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DIFFUSION IN THE FRENKEL–KONTOROVA MODEL WITH ANHARMONIC INTERATOMIC INTERACTIONS

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Low-temperature diffusion and transport properties of the generalized Frenkel–Kontorova model are investigated analytically in the framework of a phenomenological approach which treats a system of strongly interacting atoms as a system of weakly-interacting quasiparticles (kinks). The model takes into account realistic (*anharmonic*) interaction of particles subjected into a periodic substrate potential, and such a generalization leads to a series of novel effects which we expect are related to the experimentally-observed phenomena in several quasi-one-dimensional systems. Analysing the concentration dependences in the framework of the kink phenomenology, we use the renormalization procedure when the atomic structure with a complex unit cell is treated as (more simple) periodic structure of kinks. Using phenomenology of the ideal kink gas, the low-temperature states of the chain are described as those consisting of "residual" kinks supplemented by thermally-excited kinks. This approach allows us to describe the ground states of the chain as a hierarchy of "melted" kink lattices. Dynamical and diffusion properties of the system are then described in terms of the kink dynamics and kink diffusion. The motion equation for a single kink is reduced to a Langevin-type equation which is investigated with the help of the Kramers theory. Susceptibility, conductivity, self-diffusion and chemical diffusion coefficients of the chain are calculated as functions of the kink diffusion coefficient. In this way, we qualitatively analyze, for the first time to our knowledge, dependence of the different diffusion coefficients on the concentration of atoms in the chain. The results are applied to describe peculiarities in conductivity and diffusion coefficients of quasi-one-dimensional systems, in particular, superionic conductors and anisotropic layers of atoms adsorbed on crystal surfaces which were earlier investigated experimentally.

1. Introduction

The study of mass and charge transport in systems with strong interatomic interactions is an extremely difficult problem. At high temperatures transport coefficients

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can be found with the help of a perturbation technique starting from the case of non-interacting atoms. However, at low temperatures the perturbation theory breaks down and diffusional and transport characteristics may be found by computer simulations for a given choice of the system parameters. To explain results of such simulations as well as to understand at least qualitatively the system behavior, it is useful to elaborate a phenomenological approach in which a system of strongly interacting atoms is approximately treated as a system of weakly-interacting quasiparticles. In fact, in such a phenomenological approach the primary problem splits into two particular problems. First, one should introduce appropriate quasiparticles corresponding to the system of strongly interacting atoms and then calculate the parameters of these quasiparticles. Second, one has to connect the parameters which characterize the system dynamics with those of the quasiparticles.

In the present paper we use such a phenomenological approach to investigate the low-temperature diffusion in a generalized (anharmonic) Frenkel–Kontorova (FK) model. Firstly introduced to model the dynamics of one-dimensional dislocations in crystals,[1] in a rather general context, an FK type model describes a one-dimensional chain of interacting particles subjected into an effective substrate (on-site) potential. This model may describe, for example, a closely-packed row of atoms in crystals,[2] a chain of atoms adsorbed on stepped or furrowed crystal surfaces,[3] a chain of ions in a "channel" of quasi-one-dimensional conductors,[4] hydrogen atoms in hydrogen-bonded systems,[5] etc. (see, e.g., the recent review paper[6] for other applications of the FK model). In all the cases mentioned above the chain of interacting particles is a part of the whole physical system under consideration, and the remainder is modeled as an external periodic (substrate) potential and also as a thermal bath.

In the present paper we consider the generalized FK model which takes into account realistic (anharmonic) interactions between atoms in the chain. The reason for such a generalization is explained by the following. We try to describe the typical physically important situation when the mean distance between the particles in the chain varies from the value of order of the period of the substrate potential to infinity. It is clear that in this case the standard harmonic approximation for the interatomic potential looks not realistic, and one should use a realistic interaction potential. The main objective of our study is to investigate diffusion and transport characteristics of such a model as well as *to analyze the dependence of the diffusion coefficients on concentration of particles in the chain.*

The paper is organized as follows. In Sec. 2 we briefly describe our model. Section 3 introduces three diffusion coefficients which describe transport properties of the FK chain. Section 4 presents the main ideas of the renormalization procedure which, for certain cases, allows a rather complex structure of atoms at $T = 0$ to be treated as a more simple system of weakly-interacting kinks. The case of $T \neq 0$ is analysed in Sec. 5 using the approach based on the theory of the ideal kink gas. In Sec. 6 we describe diffusion of a single kink with the help of an effective Langevin equation derived for the kink's coordinate. The main purpose of this study

is to find the kink diffusion coefficient. As we show in Sec. 7, the three diffusion coefficients introduced in Sec. 3 may be found as functions of the kink diffusion coefficient and the susceptibility of the chain. In Sec. 8 we discuss temperature and concentration dependences of the diffusion coefficients. At last, Sec. 9 concludes the paper by discussing possible applications of the anharmonic FK model to describe recent experimental results on the surface diffusion of atoms adsorbed on anisotropic crystal surfaces.

2. Model

We consider a chain of particles (atoms) subjected into a periodic substrate (on-site) potential which is taken in the simplest form

$$V_{\text{sub}}(x) = \frac{1}{2}\epsilon_s \left[1 - \cos\left(\frac{2\pi x}{a_s}\right)\right] , \tag{1}$$

where ϵ_s and a_s are the height and period of the potential, respectively. Energy exchange between the chain and substrate can be approximately described by introducing a viscous friction force together with a random force which stands for random fluctuations acting on each atom. We assume that such a fluctuation force $\delta F_l(t)$ is a local Gaussian random function,

$$\langle \delta F_l(t) \rangle = 0 , \quad \langle \delta F_l(t) \delta F_{l'}(t') \rangle = 2\eta m_a k_{\text{B}} T \delta_{ll'} \delta(t - t') , \tag{2}$$

where η is the friction coefficient, m_a is the atom's mass, k_{B} is the Boltzmann constant, T is the substrate temperature, and the index l stands for the atom's number in the chain. Thus, the motion equation of the lth atom may be written in the form

$$m_a \ddot{x}_l + m_a \eta \dot{x}_l + V'_{\text{sub}}(x_l) + \sum_{l'=1}^{\infty} [V'_{\text{int}}(x_l - x_{l-l'}) - V'_{\text{int}}(x_{l+l'} - x_l)] = \delta F_l(t) , \tag{3}$$

where $x_l(t)$ is the coordinate of the lth atom, $V_{\text{int}}(x)$ is the energy of interaction between two neighboring atoms, and also $\dot{x} \equiv dx/dt$ and $V'(x) = dV/dx$. Note that the relation (2) following from the fluctuation–dissipation theorem guarantees the existence of a thermal equilibrium of a stationary state of the chain averaging over which is denoted by $\langle \ldots \rangle$.

In the present paper we consider the so-called "fixed density" FK chain consisting of N atoms uniformly distributed on the length $L = Ma_s = Na_{\text{A}}$ where M is the number of minima of the substrate potential and a_{A} is the average interatomic distance. Thus, the system is characterized by concentration of atoms, $n = N/L = a_{\text{A}}^{-1}$, or by the dimensionless "coverage" parameter θ defined as $\theta = N/M = na_s = a_s/a_{\text{A}}$. Throughout the paper we assume the limit when N, M, and $L \to \infty$ at n (or θ) fixed.

In the standard FK model[1] the interaction potential $V_{\rm int}(x)$ is approximated by a harmonic function,

$$V_{\rm int}(x) = \frac{1}{2} G_{\rm A}(x - a_{\rm A})^2 \ , \quad G_{\rm A} \equiv V''_{\rm int}(a_{\rm A}) \ , \tag{4}$$

and, moreover, only the interactions of the nearest neighbors are taken into account. However, here we will be interested in a more realistic physical situation when the coverage parameter θ is an "external" parameter which changes within the interval $0 \leq \theta \leq 1$, so that the interatomic distance $a_{\rm A}$ varies from a_s to ∞. Note that such a problem naturally corresponds to real physical objects as, for example, adsorbed layers or one-dimensional conductors. In this case the harmonic approximation for the interatomic potential (4) is not realistic and we should describe the interaction by a more realistic function which allows larger variations of the atomic displacements. For simplicity, we take the exponential interparticle interaction

$$V_{\rm int}(x) = V_0 \exp\left[-\beta\left(\frac{x}{a_s} - 1\right)\right] \ , \tag{5}$$

where V_0 ($V_0 > 0$) is the interaction energy of two atoms localed at the nearest minima of the substrate potential, and β is the dimensionless anharmonicity parameter of this potential. As a natural way to generalize the potential (5), we may add a linear attractive branch as it is for the standard Toda lattice (i.e. a chain of exponentially interacting particles without a substrate potential), but for the "fixed density" FK chain which we study here such a modification of the model is not physically important.

For the case $\eta = 0$, $T = 0$, and $\theta = 1/q$, q being integer, and for strong-coupling approximation when interatomic forces are much larger than the force $V'_{\rm sub}(x_l)$ produced by the on-site potential, the motion equation (3) with the harmonic interactions (4) reduces to the well-known sine-Gordon (SG) equation. The SG equation is exactly integrable and it admits solutions in the form of topological solitons or *kinks*. In a general case, Eq. (3) is not integrable. Nevertheless, at least at low temperatures we may describe the system dynamics in terms of kinks because the kink excitations are responsible for the mass transport along the chain and such solutions do exist as solutions of a generalized FK model. Below we use the kinks as quasiparticles which play the basic role in the phenomenological approach developed here to describe diffusional dynamics and transport properties in the FK chain.

3. Diffusion Coefficients of the FK Chain

For a uniform system in a thermodynamically equilibrium state one can introduce *three* different diffusion coefficients: the *self-diffusion* (or "tracer"-diffusion) coefficient D_s, the *collective-diffusion* (or "jump"-diffusion) coefficient D_μ, and the *chemical-diffusion* coefficient D_c. All these diffusion coefficients may be expressed

through the Laplace transform of the velocity correlation function $Q(l; t)$:

$$\bar{Q}(l; \bar{\omega}) = \int_0^\infty dt \, \exp(i\bar{\omega}t) Q(l; t) , \quad \mathrm{Im}\,\bar{\omega} > 0 , \tag{6}$$

to be

$$Q(l - l'; t - t') = \langle \dot{x}_l(t) \dot{x}_{l'}(t') \rangle . \tag{7}$$

By definition, the self-diffusion coefficient D_s is found as

$$D_s = \lim_{\bar{\omega} \to 0+i0} \bar{\mathcal{D}}_s(\bar{\omega}) , \quad \mathcal{D}_s(t) = Q(0; t) . \tag{8}$$

The value D_s describes the mean-square displacements of a given ("tagged") atom on long-time scales,

$$\langle [x_l(t) - x_l(0)]^2 \rangle = 2D_s t , \quad t \to \infty . \tag{9}$$

The function $\bar{\mathcal{D}}_s(\bar{\omega})$ describes, for example, incoherent scattering experiments for some application of the FK model.

