Commensurability in One-Dimensional Lattices at Finite Temperature

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The theory of commensurability transitions in one-dimensional atomic chains has been applied to charge density waves, mercury chain compounds, superionic conductors, etc. Previous numerical and analytical results on a model with chains of atoms with nearest neighbor interactions and periodic external potentials have dealt mainly with equilibrium and dynamical properties at $T = 0$ K. These studies are extended to nonzero temperatures. It is found that the reversible work per particle to slide the chain vanishes in the thermodynamic limit for any nonzero temperature. The mathematical pathologies associated with the commensurability transition at $T = 0$ (i.e., the "devil's stair") are absent at finite temperature; only thermodynamic evidence of low-order commensurability transitions remains.

KEY WORDS: Commensurability transition; pinning of incommensurate systems; one-dimensional charge density waves; superionic conductors; mercury chain compounds.

1. INTRODUCTION

In recent years there has been considerable interest in the statistical mechanics of systems in d dimensions with periodic external potentials. Applications range from adsorbed films on periodic substrates to "chains" of organic conducting materials.[1] A crucial feature of such systems is that when a natural lattice constant becomes commensurate with a period of the external potential the system becomes "rigid" and "pinned" to the external potential. In a sense, this is the reverse of a first-order phase transition, where the system is "soft" to compression, e.g., liquid–vapor coexistence. The nature of the critical points for commensurate transitions are not at all understood.

In 1970, Widom gave an exact solution for a chain of atoms, interacting with hard cores, in an external periodic potential.[2] McMillan has treated the commensurability transition within a Landau theory for the charge density wave problem.[3] Sacco and Sokoloff studied numerically the zero-temperature equilibrium equations of the Frenkel–Kontorova model (which consists of a chain of atoms, connected by springs, interacting with a sinusoidal potential), which is a model for such incommensurate systems.[4] It was shown that for weak external potentials there exists a sliding mode in which the chain of atoms can slide without friction with respect to the sinusoidal potential when the periods of the chain and potential are incommensurate. The present paper is an extention of these results to nonzero temperature (using methods similar to those used in Ref. 2). Our treatment, based on the transfer matrix method, is similar to that used by Guyer and Miller[5] for treating a related model. Our treatment is an improvement over Ref. 5 in that we are able to find the equation of state and the phase diagrams for the commensurate–incommensurate transition. Furthermore, we are able to discuss questions of sliding and pinning of the chain atoms by the sinusoidal potential at near-zero temperatures.

We find that although a registry transition will occur at $T = 0$ for certain critical ranges of values of the external pressure (and hence for the natural chain lengths corresponding to these values of the pressure), at any nonzero temperature a sharp registry transition will no longer occur. Furthermore, we will prove that the reversible work needed to slide the system with respect to the substrate potential is intensive (i.e., essentially zero compared to the energy of the system or the interaction energy of the system with an external field, both of which are extensive).

Here we consider one-dimensional chains of atoms ($\cdots < x_n < x_{n+1} < \cdots$) with nearest neighbor interactions $v(r)$, and external periodic potentials $\phi(x)$,

$$\phi(x + a) = \phi(x) \tag{1a}$$

$$V(x_0,\ldots, x_N) = \sum_{n=0}^{N} \phi(x_n) + \sum_{n=1}^{N} v(x_n - x_{n-1}) \tag{1b}$$

It turns out that the resulting equations of state are described by highly "pathological" functions, e.g., continuous, monotonic, and with zero derivatives almost everywhere.[6] We will see that for $T > 0$, the "pathology" vanishes.

2. THE PARTITION FUNCTION

The partition function for classical chains with a "fixed" zeroth atom is

$$Z_N(x_0; f, T) = \frac{1}{\lambda^N} \int\limits_{x_0 \le x_1 \le \ldots \le x_N \le \infty} dx_1 \cdots \int dx_N \exp - \frac{V + f|x_N - x_0|}{k_B T} \tag{2}$$

where λ is the thermal wavelength

$$\lambda = (2\pi\hbar^2/mk_BT)^{1/2} \tag{3}$$

and $f > 0$ is the "compression" force applied to the ends of the chain. It is expected (and will be proved in what follows) that the chemical potential

$$\mu(f, T) = -(k_BT) \lim_{N \to \infty} N^{-1} \ln Z_N(x_0; f, T) \tag{4}$$

will be independent of the position of the fixed zeroth atom x_0. The thermo-dynamic properties of the chain follow from

$$d\mu = -s\, dT + l\, df \tag{5}$$

where l is the mean spacing between atoms. The following recursion relation is evident from Eqs. (1) and (2):

$$Z_{N+1}(x) = \int_0^\infty \frac{dr}{\lambda} \left[\exp - \frac{\phi(x)}{k_BT} \exp - \frac{v(r) + fr}{k_BT} \right] Z_N(x + r) \tag{6}$$

For the purpose of mathematical rigor and physical clarity we place the following conditions on the potentials: $v(r)$ is repulsive, strong at short distances

$$\lim_{r \to 0+} v(r) = \infty \tag{7}$$

weak at large distances

$$\lim_{r \to \infty} v(r) = 0 \tag{8}$$

and strictly convex with second derivative

$$v''(r) > 0, \qquad 0 < r < \infty \tag{9}$$

It is also assumed that $\phi(x)$ has a bounded first derivative

$$|\phi'(x)| < \infty \tag{10}$$

i.e., the external substrate force is everywhere finite.

