{T}, \tag{24}$$

and consequently the drift velocity of the dislocation equals

$$v_{\text{dr}}\approx 2\pi D_gc_0a^3(\tilde\sigma_{xx}a/T). \tag{25}$$

Comparing (25) with (11), we obtain for the dislocation diffusion coefficient

$$D_d\approx 2\pi D_gc_0a^3. \tag{26}$$

In experiments[13] on adsorbing Kr onto graphite, the transition to the incommensurate phase occurs at a temperature $T\sim 10^2$K and at a gas pressure of ~ 1 Torr. The coefficient of diffusion of Kr gas under such conditions amounts to $D_g \sim 10$ cm^2/s, while the gas concentration is $c_0 \sim 10^{16}$ cm^{-3}. Thus, the quantity D_d in (26) comes to $\sim 5\times 10^{-6}$ cm^2/s, and is fully determined in our problem.

Let us now turn to an investigation of the other mechanism by which equilibrium could be established in the system, which we mentioned before (that is, we will assume that a new soliton line appears at the sample boundaries or at defects, and subsequently extends throughout the film). The question of diffusion of soliton lines through the film by means of the appearance and translation of kinks along a soliton line was investigated in Ref. 19. The temperature dependence of the diffusion coefficient D is determined by the factor $\exp(-\varepsilon_k/T)$ where $\varepsilon_k \sim (\lambda_1 v)^{1/2} a^2$ is the energy of a kink, or $\exp(-\varepsilon_d/T)$ with $\varepsilon_d \sim \lambda_1 a^2$ in the case of a high defect concentration. The coefficient D_0 of the exponential is a strong function of l; its characteristic value at its largest differs by the large multiplicative factor $\lambda a^3/c^2 T l_0$ from the value $\sim \omega_0 a^2$ for point defects; here, c is the defect concentration and $l_0 = a(\lambda_1/v)^{1/2}$. Similar behavior in D is observed in experiments[20] on adsorption of Ba on a Mo $\langle 110 \rangle$ substrate. A typical value of d turns out to be 10^{-6}–10^{-7} cm^2 s^{-1}. Regretably, such experiments have not been performed on graphite substrates.

Thus, in order to establish equilibrium in the incommensurate system via the "diffusion" mechanism, which is connected with the migration of solitons over distances on the order of the film dimensions L, we need a time

$$\tau_2 \sim (L^2/D_0)\exp(\varepsilon_0/T), \tag{27}$$

where $\varepsilon_0 \sim (\lambda_1 v)^{1/2} a^2$ in the case of low defect concentrations and $\varepsilon_0 \sim \lambda_1 a^2$ in the opposite case.

It is now possible to compare expressions (13) and (27), which give estimates for the characteristic times for establishing equilibrium via the two mechanisms. The small parameter al/L^2 in the quantity τ_1/τ_2 can be compensated by the ratio of exponents in the case of low defect concentration, so that the times for establishing equilibrium in the adsorbed layer for the two mechanisms can be comparable. Related to this, there has been a resurgence of interest in establishing experimentally what sort of mechanism returns the incommensurate system to equilibrium.

In our view, experimental study of the behavior of incommensurate films under time-varying stress is no less interesting than the above. That is, by varying the pulse widths and off-duty cycles in the vicinity of the times τ_1 (or τ_2), as was done in Ref. 21 to study dislocation slipping in crystals, it is possible to study the response of a film to an applied stress.

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