The collective-diffusion coefficient D_μ is introduced as

$$D_\mu = \lim_{\bar{\omega} \to 0+i0} \bar{\mathcal{D}}_\mu(\bar{\omega}) , \quad \mathcal{D}_\mu(t) = \sum_{l=1}^{N} Q(l; t) . \tag{10}$$

Because $\mathcal{D}_\mu(t)$ may be represented as

$$\mathcal{D}_\mu(t) = \langle \dot{Y}(t) \dot{Y}(0) \rangle , \tag{11}$$

where $Y(t)$ is the center of mass introduced as

$$Y(t) \equiv \frac{1}{\sqrt{N}} \sum_{l=1}^{N} x_l(t) , \tag{12}$$

the coefficient D_μ describes the long-time dynamics of the center of mass of the atoms $\langle [Y(t) - Y(0)]^2 \rangle = 2D_\mu t$, $t \to \infty$. From the definitions (8) and (10) it follows that

$$\mathcal{D}_\mu(t) = \mathcal{D}_s(t) + \frac{1}{N} \sum_{l \neq l'} \langle \dot{x}_l(t) \dot{x}_{l'}(0) \rangle . \tag{13}$$

Thus, the function $\mathcal{D}_\mu(t)$ includes an effect of *correlated motion* of interacting atoms. The coefficient D_μ is connected with the mobility coefficient $\mathcal{M}$ by the well-known Einstein relation; namely, when the particles in the FK chain have an electric charge e, the frequency-dependent conductivity $\sigma(\omega)$ is defined as

$$\sigma(\omega) = ne^2 \bar{\mathcal{M}}(\omega) , \quad \bar{\mathcal{M}}(\omega) = \frac{1}{k_B T} \bar{\mathcal{D}}_\mu(\omega + i0) . \tag{14}$$

The chemical diffusion coefficient D_c is determined through the relation

$$D_c = D_\mu/\chi \,, \tag{15}$$

where χ is the dimensionless susceptibility of the system. As a matter of fact, the coefficient D_c describes the flux $J(x,t) = \sum_l \dot{x}_l(t)\delta(x - x_l(t))$ in a nonequilibrium state when the atomic density $\rho(x,t) = \sum_l \delta(x - x_l(t))$ slightly deviates from its equilibrium value; namely, according to the second Fick law, we may write

$$\ll J(x,t) \gg \approx -D_c \frac{\partial}{\partial x} \ll \rho(x,t) \gg \,, \tag{16}$$

where $\ll \ldots \gg$ stands for the averaging over the macroscopic distances $x \gg a_A$.

For the system of noninteracting atoms all the diffusion coefficients are equal to each other, i.e. $D_s = D_\mu = D_c = D$, and one may use any definition mentioned above to calculate the only diffusion coefficient D. In particular, for the simplest case of a gas of noninteracting Brownian particles, when $V_{sub}(x) = 0$, we have $D = D_f \equiv k_B T/m_a\eta$. When $V_{sub}(x)$ is nonzero but $\epsilon_s \ll k_B T$, simple calculations based on the perturbation theory yield (see, e.g., Refs. 7–9)

$$D \approx D_f \left[1 - \frac{1}{8}\left(\frac{\epsilon_s}{k_B T}\right)^2\right] \,. \tag{17}$$

Otherwise, at low temperatures, $k_B T \ll \epsilon_s$, the coefficient D may be represented in the Arrhenius form,

$$D = \mathcal{K}\lambda^2 \,, \quad \mathcal{K} = \mathcal{K}_0 \exp(-\epsilon_s/k_B T) \,, \tag{18}$$

where $\mathcal{K}$ is the escape rate of an atom from a bottom of the potential relief, and λ is the mean length of the atomic jump. The preexponential factor $\mathcal{K}_0$ in Eq. (18) may be calculated with the help of the Kramers theory (see, e.g., Refs. 10 and 11)

$$\mathcal{K}_0 \approx \begin{cases} \epsilon_s\eta/k_B T \,, & \text{if } \eta < \eta_l \equiv \omega_0 k_B T/2\pi\epsilon_s \,, \\ \omega_0/2\pi \,, & \text{if } \eta_l < \eta < \omega_* \,, \\ \omega_0\omega_*/2\pi\eta \,, & \text{if } \eta > \omega_* \,, \end{cases} \tag{19}$$

where $\omega_0^2 = V''_{sub}(0)/m_a$ and $\omega_*^2 = -V''_{sub}(a_s/2)/m_a$. The value of λ may be estimated as[12]

$$\lambda \approx \begin{cases} a_s\eta_l/\eta \,, & \text{if } \eta < \eta_l \,, \\ a_s \,, & \text{if } \eta > \eta_l \,. \end{cases} \tag{20}$$

When interaction between atoms in the chain is taken into account, the diffusion coefficients defined above become *different*, and, in particular, they become depen-

dent on the coverage parameter θ. From the physical point of view, the role of the interatomic interactions may be characterized by the following factors.

(a) The interaction produces an order in the atoms arrangement (in one-dimensional systems such an order is short-range at $T \neq 0$). This fact results in $\chi \neq 1$ and, therefore, $D_c(\theta) \neq D_\mu(\theta)$ if $\theta \neq 0$;
(b) Each mobile atom "feels" a potential produced by other atoms and, therefore, an effective potential for a given atom depends on positions of the neighboring atoms;
(c) The motion of an atom in the chain gives rise to motion of the neighboring atoms. Such a collective motion is an analog of the "polaronic effect" in the solid state physics, and at low temperatures this collective motion may be described as motion of quasiparticles;
(d) If the model is nonintegrable, the atomic motion is always accompanied by an energy exchange between different modes of the chain leading to an intrinsic chaotization of the system dynamics. Such an effect may be approximately taken into account by assuming that the friction coefficient η includes not only a contribution of the external friction η_{ext} (which is usually introduced to account the influence of thermostat) but also a contribution of the "intrinsic" friction η_{int}, i.e. in fact, one should write $\eta = \eta_{\text{ext}} + \eta_{\text{int}}$.

The factors (a) and (b) have a static nature, while the latter two factors (c) and (d) are solely dynamical. A rigorous problem to take into account interatomic interactions in the system dynamics is rather complicated even for the case when the substrate potential is absent. At high temperatures the perturbation theory based on the Mori technique is usually used. At low temperatures, the perturbation theory does not work but, instead, we may use the phenomenological approach which we develop in the present paper.

The first step of this approach we have is to calculate the kink parameters. For the case of weakly-interacting atoms at an arbitrary value of the coverage parameter θ, as well as for the case of strongly interacting atoms but for the trivial ground state (GS) with $\theta = 1/q$ (q being integer), the kink characteristics can be found analytically. Otherwise, for a general case of $\theta \neq 1/q$ when the GS at $T = 0$ has a complex unit cell, the kink parameters may be found approximately using the renormalization procedure when the complex atomic structure is treated as a more simple structure of weakly-interacting kinks. These approaches are discussed in the next section (see also Appendix A and Table 1).

4. The $T = 0$ Ground State and Kinks

First we should describe the ground state (GS) of the FK chain at zero temperature when the atoms form a regular structure. Let us denote by GS[θ] the minimum-energy commensurate (C-) structure with the coverage parameter $\theta = s/q$, where s and q are positive integer numbers. The C-structure GS[θ] has a period $a = qa_s$,

and the elementary cell consists of s atoms. For any C-structure we can define a kink k (antikink $\bar{k}$) with a topological charge $\sigma = +1$ ($\sigma = -1$) as a minimally possible contraction (extension) of the structure when at infinity, i.e. for $l \to \pm\infty$, the arrangement of atoms relative to the minima of the substrate potential coincides with their arrangement in the GS. Kinks are elementary excitations of the GS[θ] which are spacially localized and topologically stable owing to boundary conditions. The kink has the simplest structure for the trivial GS with $\theta = 1$, when one kink (antikink) corresponds to one additional atom (vacancy) inserted into the chain, and the neighboring atoms are allowed to relax. In a general case, the kink structure is more complicated. In particular, for the GS[s/q] one additional atom (vacancy) corresponds to q kinks (antikinks).

The kink is a topologically stable quasiparticle with the following characteristics. First of all, the kink structure is conventially characterized by the displacements $u_l = x_l - x_l^{(0)}$, where x_l are the atomic coordinates for the chain with a single kink and $x_l^{(0)}$ are those for the GS. From the definition of the kink it follows that

$$\lim_{\substack{j\to+\infty \\ j'\to-\infty}} \sum_{i=1}^{s} (u_{sj+i} - u_{sj'+i}) = -\sigma a_s \ . \tag{21}$$

Following Bergman *et al.*[13] the kink's coordinate X_k may be defined as the coordinate of the center of mass of particles

$$X = q \sum_l x_l + C \ , \tag{22}$$

where the constant C is chosen in the way that the maximum deviation from the C-structure occurs at the atom with the number $l_0 = \mathrm{int}(X/a)$. The kink rest energy E_k is defined as the difference between the energy of the chain with the kink and the energy of the GS with the same number of atoms. Because the configuration $\{x_l'\} \equiv \{x_{l-s} + qa_s\}$ describes also the kink translated by a distance $a = qa_s$, i.e. by a unit cell of the C-structure), the kink may move along the chain. The amplitude of the Peierls–Nabarro (PN) barrier, ϵ_{PN}, is defined as the lowest energy barrier which must be passed for a translation $\{x_l\} \to \{x_{l'}\}$. It is necessary also to introduce the adiabatic trajectory (AT) as the curve in the $N-$dimensional configuration space of the system, which links two minimum-energy configurations $\{x_l\}$ and $\{x_{l'}\}$, passing through the nearest saddle configuration with the lowest potential energy. Such a trajectory satisfies the set of differential equations

$$\frac{dx_l(\tau)}{d\tau} = -\frac{\partial V}{\partial x_l} \ , \tag{23}$$

where V is the total potential energy of the system and τ is a parameter varying along the trajectory. Thus, the AT is the curve of the steepest descent. Physically, the AT describes the kink motion in the limit $\eta \to \infty$, when it moves adiabatically.

During the kink motion along the AT, the potential energy of the system oscillates with the amplitude ϵ_{PN}. These oscillations can be described by the function $V_{PN}(X)$ which can be interpreted as kink's potential energy. The potential $V_{PN}(X)$ may be approximately described by the function

$$V_{PN}(X) \approx \frac{1}{2}\epsilon_{PN}\left[1 - \cos\left(\frac{2\pi X}{a}\right)\right] . \tag{24}$$

At the same time, the kinetic energy of the system moving along the AT can be found as

$$K = \frac{1}{2}m_k\dot{X}^2 , \tag{25}$$

where the effective mass of the kink is introduced as the following

$$m_k = m_a \sum_l \left(\frac{\partial u_l}{\partial X}\right)^2_{x_l \in AT} . \tag{26}$$

In a general case, the kink mass m_k depends on the kink's coordinate X, but such an effect will be neglected below because oscillations of the kink's mass are usually small (see, e.g., Ref. 6).