3. ZERO EXTERNAL POTENTIAL

When $\phi(x)$ is zero, the solution to the problem is well known; it is

$$\mu_0(f, T) = -k_BT \ln \int_0^\infty \frac{dr}{\lambda} \exp - \frac{v(r) + fr}{k_BT} \tag{11}$$

It is useful to introduce the probability distribution

$$dW(r) = \frac{dr}{\lambda} \exp \frac{\mu_0 - v(r) - fr}{k_BT} \tag{12}$$

Physically, $W(r)$ is the probability that the distance between two neighboring atoms is less than r. For m successive pairs these distances are independently distributed, i.e.,

$$\langle \exp[iQ(r_{n+1} + \cdots + r_{n+m})]\rangle = M(Q)^m, \qquad r_{n+1} = x_{n+1} - x_n \quad (13)$$

where

$$M(Q) = \int_0^\infty e^{iQr} \, dW(r) \tag{14}$$

is the moment generating function. This fact enables us to easily compute the structure factor

$$S(Q) = \lim_{N \to \infty} \frac{1}{N} \sum_{n,m}^N \langle e^{iQ(x_n - x_m)}\rangle \tag{15}$$

in that Eqs. (13) and (15) imply

$$S(Q) = 1 + 2 \, \mathrm{Re} \sum_{m=1}^\infty M(Q)^m = \mathrm{Re} \frac{1 + M(Q)}{1 - M(Q)} \tag{16}$$

Long-range ordering in the density fluctuations would be present only if the denominator on the right-hand side of Eq. (16) vanished at Q equal to a reciprocal lattice vector, which would yield a Bragg peak in $S(Q)$. For finite T it is clear that

$$|M(Q; f, T)| < 1, \qquad Q > 0, \qquad T > 0 \tag{17}$$

so that this does not happen. Nevertheless as $T \to 0+$ the peaks in $S(Q)$ approach Bragg peaks. This indicates that at strictly zero temperature the chain "freezes." Let us consider this in more detail.

For potentials obeying Eqs. (7)–(9) the chemical potential $\mu_0(f, T)$ can be analytically continued in f so that $\mu_0(f - ik_BTQ, T)$ is well defined for all Q and $f > 0$. In fact Eqs. (11), (12), and (14) imply

$$\mu_0(f - ik_BTQ, T) = \mu_0(f, T) - k_BT \ln M(Q) \tag{18}$$

so that $S(Q)$ [Eq. (16)] can be constructed via the thermodynamic chemical potential (unfortunately, this only holds in one dimension). Since $\mu_0(f - ikTQ, T)$ is analytic for $f > 0$, the power series expansion in k_BTQ

$$\mu_0(f - ik_BTQ, T) = \mu_0(f, T) - ik_BTQ \frac{\partial}{\partial f} \mu_0(f, T)$$

$$- (k_BTQ)^2 \frac{1}{2} \frac{\partial^2}{\partial f^2} \mu_0(f, T) + \cdots \tag{19}$$

surely converges for

$$Q < f/k_BT \tag{20}$$

so that [see Eqs. (18) and (20)] the power series expansion in Q

$$\ln M(Q) = iQl_0 - (k_BTQ^2/2K_0) + \cdots \tag{21}$$

(with l_0 and K_0 defined in an obvious way) is asymptotically exact as $T \to 0$ with f finite. Note that the radius of convergence in Eq. (20) does not then restrict Q. Equations (21) and (16) imply that

$$S(Q) \to \left[\frac{\sinh(\tfrac{1}{2}k_B T Q^2/K_0)}{\cosh(\tfrac{1}{2}k_B T Q^2/K_0) - \cos(Ql_0)} \right] \quad \text{as} \quad T \to 0+ \qquad (22)$$

Equation (22) is a *rigorous statement* about the asymptotic "critical behavior" of density fluctuations for "freezing" at zero temperature. This expression has a very simple physical interpretation. It is precisely this structure factor that would be computed if one assumed that the chain were a simple harmonic solid with nearest neighbor springs.[7] The spring constant is obtained from the potential [note Eq. (9)],

$$K_0 = v''(l_0) \qquad (T \to 0) \qquad (23)$$

Our conclusion is that for the class of nearest neighbor potentials considered in Eqs. (7)–(9), the chain with zero external potential acts (as $T \to 0$) exactly the same as a "simple harmonic solid."

Notice that $S(Q)$ is a typical "fluidlike" structure factor when T is nonzero. As $T \to 0$, however, the smooth peaks in $S(Q)$ located at $Q_n = 2\pi n/l$ evolve into Bragg peaks which are typical of solids, i.e.,

$$S(Q_n, T) \approx A K_0 l_0^2/(2\pi n)^2 k_B T \qquad (\text{as } T \to 0) \qquad (24)$$

From the first peak one can introduce a coherence length (reciprocal width),

$$\xi \sim l_0(K_0 l_0^2/k_B T) \qquad (25)$$

One notes that the "critical index" of the coherence length for freezing is $\nu = 1$. One also sees that although the system orders as a solid only for $T = 0$ (when $\phi = 0$), the usual Landau and Lifshitz arguments[8] against ordered phases in one dimension at finite temperatures do not apply, since these arguments yield a critical index $\nu = \infty$. More precisely, the notion that "domain boundaries" of energy Δ form dilute solutions as $T \to 0$ yields a coherence length

$$\xi' \sim l_0 e^{\Delta/k_B T} \qquad (\text{as } T \to 0) \qquad (26)$$

which is valid, for example, for a one-dimensional, nearest neighbor, Ising lattice gas. For our "spring model" (with $\phi = 0$), the smaller critical index indicates that the solid melts via collective phonon excitations rather than by the formation of thermally activated domain boundaries (e.g., solitons).