Finally, when the chain contains two kinks (with the topological charges σ_1 and σ_2) separated by the distance $R = |X_1 - X_2|$, the kinks interact with the energy $v_{int}(R)$. Usually, a kink and antikink attract each other while two kinks as well as two antikinks repel each other. We would like to note that there are two mechanisms of the kink interaction. First of all, interaction between kinks arises due to the interaction of excess atoms which effectively correspond to the kinks.[16] Besides, there always exists an interaction between kinks due to overlapping of the kinks' tails because the presence of another kink nearby perturbs the kink's shape leading to a change of the kink's energy.[14] In the chain with a small density of kinks the total interaction energy may be assumed to be pairwise.[14]

Below we restrict ourselves mainly by the case $\theta \leq 1$ because this situation corresponds to the physical objects mentioned in the Introduction. The kink's characteristics can be simply found in the case of a weak interatomic interaction, $V_{int}(a_A) \ll \epsilon_s$, when in the GS all atoms are situated at the corresponding minima of the substrate potential. Namely, for the GS[θ] when the reference structure is characterized by the coverage parameter $\theta = s/q$ lying within the interval

$$(1+p)^{-1} < \theta < p^{-1} , \tag{27}$$

where p is integer, in the lowest approximation using a simple geometrical consideration we can find for the kinks and antikinks (including the case of a kink on the background with the coverage parameter $\theta = (1+p)^{-1}$ and that of an antikink on the background structure with $\theta = p^{-1}$) the following results[15,16]:

$$m_k \approx m_a/q^2 , \tag{28}$$

$$E_{k\sigma} \approx V_{\rm int}(a - \sigma a_s) - V_{\rm int}(a) \ , \tag{29}$$

$$\epsilon_{\rm PN} \approx \epsilon_s + 2V_{\rm int}\left(pa_s + \frac{1}{2}a_s\right) - V_{\rm int}(pa_s) - V_{\rm int}(pa_s + a_s) \approx \frac{1}{2}\epsilon_s(2 - \pi^2 g_p) \ , \tag{30}$$

where

$$g_p = \frac{a_s^2}{2\pi^2\epsilon_s} V''_{\rm int}\left(pa_s + \frac{1}{2}a_s\right) \ . \tag{31}$$

Because in the "fixed-density" FK chain kinks can be created only as kink–antikink pairs, we should also calculate the creation energy of the $k\bar{k}$ pair which coincides with the energy of a kink and antikink separated by an infinite distance

$$\epsilon_{\rm pair} = E_k + E_{\bar{k}} \approx V_{\rm int}(a + a_s) + V_{\rm int}(a - a_s) - 2V_{\rm int}(a) \approx 2\pi^2\epsilon_s g_a(1 - 2g_a) \ , \tag{32}$$

where

$$g_a = \frac{a_s^2}{2\pi^2\epsilon_s} V''_{\rm int}(a) \ . \tag{33}$$

It is important to note that for a given structure GS[θ] parameters of the kink and antikink are different provided the potential $V_{\rm int}(x)$ is anharmonic function as it is given by Eq. (5). Indeed, effective interaction forces for the kink (in the region of a local contraction of a chain) exceed those for the antikink (in the region of a local extension of an atomic chain). As a result, at the same values of the parameters V_0 and β a kink, in comparison with an antikink, is characterized by a larger value of the rest energy and by lower values of the effective mass and the PN potential barrier. The fact of the symmetry breaking between the kink and antikink parameters due to anharmonic interatomic interactions was firstly mentioned by Milchev and Markov.[17] In particular, the difference in the values of the PN barrier for the kink and antikink is equal to

$$\delta\epsilon_{\rm PN} = \epsilon_{\rm PN}^{\sigma=-1} - \epsilon_{\rm PN}^{\sigma=+1} \approx \left[2V_{\rm int}\left(a + \frac{1}{2}a_s\right) - V_{\rm int}(a) - V_{\rm int}(a + a_s)\right] - \left[2V_{\rm int}\left(a - \frac{1}{2}a_s\right) - V_{\rm int}(a - a_s) - V_{\rm int}(a)\right] \approx \frac{1}{2}\pi^2\epsilon_s\tilde{\beta}g_a \ , \tag{34}$$

where

$$\tilde{\beta} = -a_s V'''_{\rm int}(a)/V''_{\rm int}(a) \ . \tag{35}$$

Note that for the exponential interatomic potential (5) the dimensionless elastic constant g_a and the anharmonicity parameter $\tilde{\beta}$ are equal to

$$g_a = \frac{1}{2\pi^2}\left(\frac{V_0}{\epsilon_s}\right)\beta^2 \exp[-\beta(q-1)] , \quad \tilde{\beta} = \beta . \tag{36}$$

The another important point is that for a given GS[θ] the energies ϵ_{pair} and $\delta\epsilon_{\text{PN}}$ depend not on interaction of neighboring atoms situated on the distance $x \sim a_{\text{A}}$, but on interaction between elementary unit cells of the reference C-structure, i.e. they are determined by interatomic interactions on the distances $x \sim a = qa_s$. Therefore, the more complicated is the reference C-structure, the lower is the corresponding values of ϵ_{pair} and $\delta\epsilon_{\text{PN}}$. For example, if we consider two commensurate structures with the nearest values of the coverage parameter θ, e.g. $\theta_1 = \frac{1}{2}$ and $\theta_2 = \frac{100}{201}$, from Eq. (36) we obtain the ratio $g_a(\theta_2)/g_a(\theta_1) = \exp(-199\beta)$ and, according to Eqs. (32) and (34), the values ϵ_{pair} and $\delta\epsilon_{\text{PN}}$ for the GS[θ_2] will be lower than those for the GS[θ_1] in $\exp(199\beta)$ times.

The interaction between kinks for the FK chain with a weak coupling is exponentially small. In particular, for the GS[θ] with the coverage θ close to $\theta_0 = 1$ the potential energy of the chain can be reduced to the Ising-like form with $\theta_0 = 1$ antikinks instead of atoms.[18] In this case two antikinks separated by a distance R repel each other according to the law

$$v_{\text{int}}(R) \approx 2\pi^2\epsilon_s g_s \exp(-\xi R/d) , \tag{37}$$

where

$$\xi \approx -\sqrt{g_s}\ln g_s , \quad d = a_s\sqrt{g_s} , \quad g_s = a_s^2 V''_{\text{int}}(a_s)/2\pi^2\epsilon_s .$$

The opposite case of a strong interaction between atoms, i.e. when $V_{\text{int}}(a_{\text{A}}) \gg \epsilon_s$, is more complicated. This case can be described analytically only for the trivial GS[θ] with $\theta = 1/q$. Namely, in the strong-coupling limit we can use the continuum limit approximation, $l \to x = la$, $u_l(t) \to u(x,t)$, $\sum_l \to \int(dx/a)$, which for the exponential law (5) leads to the local SG-type equation[16]

$$\tilde{u}_{\tilde{t}\tilde{t}} + \sin\tilde{u} - (1 - \alpha\tilde{u}_{\tilde{x}})\tilde{u}_{\tilde{x}\tilde{x}} = 0 , \tag{38}$$

where the indices stand for the corresponding partial derivatives. In Eq. (38) we have introduced the dimensionless variables, $\tilde{u}(\tilde{x},\tilde{t}) = (2\pi/a_s)u(x,t)$, $\tilde{t} = \omega_0 t$, $\tilde{x} = x/d$, and

$$d = a\sqrt{g_{\text{eff}}} , \tag{39}$$

$$g_{\text{eff}} = \frac{a_s^2}{2\pi^2\epsilon_s}\sum_{l=1}^{\infty} l^2 V''_{\text{int}}(la) = g_a\frac{(1+s)}{(1-s)^3} , \tag{40}$$

$$s = \exp(-\beta q) , \tag{41}$$

and

$$\alpha = \frac{\tilde{\beta}}{2\pi\sqrt{g_a}} \left(\frac{g_a}{g_{\text{eff}}}\right)^{3/2} . \tag{42}$$

Note that continuum approximation is valid only if the effective elastic constant is large, $g_{\text{eff}} \gg 1$, and the anharmonicity parameter is small, $\alpha \ll 1$.

The kink solution of Eq. (38) is

$$u_k(x, t) = u_k^{\text{SG}}(x, t) + \delta u_k(x, t) , \tag{43}$$

where u_k^{SG} stands for the well-known shape of the SG kink,

$$u_k^{\text{SG}}(x, t) = \frac{2a_s}{\pi} \tan^{-1} \exp\{-\sigma[x - X(t)]/d\} , \tag{44}$$

and $X(t)$ describes the motion of the kink's center in the case when the "relativistic" narrowing of the kink's width is neglected. The anharmonicity-induced correction δu_k to the SG kink shape was found in Ref. 16. This effect leads to a change of the effective kink's width,

$$d \to d_{\text{eff}}^{\sigma} = d + \sigma \Delta d , \tag{45}$$

on the value Δd defined as

$$\Delta d \approx \frac{\pi}{3} \alpha d . \tag{46}$$

Knowing the perturbed kink's shape (43), we can find other characteristics of the kink, for example, the effective kink's mass,

$$m_{k\sigma} \approx m_{\text{SG}} \left(1 - \frac{\pi}{6} \sigma \alpha\right) , \tag{47}$$

where $m_{\text{SG}} = 2m_a/\pi^2 q^2 \sqrt{g_{\text{eff}}}$ is the SG kink mass, the kink's rest energy,

$$E_{k\sigma} \approx -\sigma a_s V'_{\text{int}}(a) + 4\epsilon_s \sqrt{g_{\text{eff}}} \left(1 + \frac{1}{12} \sigma \alpha\right) , \tag{48}$$

so that $\epsilon_{\text{pair}} \approx 8\epsilon_s \sqrt{g_{\text{eff}}}$, and the amplitude of the PN relief which can be estimated as

$$\epsilon_{\text{PN}}^{\sigma} \approx \epsilon_{\text{PN}}^{\text{SG}}(g_{\text{eff}}) + \sigma \Delta g \left.\frac{\partial \epsilon_{\text{PN}}^{\text{SG}}}{\partial g}\right|_{g=g_{\text{eff}}} , \tag{49}$$

where $\Delta g = (2\pi/3)\alpha g_{\text{eff}}$, and $\epsilon_{\text{PN}}^{\text{SG}}$ is the barrier of the PN relief for the standard FK model,

$$\epsilon_{\text{PN}}^{\text{SG}}(g) \approx \frac{8}{3}\pi^4 \epsilon_s g \exp(-\pi^2 \sqrt{g}) . \tag{50}$$

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Finally, the interaction energy of two kinks is equal to (see, e.g., Ref. 14)

$$v_{\rm int}(R) \approx 16\sigma_1\sigma_2\epsilon_s\sqrt{g_{\rm eff}}\exp(-R/d) \ . \tag{51}$$

Unfortunately, a general case of the GS[s/q] with $s \neq 1$ in the strong coupling limit cannot be treated analytically because the continuum approximation leads to a system of s coupled differential equations. However, this case may be investigated with the help of renormalization procedure. For example, let us consider the reference GS$\left[\frac{q-1}{q}\right]$ with $q \gg 1$. For definiteness, we call kinks for the trivial GS[1] as the trivial kinks (t-kinks) while kinks for GS $\left[\frac{q-1}{q}\right]$, as superkinks ($s$–kinks). According to Eqs. (39) to (51), the t-antikinks are characterized by the parameters

$$m_{\bar{t}k} \approx \frac{2}{\pi^2} m_a g_t^{-1/2}\left(1 - \frac{\pi}{6}\alpha_t\right) \ , \tag{52}$$

$$\epsilon_{\rm pair}^{\bar{t}k} \approx 8\epsilon_s g_t^{1/2} \ , \tag{53}$$

$$\epsilon_{\rm PN}^{\bar{t}k} \approx \epsilon_{\rm PN}^{\rm SG}(g_t) - \frac{2\pi}{3}\alpha_t g_t \frac{\partial}{\partial g}\epsilon_{\rm PN}^{\rm SG}(g)\bigg|_{g=g_t} \ , \tag{54}$$

where

$$g_t = \frac{\beta^2}{2\pi^2}\left(\frac{V_0}{\epsilon_s}\right)\frac{(1+e^{-\beta})}{(1-e^{-\beta})^3} \tag{55}$$

and

$$\alpha_t = \left[\frac{\epsilon_s}{2V_0}\frac{(1-e^{-\beta})^9}{(1+e^{-\beta})^3}\right]^{1/2} \ . \tag{56}$$

The t-antikinks may be considered as quasiparticles with the mass $m_{\bar{t}k}$ defined by Eq. (52), interacting via the exponential law

$$v_{\rm int}^{(\bar{t}k)}(\Delta X) \approx 16\epsilon_s\sqrt{g_t}\exp(-\Delta X/a_s\sqrt{g_t}) \ , \tag{57}$$

and subjected into the external periodic potential

$$v_{\rm PN}^{\bar{t}k}(X) \approx \frac{1}{2}\epsilon_{\rm PN}^{\bar{t}k}\left[1 - \cos\left(\frac{2\pi X}{a_s}\right)\right] \ . \tag{58}$$

Then, let us treat the GS $\left[\frac{q-1}{q}\right]$ as a regular lattice of the t-antikinks with the period $R = qa_s$. This lattice can be interpreted as a new ("secondary") FK model with t-antikinks instead of atoms and the coverage parameter $\theta = 1/q$. According to Eqs. (33) and (35), the dimensionless coupling constant g_s and the anharmonicity

parameter $\tilde{\beta}_s$ of the secondary FK models are equal to

$$\begin{aligned} g_s &= \frac{a_s^2}{2\pi^2 \epsilon_{\mathrm{PN}}^{\bar{t}k}} \frac{d^2}{dX^2} v_{\mathrm{int}}^{\bar{t}k}(X)\Big|_{X=R} \\ &\approx 8\pi^{-2} \left(\epsilon_s/\epsilon_{\mathrm{PN}}^{\bar{t}k}\right) g_t^{-1/2} \exp(-q g_t^{-1/2}) \\ &\approx 3\pi^{-6} g_t^{-3/2} \exp[(\pi^2 g_t - q)/\sqrt{g_t}] \end{aligned} \tag{59}$$

and

$$\tilde{\beta}_s \approx g_t^{-1/2} , \tag{60}$$

respectively. However, it is easy to see that a kink excitation of the secondary FK model consisting of t-antikinks *exactly coincides* with a kink (s-kink) excitation of the primary FK chain with $\theta = (q-1)/q$. Thus, in this way we can approximately calculate parameters of the s-kinks and s-antikinks. In particular, for $q \geq \pi^2 g_t$ the secondary FK chain has a weak coupling, i.e. $g_s \ll 1$, and Eqs. (28), (30), (32), and (34) give

$$m_{sk} \approx m_{\bar{t}k}/q^2 , \tag{61}$$

$$\epsilon_{\mathrm{pair}}^{sk} \approx 2\pi^2 \epsilon_{\mathrm{PN}}^{\bar{t}k} g_s (1 - 2g_s) , \tag{62}$$

$$\epsilon_{\mathrm{PN}}^{sk,\sigma} \approx \frac{1}{2} \epsilon_{\mathrm{PN}}^{\bar{t}k} (2 - \pi^2 g_s) - \frac{1}{2} \sigma \, \delta\epsilon_{\mathrm{PN}}^{sk} , \tag{63}$$

$$\delta\epsilon_{\mathrm{PN}}^{sk} \approx \frac{1}{2} \pi^2 \epsilon_{\mathrm{PN}}^{\bar{t}k} \tilde{\beta}_s g_s . \tag{64}$$

Otherwise, for $q < \pi^2 g_t$ when $g_s \gg 1$, from Eqs. (47) to (50) we obtain

$$m_{sk} \approx 2m_{\bar{t}k}/\pi^2 q^2 \sqrt{g_s} , \tag{65}$$

and

$$\epsilon_{\mathrm{pair}}^{sk} \approx 8\epsilon_{\mathrm{PN}}^{\bar{t}k} \sqrt{g_s} . \tag{66}$$

Analogously, we can consider kinks for a more general case of the GS[θ], if a more simple structure with θ_0 may be found provided θ_0 is close to θ and kink's parameters for the reference GS[θ_0] are known. The corresponding results of the renormalization procedure are described in Appendix A and Table 1.

Now we may describe the dependence of the kink parameters on the coverage parameter θ when the parameters V_0 and β of the interatomic interaction potential (5) are fixed. Clearly, the functions $m_k(\theta)$, $\delta m_k(\theta)$, $\epsilon_{\mathrm{pair}}(\theta)$, $\epsilon_{\mathrm{PN}}(\theta)$, and $\delta\epsilon_{\mathrm{PN}}(\theta)$ are defined only on a countable set of rational numbers θ. Besides, the functions

$m_k(\theta)$ and $\epsilon_{\rm PN}(\theta)$ take two values at each rational θ, the left-side value, $\epsilon_{\rm PN}(\theta-0) = \epsilon_{\rm PN}^{\sigma=-1}(\theta)$, and the right-side value, $\epsilon_{\rm PN}(\theta+0) = \epsilon_{\rm PN}^{\sigma=+1}(\theta)$. The functions $q^2 m_k(\theta)$ and $\epsilon_{\rm PN}(\theta)$ monotonically decrease from $m_a(0) = m_a$ and $\epsilon_{\rm PN}(0) = \epsilon_s$, to zero as θ varies from $\theta = 0$ to $\theta = \infty$, undergoing a series of jumps down at each rational value of θ, so that the corresponding dependence looks like an inverse Devil's staircase. These two functions may be defined also for irrational values of θ if we represent the irrational θ as a limit of certain rational coverages with the periods increasing to infinity. As has been explained above, the amplitude of the jump at $\theta = s/q$ is determined by anharmonicity of the potential $V_{\rm int}(x)$ on the distances $x \sim a = qa_s$. Therefore, for two C-structures with close values of the coverage parameter θ such as, for example, $\theta_1 = \frac{1}{2}$ and $\theta_2 = \frac{100}{201}$, the phase with a higher-order structure exhibits a lower jump, $\delta\epsilon_{\rm PN}(\theta_2) \ll \delta\epsilon_{\rm PN}(\theta_1)$. Besides, the largest jumps are expected to occur near that coverage θ_* where the dimensionless parameter $g_{\rm A}$, which is defined as

$$g_{\rm A} = a_s^2 V_{\rm int}''(a_{\rm A})/2\pi^2\epsilon_s \ , \tag{67}$$

is close to one. Thus, "on average" the function $\delta\epsilon_{\rm PN}(\theta)$ has a maximum at $\theta = \theta_*$. The function $\epsilon_{\rm pair}(\theta)$ increases "on average" exhibiting also an irregular structure, because for two closely taken values θ_1 and θ_2 of the coverage parameter θ the value $\epsilon_{\rm pair}$ is lower for a higher-order structure, e.g., $\epsilon_{\rm pair}(\theta_2) \ll \epsilon_{\rm pair}(\theta_1)$.

5. The $T \neq 0$ Ground State and Susceptibility

As is well known, for the one-dimensional FK model the $T = 0$ "crystalline" structure of the GS is disordered and the long-range order is destroyed at any temperature $T \neq 0$.[19] However, at low temperatures this disorder is "small", so that the short-range order still exists allowing the existence of kinks. This is the basis for the ideal kink gas phenomenology[20,21] when the low-temperature ground state of the system is considered as a regular lattice with a small number of thermally-excited phonons and kinks. Note that namely thermally-excited kink–antikink pairs destroy the long-range order of the "crystalline" structure.

Let us suppose that at low temperatures the equilibrium state of the chain contains N_k kinks and $N_{\bar{k}}$ antikinks. Because kinks and antikinks can be created only as $k\bar{k}$ pairs, this process may be considered as a "chemical reaction": phonons $\rightarrow k + \bar{k}$ vice versa.[22] Therefore, average numbers of kinks and antikinks are equal to

$$\langle N_k \rangle = \langle N_{\bar{k}} \rangle = \langle N_{\rm pair} \rangle \ , \tag{68}$$

where

$$\langle N_{\rm pair} \rangle = CL \exp(-\epsilon_k/k_{\rm B}T) \tag{69}$$

and

$$\epsilon_k = \frac{1}{2}\epsilon_{\rm pair} \ . \tag{70}$$

To calculate the preexponential factor C for Eq. (69) in a rigorous way, we should take into account kink–phonon interactions. Assuming that one kink takes away from the phonon spectrum a single degree of freedom (transforming it into the PN mode which is an analog of the Goldstone mode of a SG kink in the continuum approximation) and repeating the calculations which were done by Currie *et al.*[20] for the SG model, we obtain

$$C \approx (2\tilde{m}_k \omega_0^2 / \pi k_B T)^{1/2} , \tag{71}$$

where

$$\tilde{m}_k = \sqrt{m_k m_{\bar{k}}} . \tag{72}$$

Now let us consider the dimensionless susceptibility χ of the FK chain. This value is determined by the expression

$$\chi = \frac{\langle (\Delta \tilde{N})^2 \rangle}{\langle \tilde{N} \rangle} , \tag{73}$$

where $\tilde{N}$ is the number of atoms on a fixed length $\tilde{L}$ ($\tilde{L} \gg a_A$ but $\tilde{L} \ll L$) and $\Delta \tilde{N}$ stands for fluctuations around $\tilde{N}$. Recall that χ characterizes an "order" in the system because $\chi = 0$ for an ordered state (at $T = 0$) and $\chi = 1$ for a completely disordered state (for $T \to \infty$ or $V_{int} \to 0$).