Let us consider this in more detail. If the positions of the particles were discrete lattice sites, then it would be correct (but somewhat unusual) to

calculate the thermodynamic properties of the resulting lattice gas via Eq. (11) replacing integrals by sums,

$$\exp[\mu(f, T)] = \sum_r \exp\{-[v(r) + fr]/k_\mathrm{B}T\} \tag{27}$$

The nearest neighbor ferromagnetic Ising chain has a lattice gas equivalent potential

$$v(r) = \begin{cases} \infty & \text{for} \quad r = 0 \\ -\Delta & \text{for} \quad r = b \\ 0 & \text{for} \quad r = 2b, 3b,\ldots \end{cases} \tag{28}$$

so that

$$\mu(f, T) = fb + k_\mathrm{B}T \ln\left[e^{\Delta/k_\mathrm{B}T} + \frac{1}{e^{fb/k_\mathrm{B}T} - 1}\right] \tag{29}$$

At $T = 0$ each site is occupied by one particle, forming an ordered phase. At low temperatures the coefficient of thermal expansion

$$\alpha_T = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_f$$

obeys

$$\alpha_T = (\Delta/k_\mathrm{B}T^2)e^{-\Delta/k_\mathrm{B}T} + \cdots \qquad (\text{as } T \to 0) \tag{30}$$

The exponential factor in Eq. (30) represents the thermal activation of vacancies. These vacancies form the domain boundaries for ordered segments (of mean length ξ) of the chain. Although few in number, vacancies, due to their random distribution, prevent the occurrence of an ordered phase at finite temperature.

　　It is instructive to compare the thermal expansion in the discrete Ising chain with that of the continuous potential model. By the method of "steepest descents" one can show, for the class of potentials considered above, that

$$\lim_{T \to 0} \alpha_T = -k_\mathrm{B}[v'''(l_0)/2K_0] \tag{31}$$

The occurrence of the third derivative of the potential indicates that thermal expansion arises from anharmonic processes—in particular, the decay of one phonon into two phonons and the inverse process. This is clearly not a process which requires thermally activated domain boundaries to precipitate melting. Rather, it is a collective effect in which the thermal energy is distributed uniformly throughout the chain.[2]

　　In a true spring model, since $v'''(r) = 0$, there is no thermal expansion. However, it is reasonable to require that even in a spring model, the particles

[2] The change from continuous to Ising-like behavior has been treated in Ref. 9.

do not pass each other. The inclusion of a point hard core is sufficient to introduce anharmonicities, which fortunately can be summed to all orders. Here, the chemical potential is

$$\mu_0(f, T) = \frac{K_0 b^2}{2} + k_B T \ln\left[\frac{\hbar(K_0/m)^{1/2}}{k_B T}\right]$$

$$- \frac{1}{2K_0}(f - K_0 b)^2 - k_B T \ln\left[\frac{1}{2}\operatorname{erfc}\frac{f - K_0 b}{(2K_0 k_B T)^{1/2}}\right] \qquad (32)$$

where the term containing the complimentary error function [erfc(x)] arises from the inclusion of the point hard core. This expression will be used later. Differentiating twice, we obtain a nonzero thermal expansion for this model. It is interesting to note that the specific heat cannot show any anomalies as T approaches the melting temperature ($T = 0+$), because for low temperatures the anharmonic effects of the hard core cannot have any significant effect. The probability of a pair of atoms getting close enough for them to matter is simply too small. Thus, the specific heat must be the ordinary classical specific heat of a collection of harmonic oscillators.

4. PINNING OF THE CHAIN BY THE SUBSTRATE POTENTIAL

Suppose that we have a chain with the "zeroth" atom fixed at $x_0 = x$, and we wish to know the reversible work (i.e., the free energy change) required to push the "zeroth" atom (and thus the whole chain) to a new position $x_0 = y$. If the external potential $\phi(x)$ were zero, then the work should be strictly zero due to translational invariance. However, with a periodic external potential one must push some atoms over barriers, so that the reversible work might be extensive, i.e., proportional to the chain size. Alternately, pushing the chain might cause atoms that reside on potential maxima to slide forward into potential minima, thus towing neighboring atoms along with them with no resulting energy change.

This latter view is correct, as we will now show. The reversible work required to "push" the chain at finite T is intensive, i.e., "virtually zero," even when the chain length is macroscopically large. We reverse the question of irreversible work (i.e., friction) for a forthcoming paper on dynamics. Even for reversible work, i.e., free energy changes, it is not at first clear whether or not as $T \rightarrow 0+$ (and a "commensurate, rigid, pinned ..." phase occurs) the reversible work does remain "virtually zero."

For now let us assume that the work to push the chain reversibly via the "zeroth" atom from $x_0 = x$ to $x_0 = x + r$ is the difference $\psi(x + r) - \psi(x)$ between intensive free energies. Now add a new particle (the minus first) at $x_{-1} = x$, i.e., where the "zeroth" used to be. This requires an additional energy $v(r) + fr + \phi(x)$ due to nearest neighbor interactions, compression,

and the external potential. Allowing r to fluctuate, we find the free energy change μ arising from the addition of one particle to be given by

$$e^{-\mu/k_B T} = \int_0^\infty \frac{dr}{\lambda} \exp\left\{-\frac{1}{k_B T}[\psi(x+r) - \psi(x) + v(r) + fr + \phi(x)]\right\} \quad (33)$$

But this is recognized as a transfer matrix eigenvalue problem with

$$z = e^{-\mu/k_B T} \quad (34a)$$

as the eigenvalue and

$$g(x) = e^{-\psi(x)/k_B T} \quad (34b)$$

as the eigenvector. The eigenfunction $g(x)$ determines the intensive free energy ["end effect" $\psi(x)$] that the chain has because the "zeroth" atom is at position x (held fixed), To prove that this is indeed the case, it must be shown that $\psi(x) - \psi(y)$ is really the work done reversibly to move the chain from $x_0 = x$ to $x_0 = y$, i.e.,

$$\psi(x) - \psi(y) = k_B T \lim_{N \to \infty} \ln[Z_N(x; f, T)/Z_N(y; f, T)] \quad (35)$$

In fact Eqs. (33) and (35) follow directly from Eq. (4) and the recursion Eq. (6).

   The physical interpretation that $\psi(x)$ is the free energy to hold the "zeroth" atom at $x_0 = x$ requires that $\psi'(x)$ be the force to push the chain quasistatically. This leads to the following definitions: If $\psi'(x)$ goes to a finite limit as $T \to 0+$, then the chain is said to be "free." If $|\psi'(x)|$ diverges as $T \to 0+$, then the chain is said to be "pinned." If, and only if, the chain goes from a "pinned" state to a "free" state (or the reverse) when the compression force f changes is a "commensurability transition" said to occur. Presumably, in dimension $d > 1$ the same sort of definition would hold with $T \to 0+$ replaced by $T \to T_c+$, where T_c is the "critical" temperature.

5. FREE CHAINS AT $T = 0$

   Having defined a free chain as that for which

$$\lim_{T \to 0+} \text{Max}_x |\psi'(x; f, T)| < \infty \quad (36)$$

so that the chain at zero temperature can be "pushed" quasistatistically with "virtually zero work" through the external potential, it becomes important to derive sufficient conditions for a chain to be free. This is possible by applying "steepest descent" to the eigenvalue problem [in the form of Eq. (33)] as $T \to 0+$ to evaluate μ at zero temperature. This leads to the zero-temperature equation

$$\mu = \phi(x) - \psi(x) + \text{Min}_{0 < r < \infty} [v(r) + fr + \psi(x + r)] \quad (37)$$

We now have a well-defined mathematical problem at $T = 0$. Find a function $\psi(x)$ [periodic $\psi(x + a) = \psi(x)$] with finite derivative everywhere

$$\text{Max}_x |\psi'(x)| < \infty \tag{38}$$

such that [for given compression force f and external potential $\phi(x)$] the right-hand side of Eq. (37) does not depend on x.

In minimizing the expression on the right-hand side of Eq. (37) with respect to r we have the sum of a convex function $v(r) + fr$ restricted by Eqs. (7)–(9) and a differentiable periodic function of r, i.e., $\psi(x + r)$ restricted by Eq. (38). It is not difficult to prove that for this minimum to exist (i) $\psi(x)$ must be twice differentiable, (ii) a function $R(x)$ must exist such that for an extremum

$$v'[R(x)] + f + \psi'[x + R(x)] = 0 \tag{39}$$

and (iii) the second derivative condition for minimization

$$v''[R(x)] + \psi''[x + R(x)] > 0 \tag{40}$$

must hold. Equation (35) can be solved because of the convexity condition on $v(r)$ in the form

$$R(x) = l_0[f + \psi'(x + R(x))] \qquad [v'(l_0) + f = 0] \tag{41}$$

where $l_0(f) \equiv \lim_{T \to 0+} l_0(f, T)$ is the mean spacing between atoms when the substrate potential $\phi(x) = 0$.

The chemical potential (for free chains) at $T = 0$ is thus [see Eq. (37)]

$$\mu = \phi(x) - \psi(x) + v[R(x)] + fR(x) + \psi[x + R(x)] \qquad T = 0 \tag{42}$$

For the right-hand side of Eq. (42) to be independent of x, $R(x)$ must be differentiable; $\partial\mu/\partial x = 0$ then requires that

$$\psi'(x) = \phi'(x) + \psi'[x + R(x)] \tag{43}$$

and Eq. (41) becomes

$$R(x) = l_0[f + \psi'(x) - \phi'(x)] \tag{44}$$

Equations (43) and (44) are the rather complicated functional equations that must be solved in order to compute the $T \to 0+$ equations of state for free chains. A simple physical interpretation of these equations will now be given.

6. EQUILIBRIUM CONFIGURATIONS OF FREE CHAINS

An "equilibrium configuration" sequence $\cdots < x_{n-1} < x_n < x_{n+1} < \cdots$ of a free chain is a sequence that obeys

$$x_{n+1} = x_n + R(x_n) \tag{45}$$

From Eqs. (45) and (39), one sees that for such sequences

$$v'(x_n - x_{n-1}) + f + \psi'(x_n) = 0 \tag{46}$$

but from Eqs. (43) and (45),

$$\psi'(x_n) = \phi'(x_n) + \psi'(x_{n+1}) \tag{47}$$

Together Eqs. (46) and (47) imply the equation of mechanical equilibrium at $T = 0$,

$$v'(x_n - x_{n-1}) - v'(x_{n+1} - x_n) + \phi'(x_n) = 0 \tag{48}$$

(The numerical solution of these equations was the subject of Ref. 4.) Thus the functional equations of statistical physics at nonzero T generate as $T \to 0+$ the solutions [via Eq. (45)] of a quite complicated nonlinear equilibrium difference equation for free chains. It is important to realize that these solutions must be the *stable* solutions of *lowest energy* by the physical nature of $T \to 0+$ limit. [The higher energy solutions of Eq. (48) are eliminated by the Boltzmann factor $e^{-v/k_B T}$ of statistical mechanics as "improbable."] Let us consider this stability, which is difficult to obtain if strictly $T = 0$ theories are considered. For free chains the stability condition is Eq. (40), which [by differentiating with respect to x in Eqs. (43) and (44) and using a little algebra] takes the form

$$1 + R'(x) > 0 \tag{49}$$

For small deformations in the equilibrium configurations

$$\delta x_{n+1} = [1 + R'(x_n)] \, \delta x_n \tag{50}$$

free chains are characterized by all δx_n having the same sign, i.e., they can be easily "pushed" without "crunching." When this cannot be done, i.e., $\psi'(x)$ does not exist at $T = 0$, the chain is "pinned." Thus, whether or not a chain is pinned is reduced mathematically to proving an "existence theorem" for Eqs. (43) and (44).