The susceptibility χ can be easily found with the help of the ideal kink gas approach.[23] Namely, let us assume that on the length $\tilde{L}$ there are $\tilde{N}$ atoms, $\tilde{N}_k$ kinks, and $\tilde{N}_{\bar{k}}$ antikinks with $\tilde{N}$, $\tilde{N}_k$, $\tilde{N}_{\bar{k}} \gg 1$. At low temperatures, when the concentration of kinks is small and they may be considered as noninteracting quasiparticles, the corresponding probability distributions should be Poissonian-like giving the following relations,

$$\langle \tilde{N}_k^2 \rangle - \langle \tilde{N}_k \rangle^2 = \langle \tilde{N}_k \rangle ,$$

$$\langle \tilde{N}_{\bar{k}}^2 \rangle - \langle \tilde{N}_{\bar{k}} \rangle^2 = \langle \tilde{N}_{\bar{k}} \rangle , \tag{74}$$

$$\langle \tilde{N}_k \tilde{N}_{\bar{k}} \rangle = \langle \tilde{N}_k \rangle \langle \tilde{N}_{\bar{k}} \rangle . \tag{75}$$

Recalling that each kink corresponds to $1/q$ excess atoms, and each antikink, to the same quantity of vacancies, we can write the number of atoms on the length $\tilde{L}$ as

$$\tilde{N} = \tilde{N}_0 + \frac{1}{q}(\tilde{N}_k - \tilde{N}_{\bar{k}}) , \tag{76}$$

where $\tilde{N}_0 = n\tilde{L}$ is the number of atoms at $T = 0$. Substituting Eq. (76) into Eq. (73) and using Eq. (75), we obtain the result

$$\chi = \frac{\langle N_{tot} \rangle}{q^2 \langle N \rangle} , \tag{77}$$

where $\langle N_{\rm tot}\rangle = \langle N_k\rangle + \langle N_{\bar{k}}\rangle$, and all the tildes are finally omitted. Thus, at low temperatures the susceptibility behaves as the following:

$$\chi \approx \frac{2\omega_0}{q^2 n}\left(\frac{2\tilde{m}_k}{\pi k_{\rm B}T}\right)^{1/2}\exp\left(-\frac{\epsilon_{\rm pair}}{2k_{\rm B}T}\right) . \tag{78}$$

The results obtained above are valid provided $k_{\rm B}T \ll \epsilon_k$, when the concentration of thermally-excited kinks is small so that they can be considered as noninteracting quasiparticles.

For $k_{\rm B}T \geq \epsilon_k$ the concentration of thermally-excited $k\bar{k}$ pairs becomes so large that they "melt" the reference C-structure and the approach based on the ideal kink gas breaks down. However, if $\theta \neq 1/q$, i.e. the $T = 0$ GS$[\theta]$ is nontrivial, the approach using the kink gas theory remains useful up to temperatures $k_{\rm B}T \leq \epsilon_{tk}$. For example, let us consider again the case $\theta = (q-1)/q$ with $q \gg 1$ when the $T = 0$ GS$[\theta]$ may be treated as a regular structure of t-antikinks with the number N_w (these t-antikinks are known as the "residual" t-antikinks). Analogously to Eq. (70) we can introduce the energies $\epsilon_{sk} = \frac{1}{2}\epsilon^{sk}_{\rm pair}$ and $\epsilon_{tk} = \frac{1}{2}\epsilon^{tk}_{\rm pair}$. Comparing Eq. (62) or (66) with Eq. (53), we see that $\epsilon_{sk} \ll \epsilon_{tk}$ provided $q \geq \sqrt{g_t}$. Thus, there may exist wider temperature interval,

$$\epsilon_{sk} < k_{\rm B}T < \epsilon_{tk} , \tag{79}$$

where the trivial $\theta = 1$ structure of atoms still exists while the original $\theta = (q-1)/q$ atomic superstructure is disordered. Thus, in the temperature interval (79) the lattice of t-antikinks is "melted" and, therefore, the t-antikinks can be considered as a gas of weakly-interacting quasiparticles. Now, repeating the calculations similar to those we have done above, we obtain for the interval (79) the expression

$$\chi \approx \frac{\langle N_{\rm tot}\rangle}{\langle N\rangle} , \tag{80}$$

where now $N_{\rm tot}$ is the total number of trivial kinks and antikinks. As was shown by Currie *et al.*,[22] the average number of $N_{\rm tot}$ is given by the formula

$$\langle N_{\rm tot}\rangle = \left[\langle N_w\rangle^2 + \langle 2N_{\rm pair}\rangle^2\right]^{1/2} , \tag{81}$$

where $\langle N_w\rangle = N_w$ is the number of residual t-antikinks and $\langle N_{\rm pair}\rangle$ is the average number of thermally-created trivial $k\bar{k}$ pairs determined by Eqs. (69), (71) with ϵ_{tk} instead of ϵ_k and $\tilde{m}_{tk} = \sqrt{m_{tk}m_{t\bar{k}}}$ instead of $\tilde{m}_k$. From Eqs. (81), (69), and (71) it follows that on the left-hand-side of the interval (79) the function $\chi(T)$ has a plateau $\chi \approx w \equiv N_w/N$ (the value w is known as the "window number"), and on the right-hand side, $\chi(T)$ increases exponentially due to thermal excitation of the $k\bar{k}$ pairs which join those already present from the "melted" t-antikink lattice.

With the help of the renormalization arguments presented in the previous section, we may describe in the similar way the temperature dependence of $\chi(T)$ for

more complicated structures with $\theta = s/q$ where $s \neq 1$ and $s \neq (q-1)$. Considering the system as an hierarchy of the consequently melted superkink lattices, we can divide the whole temperature interval $0 < k_B T < \epsilon_{tk}$ into subintervals, at each of them more complex superkink structure is already melted, but more simple structure still exists and it allows strong definition of the corresponding s-kinks and s-antikinks which are approximately noninteracting in this temperature subinterval. Within each subinterval the susceptibility is defined by Eq. (77), (81), (69) to (72), where the parameters q and N_w characterize a more simple structure, and ϵ_{pair} and m_k, $m_{\bar{k}}$ correspond to kinks defined on the basis of this reference structure. Thus, the function $\chi(T)$ has to display a series of plateaus at low-temperature sides of these subintervals, and it changes exponentially between the plateaus. We would like to note that computer simulations of Gillan and Halloway[24] are in a good agreement with the results of our phenomenological approach.

With futher increasing of temperature, $k_B T > \epsilon_{tk}$, the function $\chi(T)$ for the standard FK model tends to its asymptotic value $\chi(T) \to k_B T/G_A a_A^2$. However, in the limit $T/G_A \to \infty$ this asymptotic dependence gives the unphysical result $\chi \to \infty$ instead of the correct one, $\chi \to 1$. The reason of that can be explained by the fact that for $k_B T \geq G_A a_A^2$ mutual displacements of atoms are not small, and the harmonic approximation (4) for $V_{\text{int}}(x)$ becomes not valid anymore. As is shown in Appendix A, the accurate accounting of anharmonicity effects of $V_{\text{int}}(x)$ restores the correct limit $\chi \to 1$ for $T \to \infty$.

At last, here we will estimate also the "melting" temperatures of the hierarchy of superkink lattices. Let us consider a regular lattice of interacting quasiparticles (atoms, trivial kinks, superkinks, etc.; below we will call them "atoms") interpreted as the reference structure which is characterized by an effective value of the coverage parameter $\tilde{\theta} = \tilde{s}/\tilde{q}$ and by an effective external potential with the period $\tilde{a}_s$. We assume that the system has a small quantity of approximately noninteracting topological excitations (trivial kinks, superkinks, super-superkinks, etc., below we will call them as "kinks") which are characterized by the width $\tilde{d}$ and the mean rest energy $\tilde{\epsilon}_k$. Note that the "kinks"may be both residual as well as thermally-excited. According to the definition of the susceptibility χ, this value describes the mean square fluctuations of the relative atomic displacements $x_{l'+l} - x_{l'}$,[23]

$$\Lambda_l \equiv \frac{1}{N} \sum_{l'} \langle [(x_{l'+l} - x_{l'}) - \langle x_{l'+l} - x_{l'} \rangle]^2 \rangle = \chi a_A^2 |l| \,. \tag{82}$$

Thus, mutual positions of two "atoms" separated by the distance x, $x = l a_A$, fluctuate with the amplitude $\delta(x) = \sqrt{\Lambda_l} = \sqrt{\chi a_A x}$. In order to construct "kinks" for the reference structure with $\tilde{\theta} = \tilde{s}/\tilde{q}$, mutual fluctuations must be assumed small, $\delta(x) \leq \tilde{a}_s/\tilde{s}$, at least on distances of order of the "kink" width, $\tilde{x} \geq \tilde{d}$. In this way we obtain the upper limit when a given reference structure may be considered as a regular one; the corresponding equation is $\delta(\tilde{d}) = \tilde{a}_s/\tilde{s}$, or

$$\chi(T) a_A \tilde{d} \tilde{s}^2 = \tilde{a}_s^2 \,. \tag{83}$$

A solution of Eq. (83) defines the temperature $\tilde{T}_{\text{melt}}$, above which the short-range order in the given reference structure is completely destroyed by thermal fluctuations. Using the expression (77) for $\chi(T)$, we can see that at $T = \tilde{T}_{\text{melt}}$ the average distance $\tilde{R}$ between "kinks" is equal to $\tilde{d}$, so that at $T > \tilde{T}_{\text{melt}}$ the total concentration of such "kinks" becomes so large that they begin to overlap.

When the reference structure has no residual "kinks" (i.e., for the lowest temperature interval in the kink–lattice hierarchy), Eq. (83) leads to the result

$$k_{\text{B}}\tilde{T}_{\text{melt}} \approx \tilde{\epsilon}_k \ . \tag{84}$$

However, when the quantity of residual "kinks" is nonzero, it follows that $k_{\text{B}}\tilde{T}_{\text{melt}} < \tilde{\epsilon}_k$ because the residual "kinks" supplement thermally-excited "kink–antikink" pairs and, therefore, the criterion $\tilde{R} = \tilde{d}$ will be achieved at lower temperatures.

Thus, the more complex (higher-order) is the reference structure, the lower is the energy $\tilde{\epsilon}_k$ of its topological excitations and, therefore, the lower is its "melting" temperature $\tilde{T}_{\text{melt}}$.