Equation (43), which determines $\psi(x)$ [and hence $R(x)$], can be solved numerically. This was the subject of a previous paper[4] and will not be discussed further. The equation can also be studied analytically via perturbation theory. Writing

$$\psi(x) = \psi_1(x) + \psi_2(x) + \psi_3(x) + \cdots \tag{51}$$

where ψ_n is nth order in $\phi(x)$, results in a sequence of equations

$$\psi_n'(x) = \psi_n'[x + l_0(f)] + g_n(x), \qquad n = 1, 2,\ldots \tag{52}$$

The first few orders are

$$g_1(x) = \phi'(x)$$

$$g_2(x) = -\frac{1}{K_0(f)} [\psi_1'(x) - \phi'(x)]\psi_1''[x + l_0(f)]$$

$$g_3(x) = -\frac{1}{K_0} [\psi_1'(x) - \phi'(x)]\psi_2''(x + l_0) - \frac{1}{K_0} \psi_1''(x + l_0)\psi_2'(x)$$

$$+ \frac{1}{2K_0{}^2} [\psi_1'(x) - \phi(x)]^2[\psi_1'''(x + l_0) + \frac{\partial K_0(f)}{\partial f} \psi_1''(x + l_0)]$$

In general if $\phi(x)$ has m distinct, positive Fourier components, then $g_n(x)$ will have at most mn distinct, positive Fourier components,

$$g_n(x) = \sum_{k \neq 0} g_{nk} e^{2\pi i k x/a} \tag{53}$$

Equation (52) then yields

$$\psi_n'(x) = \sum_{k \neq 0} \frac{g_{nk}}{1 - e^{2\pi i k l_0/a}} e^{2\pi i k x/a} \tag{54}$$

Notice that $\psi_n'(x)$ diverges when

$$g_{nk} \neq 0, \qquad l_0 = (j/k)a, \qquad j = 0, 1, 2,...$$

Therefore, if $l_0(f)$ is irrational, there exists no divergence in the nth order $\psi_n'(x)$ for any n.[10] However, if $l_0(f)/a = N/M$ is rational, then one expects a divergence in $\psi_n'(x)$ for $n \geq M$. These divergences in $\psi_n'(x)$, however, arise from deficiencies of the perturbation expansion and can be eliminated by imposing the stability condition (i.e., doing a Maxwell construction to guarantee that μ have the proper convexity). This results in a registry transition for l_0/a close to a rational value.

From the previous equations, it follows (by differentiating the resulting expression for μ with respect to f and doing some tedious algebra) that the mean spacing per atom is

$$\frac{l(f)}{a} = \frac{l_0(f)}{a} - \frac{\pi\lambda^2 \cos(\pi l_0/a)}{8 \sin^3(\pi l_0/a)} + \frac{\lambda^2 \partial(K_0 a)/\partial f}{16 \sin^2(\pi l_0/a)} + \cdots \tag{55}$$

where

$$\lambda = \pi w/K_0 a^2 \tag{56}$$

This expression will be used in a later section.

7. EXISTENCE OF PINNING AT $T = 0$

In this section, we will show that the right-hand side of Eq. (42) always depends on x, which (as was stated earlier) implies the chain is always pinned

at $T = 0$. Our method of proof consists in showing that the assumption that the equilibrium properties of the chain be independent of the position of the first atom (call it x_0) leads to an inconsistency. Our proof depends on the fact that for sufficiently weak external "pressure" f, the chain will certainly be pinned. This statement is true because the assumption that $v(r)$ be strictly repulsive leads to a natural chain length per particle l_0 which is a monotonically decreasing function of f. Thus, for very weak f, l_0 can become enormous, leading to a situation in which the atoms interact with very weak forces. Then, each atom will lie near a minimum of $\phi(x)$, and the chain is obviously pinned.

The second atom in the chain (at position x_1) experiences a force $-v'(x_1 - x_0)$ due to the first atom (at x_0). If we set $n = 0$ in Eq. (48) and identify $-v'(x_0 - x_{-1})$ with the external force f, the condition for equilibrium of the first atom becomes

$$-v'(x_1 - x_0) = f - \phi'(x_0) \tag{57}$$

Thus, the atom at x_1 experiences a force $f - \phi'(x_0)$. If we assume that the chain is not pinned, x_0 can take on any value without changing the value of the free energy and hence may be chosen so that $f - \phi'(x_0) < f$. Now relabel the atoms so that $x_1 \to x_0$, etc. It follows that if the chain were not pinned for an external force f, it will also not be pinned for a smaller force. We conclude by induction that the chain would be not pinned for even a very small external force, which we have argued earlier is not true. Thus the chain must have been pinned, and x_0 can only take on a few discrete values consistent with minimum free energy.

Since we can always add atoms to the chain in such a way that x_0 will experience the same force on it as it had before these atoms were added, x_0 can be considered the position of an atom away from the end of the chain. It follows that each atom can take on only a few discrete values which must periodically repeat. Thus, the chain is in registry with the substrate (i.e., l_0/a is a rational number). This means that the l versus f (or l_0) curve consists entirely of discrete, flat steps. In Aubry's language, we say that the "devil's stair" is complete.[6]

It will now be shown by a simple example that although in a technical mathematical sense the "devil's stair" is complete, most of the steps can be so small that for all purposes the chain may be considered incommensurate with the substrate. Let us consider a model in which the substrate potential $\phi(x)$ is given by

$$\phi(x) = -\tfrac{1}{2}w \cos(\pi x/a) \tag{58}$$

and the interatomic potential $v(x)$ is a spring potential,

$$v(x) = \tfrac{1}{2}K_0(x - b)^2 \tag{59}$$

where b is the natural spring length.