6. Kink Diffusion

In this section we study the system dynamics when the FK chain contains a single kink only. Namely, we impose the periodic boundary conditions, $u_{N+1} = u_1 - \sigma a_s$, and suppose that temperature is low enough, i.e. $k_{\text{B}}T \ll \epsilon_k$, so that the probability of thermal creation of $k\bar{k}$ pairs is negligible.

Using a phenomenological approach we may consider a kink as a quasiparticle of the mass m_k which is characterized by the coordinate $X_k(t)$ and has the kinetic energy $\frac{1}{2}m_k\dot{X}_k^2$ moving in the potential relief $V_{\text{PN}}(X_k)$. Thus, it is reasonable to suppose that the kink's coordinate $X_k(t)$ satisfies the Langevin-type equation

$$m_k\ddot{X}_k + m_k\eta_k\dot{X}_k + V'_{\text{PN}}(X_k) = \delta F_k(t) \ . \tag{85}$$

It is clear that Eq. (85) is an approximate equation and, therefore, it can not be rigorously derived from the primary motion equation (3). However, in order to find the kink friction coefficient η_k and the fluctuation force $\delta F_k(t)$, below we briefly outline a way how to reduce Eq. (3) to the form given by Eq. (85).

In Sec. 2 we have introduced the adiabatic trajectory $x_l(\tau)$ as a solution of the system of equations (23). When the FK chain contains a single kink only, we can uniquely put into correspondence the value $X(\tau)$ from Eq. (22) to each point of the AT. Thus, we can introduce the functions $u_l^{\text{kink}}(X_k)$ according to the equation

$$u_l^{\text{kink}}(X_k) = x_l(\tau)\Big|_{X(\tau)=X_k} - x_l^{(0)} \ . \tag{86}$$

The functions $u_l^{\text{kink}}(X_k)$ describe atomic displacements in the FK chain with a single (adiabatically-slowly moving) kink. Then, let us suppose that the system can move

strictly along the AT only, looking for a solution of the motion equation (3) in the form

$$u_l(t) = u_l^{\text{kink}}[X_k(t)] \,. \tag{87}$$

Suppose now that during a short time interval Δt, the fluctuation forces $\delta F_l(t)$ and $\delta F_k(t)$ are constant, while the atoms and the kink are shifted on small distances Δx_l and ΔX_k, respectively. From Eq. (86) it follows that Δx_l and ΔX_k are coupled by the relation

$$\Delta x_l = \frac{du_l^{\text{kink}}(X_k)}{dX_k} \Delta X_k \,. \tag{88}$$

The work done by the fluctuation forces can be written as

$$\delta F_k \Delta X_k = \sum_l \delta F_l \Delta x_l \,. \tag{89}$$

Substituting Eq. (88) into Eq. (89), we obtain

$$\delta F_k(t) = \sum_l \frac{du_l^{\text{kink}}(X_k)}{dX_k} \delta F_l(t) \,. \tag{90}$$

Now, using Eq. (2) for $\delta F_l(t)$ and taking into account the definition (26) for the kink's mass, we find correlation functions for the kink fluctuation force,

$$\langle \delta F_k(t) \rangle = 0 \,, \quad \langle \delta F_k(t) \delta F_k(t') \rangle = 2\eta_k m_k k_B T \delta(t - t') \,, \tag{91}$$

where $\eta_k = \eta$.

To find the friction force acting on the kink, let us take the sum over l for the first two terms in the motion equation (3),

$$(q m_k / m_a) \sum_l (m_a \ddot{x}_l + m_a \eta \dot{x}_l) = m_k \ddot{X}_k + m_k \eta \dot{X}_k \,, \tag{92}$$

where we have used Eq. (22) to introduce $X \equiv X_k$. Comparing Eqs. (85) and (92), we see that the friction coefficient η_k in Eq. (85) exactly coincides with the atomic friction coefficient η.

It should be emphasized that the parameters m_k, η_k, and the function $V_{\text{PN}}(X)$ in Eqs. (85), (91) coincide with those calculated for the kink only if the atoms move strictly along the AT. As a matter of fact, a real trajectory deviates from the AT. For example, even at $T = 0$ a moving kink radiates phonons, and this leads to an additional damping of the kink's velocity. Besides, at $T \neq 0$ the system contains a certain number of thermally-excited phonons. Thus, more rigorously we should look for a solution of Eq. (3) in the form $u_l(t) = u_l^{\text{ph}}(t) + u_l^{\text{kink}}[X_k(t)]$, where $u_l^{\text{ph}}(t)$ describes a contribution of phonons to the atomic displacements. It is convenient to consider X_k and $P_k = m_k \dot{X}_k$ as two canonical variables. In this case we must impose two Dirac's constrains on the variables u_l^{ph} in order to keep the dimensionability of the phase space unchanged (see details in Ref. 25). The motion equation of

the type (85) is then obtained after averaging over the phonon coordinates $u_l^{\rm ph}(t)$. Collisions of a kink with thermally-excited phonons lead to energy and momentum exchange between them, the rate of this exchange may be approximately described by introducing an additional "intrinsic" viscous friction $\eta_{\rm int}$. Of course, $\eta_{\rm int}$ cannot be calculated exactly, but it can be estimated by the perturbation technique. At low temperatures the perturbation approach gives the result (see, e.g., Refs. 26–31)

$$\eta_{\rm int} \approx C_\eta \omega_0 (k_{\rm B}T/\epsilon_k)^2 , \tag{93}$$

where the dimensionless factor C_η depends on the type of the model under consideration. Note that for the exactly integrable SG model $\eta_{\rm int} = 0$.[26,31] But any deviation from the pure SG model, such as nonsinusoidal substrate potential, anharmonic interatomic interaction, discreteness effects (especially, for a nontrivial GS[θ] with $\theta \neq 1/q$) which destroy exact integrability of the model, will lead to $\eta_{\rm int} \neq 0$. Besides, kink–phonon interactions may increase the effective kink mass (due to a phonon "dressing") and decrease the height of the effective PN barrier (analogously to the so-called Debay–Waller effect). Thus, the parameters m_k, $\eta_k = \eta + \eta_{\rm int}$, and $\epsilon_{\rm PN}$ used in Eqs. (85), (91) are effective parameters which in a general case depend on T. However, these effects can be neglected when the kink–phonon interaction is small in comparison with interaction with the substrate, i.e. if $\eta_{\rm int} \ll \eta_{\rm ext}$. In real physical objects, when the FK chain is only a part of the whole three-dimensional system, the latter inequality is usually fulfilled.

Note that for the trivial GS[θ] with $\theta = 1$ the Langevin equation (85) was introduced earlier (see Refs. 32–35) where, however, instead of the AT-kink shape it was taken the SG kink profile, the latter being rigorous only for the FK chain with a strong interparticle coupling.[36,37]

When the parameters of Eq. (85) are known, the kink diffusion coefficient can be found as

$$D_k = \lim_{\bar\omega \to 0+i0} \mathcal{D}_k(\bar\omega) = \int_0^\infty dt\, e^{i\bar\omega t} \langle \dot X_k(t) \dot X_k(0) \rangle . \tag{94}$$

According to Eqs. (18) to (20), at low temperatures, i.e. when $k_{\rm B}T < \epsilon_{\rm PN}$, the kink diffusion coefficient should have the Arrhenius form,

$$D_k = D_{k0} \exp(-\epsilon_{\rm PN}/k_{\rm B}T) , \tag{95}$$

where

$$D_{k0} \approx \begin{cases} a^2 \omega_{\rm PN}/2\pi , & \text{if } \eta_{lk} < \eta < \omega_{\rm PN}^* , \\ a^2 \omega_{\rm PN} \omega_{\rm PN}^*/2\pi\eta_k , & \text{if } \eta > \omega_{\rm PN}^* . \end{cases} \tag{96}$$

Here $\omega_{\rm PN} = \sqrt{V_{\rm PN}''(0)/m_k}$, $\omega_{\rm PN}^* = \sqrt{-V_{\rm PN}''(a/2)/m_k}$, and $\eta_{lk} = \omega_{\rm PN} k_{\rm B}T/2\pi\epsilon_{\rm PN}$. The activated kink diffusion for the trivial GS was predicted by Pietronero and Strässler[33] (see also Refs. 34 and 35) and observed in molecular-dynamics simulation by Combs and Yip.[38]

In the FK chain with a strong coupling, for a GS[θ] with a simple elementary cell the inequality $\epsilon_{PN} < \epsilon_k$ may be easily fulfilled. According to Eq. (17), in the temperature interval $\epsilon_{PN} < k_B T \ll \epsilon_k$ the kink diffusion coefficient may be found in the form (see, e.g., Refs. 32, 13 and 37)

$$D_k \approx \frac{k_B T}{m_k \eta_k} \left[1 - \frac{1}{8} \left(\frac{\epsilon_{PN}}{k_B T} \right)^2 \right] . \tag{97}$$

When GS[θ] of the system is nontrivial, i.e. $\theta \neq 1/q$, the phenomenological approach is useful not only to be applied for the lowest temperature subinterval in the hierarchy of the kink lattices, but also at the left-hand side of any of these subintervals. For example, for $\theta = (q-1)/q$ with $q \gg 1$ for temperature $\epsilon_{*\bar{t}} \leq k_B T \ll \epsilon_{\bar{t}k}$ the GS may be considered as a system consisting of N_w weakly-interacting residual t-antikinks. If collisions of these kinks are approximately elastic (as they do in the standard SG model), the kink collective diffusion coefficient

$$D_{\mu k} \equiv \int_0^\infty dt \, \frac{1}{N_w} \sum_{kk'}^{N_w} \langle \dot{X}_k(t) \dot{X}_{k'}(0) \rangle$$

coincides with the diffusion coefficient of a single kink for the same reference structure (namely, with the diffusion coefficient of a single t-antikink). On the other hand, the chemical diffusion coefficient of the kink is equal to

$$D_{ck} = D_{\mu k} / \chi_k , \tag{98}$$

where χ_k is the dimensionless susceptibility of the t-antikink system. When the PN barrier for the t-antikinks may be neglected, that is valid for $\epsilon_{PN}^{t\bar{k}} \ll k_B T$, the susceptibility χ_k is calculated with the help of the perturbation theory[39] and the result is given by the integral,

$$\chi_k \approx \left[1 + \frac{n_w}{k_B T} \int_{-\infty}^{\infty} dX \, v_{int}(X) \right]^{-1} , \tag{99}$$

where $n_w = N_w / L$ is the concentration of the residual t-antikinks. Otherwise, for $k_B T \ll \epsilon_{PN}^{t\bar{k}}$ the system Hamiltonian reduces to that for an effective lattice gas, and χ_k is found as

$$\chi_k \approx 1 - \theta_w , \tag{100}$$

where $\theta_w = N_w / M$ corresponds to the concentration of t-antikinks.