Then, the equilibrium equation [Eq. (48)] for an atom other than an end atom in the chain is

$$-K_0(2x_n - x_{n+1} - x_{n-1}) - (\pi/a)w \sin[(2\pi/a)x_n] = 0 \tag{60}$$

The equilibrium equations for the first and last atoms in the chain (the ones at positions x_0 and x_N) are, respectively,

$$f - K_0(x_0 - x_1 + b) - (\pi/a)w \sin[(2\pi/a)x_0] = 0 \tag{61}$$

and

$$-f - K_0(x_{N-1} - x_{N-2} - b) - (\pi/a)w \sin[(2\pi/a)x_{N-1}] = 0 \tag{62}$$

Ying has argued that for weak substrate, Eq. (60) has a solution of the form[11]

$$x_n = nl + d + \sum_{p=1}^{\infty} t(p) \sin[2\pi p(nl + d)/a] \tag{63}$$

where d is an arbitrary distance less than l. Substituting in Eqs. (61) and (62) yields

$$K_0(l - b - l_0) + \sum_{p=1}^{\infty} t(p)\left\{ \sin\left(\frac{2\pi p}{a} d\right) - \sin\left[\frac{2\pi p}{a}(d - l)\right]\right\} = 0 \tag{64a}$$

$$K_0(l - b - l_0) + \sum_{p=1}^{\infty} t(p)$$

$$\times \left(\sin\left[\frac{2\pi p}{a}(d + Nl)\right] - \sin\left\{\frac{2\pi p}{a}[d + (N-1)l]\right\}\right) = 0 \tag{64b}$$

where $l_0 = -f/K_0$.

The first equation shows that there only exists an equilibrium solution for a given value of f and b for one value of d, and hence for a given value of x_0. The second equation will only be consistent with the first if

$$Nl = Ma$$

where M is an integer. Thus, we see that the boundary conditions demand that the chain of atoms be pinned in place and commensurate, as expected. Substituting Eq. (63) for the equilibrium positions in Eq. (1), using Eqs. (57) and (59), gives a potential energy per atom

$$V = \frac{1}{2} K_0 \sum_{p} t^2(p) \sin^2 \frac{\pi p l}{a} + \frac{1}{2} K_0(l - l_0)^2$$

$$- \frac{w}{2} \sum_{p} \text{Re}\left\{ \exp\left[i\frac{2\pi}{a}(nl + d)\right]\right.$$

$$\times \left. \prod_{p=1}^{\infty} \sum_{m=-\infty}^{\infty} J_m\left[\frac{2\pi}{a} t(p)\right] \exp\left[imp \frac{2\pi}{a}(nl + d)\right]\right\} \tag{65}$$

This expression is an oscillatory function of d, which for weak substrate has an amplitude of the order of

$$\frac{w}{2^q(q-1)} \left[\frac{2\pi}{a} t(1)\right]^{q-1} \tag{66}$$

where q is the order of the commensurability (i.e., if $l/a = M/N = m/q$, where m and q are prime to each other). Thus, we see that although we have argued that the "devil's stair" is complete[6] and the chain of atoms is pinned, l/a can be a ratio of large integers. Since for sufficiently weak substrate potential and very high order commensurability (i.e., large q), $(2\pi/a)t(1)$ is less than one, Eq. (66) shows that the amplitude of the oscillations of V with d can be negligibly small. Hence, we conclude that although the system goes into a commensurate state at $T = 0$, it can be a very high-order commensurate state for which d dependence (i.e., x_0 dependence) of the potential energy is negligible (i.e., there exists a continuum of nonequilibrium states nearly degenerate with the ground state). In such circumstances it should be physically, if not mathematically, correct to replace a high-order commensurate state by an incommensurate state. For strong substrate these oscillations with x_0 will no longer have small amplitude, and thus, even the very high-order commensurate states are completely pinned, since the atoms all lie at the bottom of the substrate potential walls. In any case, we will see in the next section that all zero-temperature mathematical "pathologies" disappear at nonzero temperature.

It is interesting to note that the preceding argument explains the apparent differences found between chains with free and periodic boundary conditions in Ref. 4. In Ref. 4, the lowest energy equilibrium states for free end boundary conditions were found not to be continuously degenerate in the thermodynamic limit as were the lowest energy equilibrium states for the periodic boundary condition problem. We see here that although this result is indeed correct, for the case in which l_0/a approaches an irrational number, there exists a continuum of nonequilibrium states which are nearly degenerate with the correct equilibrium ground state, so that the free-end chain does actually slide in the incommensurate thermodynamic limit.

It should be noted that if there exist more than one commensurate solution to the equilibrium equations, the lowest energy solution should be taken. Thus, we will never get overlapping steps in the "devil's stair," and although most of the steps will have negligible width, steps corresponding to the first few low-order commensurate states will have reasonable size. This is consistent with the mean field theory results found by von Boehm and Bak for a different system.[12]

8. FINITE-TEMPERATURE EFFECTS

Here we will show that the registry transitions at zero temperature and the mathematical pathologies associated with them vanish at finite temperature. It will be seen that the mechanism responsible for the destruction of registry is not a simple thermal activation process such as the formation of domain boundaries, but rather an anharmonic effect that produces a thermal expansion of the chain which "unlocks" the atoms. In this regime no reversible work is required to translate the chain relative to the substrate.

To illustrate these points it is convenient to consider the strong spring–weak substrate regime, where the continuum approximation of Frank and Van der Merwe is known to be applicable.[13] Here, the free energy required to translate the first atom $\psi(x)$ [or equivalently $R(x)$] is taken to be a slowly varying, periodic function of position. If, in Eq. (33), $\psi(x + r)$ is expanded to first order in r, one obtains

$$\mu(f, T) = \varphi(x) + \mu_0(f + \psi'(x), T) \tag{67}$$

where $\mu_0(f, T)$ is the free energy in the absence of the substrate [Eq. (11)]. Now $\mu_0(f, T)$ is a monotonic function of f and is hence invertible, i.e.,

$$f = f_0[\mu_0, T] \tag{68}$$

Equation (67) can then be inverted to yield an equation which explicitly depends upon $\psi'(x)$,

$$f + \psi'(x) = f_0[\mu_0 = \mu - \varphi(x), T] \tag{69}$$

Owing to the periodicity of $\psi(x)$, the explicit $\psi'(x)$ dependence in this equation can be eliminated by averaging over a cell. Thus,

$$f(\mu, T) = \langle f_0[\mu_0 = \mu - \phi(x), T]\rangle_{\text{cell}} \tag{70}$$

Since $l_0^{-1}(t) = (\partial f/\partial \mu_0)_T$, it follows that

$$l^{-1}(\mu, T) = \langle l_0^{-1}[\mu_0 = \mu - \phi(x), T]\rangle_{\text{cell}} \tag{71}$$

An equation of state can be obtained from these two "Thomas–Fermi"-like equations by eliminating μ.