7. Calculation of the Diffusion Coefficients D_S, D_μ, and D_C

In order to find the system diffusion coefficients in the framework of the phenomenological approach, let us suppose that at low temperatures the GS of the FK chain contains a certain number of phonon modes, kinks, and antikinks, neglecting mutual influence of one excitation on others. In this case the atomic displacements can

be represented as the sum

$$u_l(t) = u_l^{\mathrm{ph}}(t) + \sum_{j=1}^{N_{\mathrm{tot}}} u_l^{\mathrm{kink}}[\sigma_j, X_j(t)] , \tag{101}$$

where $u^{\mathrm{kink}}(\sigma, X)$ stands for the shape of a slowly moving kink with the coordinate X and the topological charge σ, and u^{ph} describes phonons adjusted to the kinks. From Eq. (101) we obtain for the atomic velocities the expression

$$\dot{u}_l(t) = \dot{u}_l^{\mathrm{ph}}(t) + \sum_{j=1}^{N_{\mathrm{tot}}} \dot{X}_j(t) w_l[\sigma_j, X_j(t)] , \tag{102}$$

where $w(\sigma, X) = \frac{\partial}{\partial X} u^{\mathrm{kink}}(\sigma, X)$.

Substituting Eq. (102) into Eq. (10) for $\mathcal{D}_\mu(t)$, we obtain three types of terms. A contribution from the phonon correlation function $\langle \dot{u}^{\mathrm{ph}}(t) \dot{u}^{\mathrm{ph}}(0) \rangle$ is

$$\Delta \bar{\mathcal{D}}_\mu^{\mathrm{ph}}(\bar{\omega}) = D_f \sum_\kappa \frac{i\bar{\omega}\eta}{[i\bar{\omega}\eta + \bar{\omega}^2 - \omega_{\mathrm{ph}}^2(\kappa)]} , \tag{103}$$

where κ stands for the phonon modes with the frequencies $\omega_{\mathrm{ph}}(\kappa)$. Because the phonon spectrum of the FK chain is optical, the contribution (103) tends to zero in the limit $\bar{\omega} \to 0$. The mixed correlation functions $\langle \dot{u}^{\mathrm{ph}}(t) \dot{X}_j(0) \rangle$ describe kink–phonon interactions. However, a rigorous calculation of these functions is too complicated. But in the phenomenological approach we may assume that these interactions are already taken into account if the kink concentration and the kink friction coefficient η_k are calculated in a way which includes the kink–phonon interactions. Finally, in order to find the last contribution, let us assume that the kink concentration is small, $n_{\mathrm{tot}} \ll n$, so that kinks can be considered as independent quasiparticles. This assumption yields

$$\int_0^\infty dt \langle \dot{X}_j(t) \dot{X}_{j'}(0) \rangle = \delta_{jj'} D_{k(\bar{k})} , \tag{104}$$

where $D_{k(\bar{k})}$ is the diffusion coefficient for a single kink (antikink). Then, substituting Eq. (102) into Eq. (10), and using Eq. (104) and the equality

$$\sum_l w_l(X) = \frac{d}{dX} \sum_l u_l^{\mathrm{kink}}(X) = \frac{d}{dX} \left(\frac{X}{q} \right) = \frac{1}{q} \tag{105}$$

which follows from Eq. (22), we obtain the approximate expression for the collective diffusion coefficient D_μ,

$$D_\mu \approx \frac{1}{q^2 N} \left(\langle N_k \rangle D_k + \langle N_{\bar{k}} \rangle D_{\bar{k}} \right) . \tag{106}$$

Thus, the conductivity of the FK chain is directly proportional to the total kink concentration (see also Refs. 33, 32 and 40).

The result (106) can be also directly obtained from Eq. (11) if we rewrite the expression (12) for $Y(t)$ in the form

$$Y(t) \approx \text{Const} + \frac{1}{q\sqrt{N}} \sum_{j=1}^{N_{\text{tot}}} X_j(t) \,. \tag{107}$$

For the standard FK model with the trivial GS at $\theta = 1$, in the limit when the SG equation is valid, we can take $D_k = D_{\bar{k}} = k_B T/m_k \eta$, so that $\langle N_k \rangle = \langle N_{\bar{k}} \rangle = N a_s \omega_0 \sqrt{2m_k/\pi k_B T} \exp(-\epsilon_k/k_B T)$, $m_k = 2m_a/\pi^2\sqrt{g_a}$, and $\epsilon_k = 4\epsilon_s\sqrt{g_a}$, thus obtaining from Eq. (106) the following expression

$$D_\mu^{(\text{SG})} \approx D_f (\pi m_a \omega_0^2 a_s^2/\epsilon_s)^{1/2} (\epsilon_k/k_B T)^{1/2} \exp(-\epsilon_k/k_B T) \,. \tag{108}$$

This result was firstly obtained by Büttiker and Landauer[41] with the help of the generalized rate theory (see also Ref. 18).

While the collective-diffusion coefficient is known, the chemical diffusion coefficient can be obtained as $D_c = D_\mu/\chi$. Using Eq. (77) for χ, we can find from Eq. (106) that

$$D_c \approx \frac{\langle N_k \rangle D_k + \langle N_{\bar{k}} \rangle D_{\bar{k}}}{\langle N_k \rangle + \langle N_{\bar{k}} \rangle} \,. \tag{109}$$

We should note that by kinks (antikinks) in Eqs. (106) and (109) we must understand those "kinks" (trivial kinks, superkinks, super-superkinks, etc) which are well defined as quasiparticles at a given temperature interval for a given coverage parameter θ.

For the lowest temperature interval of the kink–lattice hierarchy, Eq. (109) leads to

$$D_c \approx \frac{1}{2}(D_k + D_{\bar{k}}) \,. \tag{110}$$

When the GS[θ] is nontrivial, i.e. $\theta \neq 1/q$, Eq. (109) allows us to find the chemical diffusion coefficient at the left-hand side of each temperature subinterval of the hierarchy. Indeed, in this case the number of residual kinks (or antikinks) exceeds the number of thermally-excited kink–antikink pairs, $\langle N_w \rangle \gg \langle N_{\text{pair}} \rangle$, and, therefore, using the condition $\langle N_k \rangle \gg \langle N_{\bar{k}} \rangle$ (or $\langle N_k \rangle \ll \langle N_{\bar{k}} \rangle$) in Eq. (109), we obtain

$$D_c \approx D_k \text{ (or } D_{\bar{k}}) \,. \tag{111}$$

For example, let us consider the coverage defined by $\theta_\pm = (q \pm 1)/q$ with $q \gg 1$, which are close to the trivial coverage $\theta_0 = 1$. According to Eq. (111), we should have $D_c(\theta_+) \approx D_{tk}$ and $D_c(\theta_-) \approx D_{\bar{t}k}$ at the temperature interval $\epsilon_{sk} < k_B T \ll \epsilon_{tk}$.

The result (111) has a simple physical meaning. Indeed, for $k_B T \leq \epsilon_k$ the mass transport along the chain is carried out by kinks. Because the concentration of kinks is proportional to the concentration of atoms, the ratio of the flux of kinks to the gradient of the kink concentration (which determines the coefficient D_{ck}) is exactly equal to the ratio of the atomic flux to the atomic gradient (which defines the coefficient D_c according to Fick's law (16)). Moreover, this explanation shows that in order to take into account kink–kink interactions, we should use, instead of Eq. (111), the equation

$$D_c \approx D_{ck} (\text{or } D_{c\bar{k}}) , \tag{112}$$

where D_{ck} is the chemical diffusion coefficient for kinks determined by Eqs. (98) to (100).

At last, to find the self-diffusion coefficient D_s with the help of the phenomenological approach developed here, we substitute the atomic velocities (102) into Eq. (8), thus obtaining a value $D_s^* \neq 0$. For example, for the standard FK model in the SG limit we obtain in this way the result

$$D_s^* \approx (a/d) D_\mu . \tag{113}$$

However, the coefficient D_s^* describes diffusion of a tagged atom provided the time scales are not too large, $t \ll t^*$, because we have ignored completely kink–kink interactions. To estimate the value of t^*, let us again consider the $T \neq 0$ GS of the FK chain as a system of quasiparticles (kinks) separated by an average distance R_0 and interacting via a potential $v_{\text{int}}(R)$. Expanding $v_{\text{int}}(R)$ into the Taylor series, $v_{\text{int}}(R) \approx \ldots + \frac{1}{2} m_k \omega^2 (R - R_0)^2$, we can interpret the kink system as a harmonic chain of Brownian quasiparticles studied earlier (see, e.g., Refs. 42 and 43). In this way, we obtain $t^* = \eta_k / \omega^2$, or

$$t^* \approx m_k \eta_k / v''_{\text{int}}(R_0) . \tag{114}$$

The long-time-scale behavior of the kink chain depends on the interatomic potential which may be bounded or unbounded. In the former case, when $V_{\text{int}}(x) \to \infty$ for $|x| \to +\infty$, the rigorous sequence of atoms in the chain can not be violated. As a result, it follows that $D_s = 0$ because the long-time-scale behavior of a given atom is subdiffusional,[44–47]

$$\langle [x_l(t) - x_l(0)]^2 \rangle \approx \alpha_s \sqrt{t} , \quad t \gg t^* . \tag{115}$$

The coefficient α_s in Eq. (115) was found in several works (see, e.g., Refs. 43, 48, 49 and 23, and it is defined as

$$\alpha_s = 2 a_A \chi \sqrt{D_c / \pi} = 2 a_A \sqrt{\chi D_\mu / \pi} = 2 a_A D_\mu / \sqrt{\pi D_c} , \tag{116}$$

where χ, D_c, and D_μ were calculated above.

For realistic physical models it is reasonable to assume that the potential $V_{\rm int}(x)$ depends on the modulus of the interatomic distance, $V_{\rm int}(x) = V_{\rm int}(|x|)$, and $V_{\rm int}(|x|) \to 0$ as $|x| \to \infty$. If the potential $V_{\rm int}(x)$ is bounded, i.e. if $\epsilon^* < \infty$, where $\epsilon^* \equiv V_{\rm int}(0) - V_{\rm int}(a_{\rm A})$, the ordered sequence of atoms in the chain may be destroyed because any two atoms may exchange their sites. The rate $\mathcal{K}_{\rm exc}$ of "site-exchange" events for two given nearest-neighbor atoms can be estimated for $k_{\rm B}T \ll \epsilon^*$ as

$$\mathcal{K}_{\rm exc} \approx \begin{cases} (\omega_{\max}/2\pi)\exp(-\epsilon^*/k_{\rm B}T)\,, & \text{if } \eta < \omega_{\max}\,, \\ (\omega_{\max}^2/2\pi\eta)\exp(-\epsilon^*/k_{\rm B}T)\,, & \text{if } \eta > \omega_{\max}\,, \end{cases} \tag{117}$$

where the frequency $\omega_{\max}$ corresponds to the out-of-pahse vibrations of these two atoms, i.e. $\omega_{\max}$ is the maximum (cut-off) frequency of phonons in the model under consideration.