We first show that these equations yield the continuum model results of Frank and Van der Merwe[12] in the limit of zero temperature. Consider a system of point hard-core atoms interacting with spring potentials in the presence of a sinusoidal substrate potential. At zero temperature it is found by inverting Eq. (32) that

$$f_0(\mu_0) = K_0 b - K_0 b[1 - (2\mu_0/K_0 b^2)]^{1/2} \tag{72}$$

where b is the natural spring length (i.e., the value of l_0 for $f = 0$). Also, by differentiating Eq. (68) with respect to μ_0,

$$l_0^{-1}(\mu_0) = \frac{1}{b(1 - 2\mu_0/K_0 b^2)^{1/2}} \tag{73}$$

Replacing μ_0 by $\mu - \phi(x)$ and integrating over a cell yields

$$l_0(k) = 2aE(k)/\pi\xi_0 k \tag{74}$$

$$l(k) = \pi a/2\xi_0 k K(k) \tag{75}$$

Here $K(k)$ and $E(k)$ are the complete elliptic functions of the first and second kind and

$$\xi_0^2 = K_0 a^2/2W \tag{76}$$

$$k^2 = W/(W - \mu + \tfrac{1}{2}K_0 b^2) \tag{77}$$

These are precisely Frank and Van der Merwe's equations for the continuum model at zero temperature.[13]

Second, we show that harmonic phonons alone cannot be responsible for the elimination of the registry transition at finite temperature. Consider the temperature dependence of $\mu_0(f, T)$ shown in Eq. (32). The first temperature term arises from harmonic phonons, whereas the second temperature term arises from the anharmonicity produced by the point hard-core interaction. It is evident that if the anharmonic term is neglected, the registry transition will persist at all temperatures [since $l_0 = (\partial\mu_0/\partial f)_T$ is then temperature independent]. The harmonic term merely alters k, the argument of the elliptic functions, which cannot affect the registry. The point here is that harmonic phonons cannot produce the thermal expansion in the chain that precipitates "melting."

To treat the anharmonic term correctly, Eq. (67) must be inverted numerically. The results are displayed in Fig. 1. Notice that the slightest temperature will cause the "kink" in l versus l_0 to "round out." That is, the l versus l_0 curve, instead of having a flat region for a range of l_0 values around perfect registry, at $T > 0$, has an inflection point at registry (i.e., a second-order phase transition at $T = 0$). For low T, however, the curve is almost flat.

It should be noted that any analytical approach to the inversion of $l_0(f, T)$ that iterates the anharmonic term will ultimately encounter negative values of $l(f, T)$ for small values of l_0, which when Maxwell constructed to give proper convexity, produce a fictitious registry transition at finite temperature in contradiction with the "exact" numerical calculation. However, extensions of such iterative calculations to higher order will "improve" the results by decreasing the slope of the fictitious registry "kink" while moving its location toward the origin. In this sense an iterative approach can be used to obtain the qualitative features of $l(f, T)$.
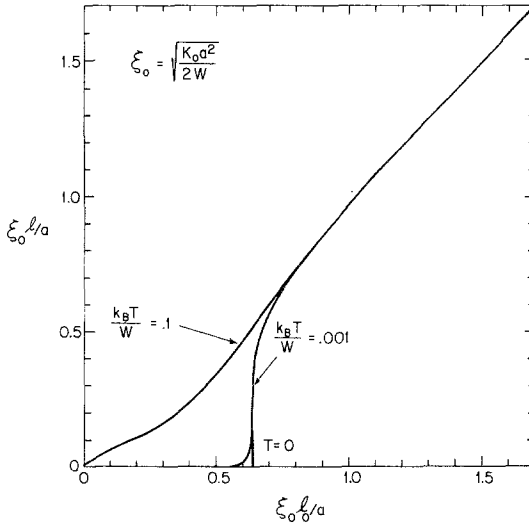
Fig. 1. The dimensionless quantity $l\xi_0/a$ plotted as a function of $l_0\xi_0/a$ for three values of $k_{\mathrm{B}}T/W$.

The previous remarks about the destruction of registry at finite temperature were shown to be valid for the "continuum" model. We should be able to obtain similar effects in the discrete model. The extreme, nonlinear character of the equations makes perturbation theory the only viable computational tool. However, as in the continuum model, perturbation theory will fail to describe the physics of the system unless carried to all orders. Truncation of the expansion will again lead to convexity problems in $l(f, T)$ which produce fictitious registries at finite temperature. To show this, consider again the strong spring–weak substrate limit. The chemical potential can be (cluster) expanded in powers of substrate interaction, i.e.,

$$\mu(f, T) = \mu_0(f, T) + \phi_{K=0} - \frac{1}{k_{\mathrm{B}}T} \sum_K S_0(K)|\phi_K|^2 + \cdots \qquad (78)$$

where ϕ_K is the Kth Fourier component of the substrate potential and $S_0(K)$ is the substrate-free structure factor. Differentiating this expansion with respect to f, one finds the mean spacing per atom at low temperatures to be

$$l(f, T) = l_0(f, T) - \frac{a\pi^3}{16\xi_0^4} \frac{\sin[2\pi l_0(0)/a]}{\{\cosh(2\pi^2 k_0 T/K_0 a^2) - \cos[2\pi l_0(0)/a]\}^2} + \cdots \qquad (79)$$

Notice that the singular denominators that occur in the zero-temperature expansion [i.e., Eq. (55)] are "cut off" by Debye–Waller factors. These cutoffs, however, are not sufficient to avoid convexity problems in low-order

expansions (as evidenced by negative l values for l_0/a nearly rational). As the temperature is decreased, the system can be shown via a Maxwell construction to undergo a fictitious registry transition as in the continuum model. Here the source of the convexity problems arising in the perturbation expansions is twofold: First, as in the continuum model, the anharmonicity of the hard-core interaction must be included to all orders. Second, all the higher order terms (which vary with ξ_0 as ξ_0^{-4n}, where n is the order of the registry) contribute to the primary registry. As in the continuum model, the higher order terms will improve the calculation by decreasing the slope of the registry "kink" and displacing its location toward the origin.

We have calculated the entropy for this model at low temperatures for the fundamental registry (i.e., $l = a$) as a function of temperature. The entropy was found to exhibit no anomalies at $T = 0$ (remember that we are using classical mechanics and hence the entropy need not go to zero). This is consistent with the behavior of the entropy for the substrate-free case discussed at the end of Section 3.

9. THE STATIC STRUCTURE FACTOR IN THE INCOMMENSURATE PHASE

As mentioned in Section 2, the structure factor $S(Q)$ for the one-dimensional chain of atoms at nonzero temperature in the absence of a substrate is liquidlike. That is, it exhibits finite peaks of successively increasing width. As $T \to 0$, these peaks narrow and increase in height, becoming Bragg peaks at $T = 0$. To find $S(Q)$ in the presence of a substrate, we consider a subsection of the chain with m atoms and put a "pressure" p on the end atoms of this subsection. Then, the change in Gibbs free energy of this subsection due to this pressure $mg_m(p)$ is given by

$$\exp[-mg_m(p)/k_BT] = \langle \exp(-p|x_{m+n} - x_n|/k_BT) \rangle \tag{80}$$

(The thermal average clearly includes an average over the center of mass of the chain.) Then, we may write

$$S(Q) = 1 + 2 \operatorname{Re} \sum_{m=1}^{\infty} \exp[-mg_m(p = -ik_BTQ)/k_BT] \tag{81}$$

Using the small-p asymptotic expansion,

$$g_n(p) = l_n p - \tfrac{1}{2}K_n^{-1}p^2 + \cdots$$

where

$$l_n = (\partial g_n/\partial p)_T, \qquad K_n^{-1} = -(\partial l_n/\partial p)_T$$

We find that for low temperatures and relatively small values of Q

$$S(Q) = 1 + 2 \sum_{m=1}^{\infty} \cos(Qml_m) \exp(-2K_m^{-1}k_BTQ^2m) \tag{82}$$

This expression gives the diffuse scattering. Away from a registry transition and for weak substrate potentials, $K_{n-n'}$ is to a good approximation the force constant for the interaction potential between a pair of atoms [i.e., $(\partial^2 v/\partial x^2)$]. We see, as with the substrate-free case, that the diffuse peaks narrow into Bragg peaks at $T = 0$. At any temperature there occur diffuse scattering peaks for $Q = (2\pi/a)q_1 + (2\pi/a)q_2$, where q_1 and q_2 are positive or negative integers. If the chain is in a registry phase, since we showed earlier that K_m^{-1} (which becomes the compressibility for large m) becomes zero, we see that the diffuse peaks become Bragg peaks.

In addition to the diffuse scattering, there will occur Bragg scattering for $Q = (2\pi/a)q_1$ because the substrate induces its periodicity in the chain. For example, to lowest order in the substrate potential, we get a reduced Fourier component of strength

$$\rho_{2\pi/a} = \frac{S_0(2\pi/a)}{2kT} \phi_{2\pi/a} \tag{83}$$

where $S_0(Q)$ is the substrate-free structure factor and $\phi_{2\pi/a}$ is the $2\pi/a$ Fourier coefficient of the substrate potential. Thus, we conclude that x-ray or neutron scattering from the chain will exhibit Bragg scattering at the substrate reciprocal lattice vectors and diffuse scattering at the reciprocal lattice vectors of the chain, the diffuse scattering becoming Bragg scattering at $T = 0$. The lack of Bragg scattering at the chain reciprocal lattice vectors is, of course, due entirely to the one-dimensional nature of the system.

10. CONCLUSIONS

We conclude that at $T = 0$, the lattice constant l of the chain versus the compression force f is a "devil's stair" (i.e., there exists a registry phase transition at each value of f). Of course, most of the "steps" have negligibly small width, leading to the appearance of a smooth curve, with only the lowest order registries giving sizable steps. Each "step" can be thought of as a first-order phase transition turned 90°, leading to the result that $\partial l/\partial f = 0$ (i.e., the lattice hardens rather than softens when registry occurs). We also conclude that the chain is always pinned at $T = 0$, in that it requires an extensive energy to slide it, but for most values of f this energy is negligibly small (i.e., for all purposes zero).

At nonzero temperature, however, all the registry transitions round out into a smooth transition and the chain only requires an intensive free energy

to slide it (i.e., it is not pinned). This does not, of course, mean that the chain can slide without resistance, because there can still be considerable irreversible work, which is not included in our equilibrium statistical mechanical treatment. This will be the subject of a later paper on dynamics. The occurrence of a smooth (i.e., second order) registry transition for nonzero T is consistent with similar results found for two-dimensional models for registry transitions by Pokrovsky and Talapov[14] and McMillan.[3]

It is interesting to note that our result that the system can go from a registered solid phase at $T = 0$ to an incommensurate liquid phase at $T \neq 0$ (see Section 9) is consistent with the experimental results of Clarke et al.,[15] who find a similar result when a two-dimensional intercalate in a graphite intercalation compound melts.

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