Because during $t \sim t_{\rm exc} = \mathcal{K}_{\rm exc}^{-1}$ a given atom passes a mean distance $l_{\rm exc}$ which can be estimated from Eqs. (113) or (115) as

$$l_{\rm exc}^2 \approx \begin{cases} 2D_s^* t_{\rm exc}\,, & \text{if } t_{\rm exc} < t^*\,, \\ \alpha_s\sqrt{t_{\rm exc}}\,, & \text{if } t_{\rm exc} > t^*\,, \end{cases} \tag{118}$$

the self-diffusion coefficient D_s for the FK model with the bounded interatomic potential can be estimated as

$$D_s \approx \mathcal{K}_{\rm exc} l_{\rm exc}^2\,. \tag{119}$$

Thus, to find the diffusion coefficients of the FK chain, first we have to determine the parameters of kinks which are well-defined and slowly interacting at a given value of the coverage parameter θ and temperature T, then to calculate the susceptibility χ and the kink diffusion coefficient D_k (or D_{ck}) and, finally, to obtain $D_{\rm c}$ and then D_μ as $D_\mu = \chi D_{\rm c}$.

8. Discussions

Now we can qualitatively describe dependences of the diffusion coefficients $D_{\rm c}$ and D_μ on temperature T and the atomic concentration n. Let us begin from the temperature dependence. For definiteness, we consider a physically important case when $\theta \le 1$, namely $\theta = (q-1)/q$ with $q \gg 1$. Recall that the $T = 0$ GS of the chain is the commensurate structure with the period $a = qa_s$, and topologically stable excitations are s-kinks (s-antikinks) which are characterized by the effective mass m_{sk} and the half-pair creation energy ϵ_{sk}. The adiabatically slow motion of the s-kinks is carried out in the PN periodic relief described by $V_{s\,\rm PN}(X) \approx \frac{1}{2}\epsilon_{s\,\rm PN}[1-\cos(2\pi X/a)]$ with the height $\epsilon_{s\,\rm PN}$, and small vibrations of the kink at a bottom of the PN potential are characterized by the PN frequency $\omega_{s\,\rm PN} \approx \sqrt{\epsilon_{s\,\rm PN}/2q^2 m_{sk}}$. An effective friction for a moving s-kink we denote by η_{sk}. According to the renormalization arguments of Sec. 2, the described $T = 0$ GS can be treated as a regular lattice of trivial ($\theta = 1$) antikinks.

When the temperature increases to be above the "melting" temperature $T_{sk} \approx \epsilon_{sk}/k_B$, this lattice becomes disordered due to thermal creation of a large quantity of sk–$\bar{sk}$ pairs. According to the kink-lattice-hierarchy ideology of Sec. 3, within the temperature interval $\epsilon_{sk} < k_B T < \epsilon_{tk}$ the equilibrium state of the FK chain can be considered as a commensurate structure with the period a_s where, however, there exists $N_w = N/q$ residual t-antikinks and N_{pair} thermally-created tk–$\bar{tk}$ pairs. Let ϵ_{tk} denotes the half-pair creation energy of the $\theta = 1$ kinks, m_{tk} denotes their effective mass, $V_{t\,PN}(X) \approx \frac{1}{2}\epsilon_{t\,PN}[1 - \cos(2\pi X/a_s)]$ denotes the shape of the PN relief, so that $\omega_{t\,PN} \approx \sqrt{\epsilon_{t\,PN}/2m_{tk}}$ is the PN frequency, and η_{tk} stands for the corresponding friction coefficient. The parameters of s-kinks and t-kinks satisfy two inequalities, $\epsilon_{s\,PN} < \epsilon_{t\,PN} < \epsilon_s$ and $\epsilon_{sk} < \epsilon_{tk}$. For definiteness, let us assume also that ϵ_{sk} is the lowest energetic parameter of the system (that is always true at least for $q \gg 1$), and that anharmonicity of the potential $V_{int}(x)$ is small so that the energy ϵ_{anh} introduced in Appendix A is the largest energetic parameter. Now we can describe the functions $D_c(T)$ and $D_\mu(T)$ for various temperature intervals.

At very low temperature,

$$0 < k_B T < \epsilon_{sk} , \tag{120}$$

mass transport along the chain is carried out by s-kinks, and the chemical diffusion coefficient is equal to

$$D_c \approx \mathcal{K}_{sk}(qa_s)^2 \exp(-\epsilon_{s\,PN}/k_B T) , \tag{121}$$

where

$$\mathcal{K}_{sk} \approx \begin{cases} \omega_{s\,PN}/2\pi , & \text{if } \eta_{sk} < \omega_{s\,PN} , \\ \omega_{s\,PN}^2/2\pi\eta_{sk} , & \text{if } \eta_{sk} > \omega_{s\,PN} , \end{cases} \tag{122}$$

while the collective-diffusion coefficient is determined by the expression

$$D_\mu \approx D_c \frac{(\langle N_{sk}\rangle + \langle N_{\bar{sk}}\rangle)}{q^2\langle N\rangle} \propto \exp[-(\epsilon_{s\,PN} + \epsilon_{sk})/k_B T] . \tag{123}$$

Notice that both D_c and D_μ have the Arrhenius form but they are determined by different activation energies. When temperature increases, $k_B T \to \epsilon_{sk}$, the number of thermally-excited sk–$\bar{sk}$ pairs also increases, and their mutual attraction should decrease the values of D_c and D_μ in comparison with those given by Eqs. (121) to (123).

At low temperatures,

$$\epsilon_{sk} < k_B T < \min(\epsilon_{t\,PN}, \epsilon_{tk}) , \tag{124}$$

superkinks are likely destroyed by thermal fluctuations, but the trivial kinks still exist, and this time they are responsible for the mass transport. Neglecting interactions of t-kinks, we obtain

$$D_c \approx \mathcal{K}_{tk} a_s^2 \exp(-\epsilon_{t\,\mathrm{PN}}/k_B T) , \tag{125}$$

$$\mathcal{K}_{tk} \approx \begin{cases} \omega_{t\,\mathrm{PN}}/2\pi , & \text{if } \eta_{tk} < \omega_{t\,\mathrm{PN}} , \\ \omega_{t\,\mathrm{PN}}^2/2\pi\eta_{tk} , & \text{if } \eta_{tk} > \omega_{t\,\mathrm{PN}} , \end{cases} \tag{126}$$

$$D_\mu \approx \frac{D_c}{q}\left(1 + \frac{4q^2 m_{tk}\omega_0^2 a_s^2}{\pi k_B T} e^{-\epsilon_{tk}/k_B T}\right) . \tag{127}$$

The mutual repulsion of the residual t-antikinks increases the values of D_c and D_μ in comparison with those defined by Eqs. (125) to (127).

Analogously, we may describe the case of the GS$[s/q]$ with $2 \le s \le q-2$, when the kink–lattice hierarchy consists of more than two temperature intervals.

The limits of the intermediate temperature interval depend on the model parameter g_s. Namely, when $g_s \ge 1$, there exists the temperature interval

$$\epsilon_{t\,\mathrm{PN}} < k_B T < \epsilon_{tk} , \tag{128}$$

within which t-kinks still exist, but their motion is not thermally activated. In this case we have

$$D_c \approx \frac{k_B T}{m_{tk}\eta_{tk}}\left[1 - \frac{1}{8}\left(\frac{\epsilon_{t\,\mathrm{PN}}}{k_B T}\right)^2\right] \tag{129}$$

and

$$D_\mu \approx D_c \frac{\langle n_{\mathrm{tot}}\rangle}{\langle n\rangle} \propto \exp(-\epsilon_{tk}/k_B T) . \tag{130}$$

The described analytical predictions are in a good agreement with molecular dynamics simulations of Holloway and Gillan[50,24] carried out for the standard undamped FK chain, if we put in Eq. (129) $\eta_{tk} = \eta_{\mathrm{int}} \approx 0.028\omega_0$.

If $g_s \ll 1$, the intermediate temperature interval is determined as

$$\epsilon_{tk} < k_B T < \epsilon_{t\,\mathrm{PN}} . \tag{131}$$

Within this interval the diffusion coefficient can be found only numerically. It may be expected, however, that D_c and D_μ will have the Arrhenius behavior with the activation energy $\epsilon_s^{\mathrm{eff}}$ where $\epsilon_{t\,\mathrm{PN}} < \epsilon_s^{\mathrm{eff}} < \epsilon_s$.[51]

At high temperatures,

$$\max(\epsilon_s, \epsilon_{tk}) < k_B T < \epsilon_{anh} , \tag{132}$$

a perturbation theory approach may be used and it leads to the result

$$D_\mu \approx D_f \left\{ 1 + \frac{1}{8} \left[\frac{(\epsilon_s/k_B T) \sinh(k_B T/\epsilon_s g_A)}{\cosh(k_B T/\epsilon_s g_A) - \cos(2\pi a_A/a_s)} \right]^2 \right\}^{-1} , \tag{133}$$

and the analogous expression for D_c with the factor $G_A a_A^2/m_a\eta$ instead of D_f.

Finally, at very high temperatures, $k_B T > \epsilon_{anh}$, contributions of both $V_{sub}(x)$ and $V_{int}(x)$ become negligible, and the diffusion coefficients D_μ and D_c are close to the value $D_f = k_B T/m_a\eta$.

Let us describe now the behavior of the diffusion coefficients as functions of the coverage parameter $\theta \equiv a_s/a_A$. As can be seen from Eq. (133), at high temperature within the interval (132) the collective diffusion coefficient $D_\mu(\theta)$ shows oscillations as a function of θ, achieving minima for the trivial ground states when $\theta = 1/q$, where the atoms are situated at the bottom of the substrate potential wells. On the other hand, maxima of $D_\mu(\theta)$ occur at $\theta = 2/(2q-1)$ where the atoms in the GS are displaced from the bottoms that are closer to the potential tops. Maxima and minima of $D_\mu(\theta)$ become more pronounced with increasing of the interatomic interaction and decreasing of temperature. Because for the exponential interaction (5) the parameter g_A (see Eq. (67)) defined as

$$g_A = \frac{1}{2\pi^2} \left(\frac{V_0}{\epsilon_s} \right) \beta^2 e^\beta \exp(-\beta/\theta) \tag{134}$$

increases with θ, the amplitude of the oscillations of the diffusion coefficient $D_\mu(\theta)$ will also increase with θ. Thus, the dc conductivity of the FK chain as a function of θ, $\sigma(\theta) \propto \theta D_\mu(\theta)$, is expected to have the absolute maximum within the interval $0 \leq \theta \leq 1$ at the concentration value θ between 0.75 and 0.80 (cf. Ref. 52). On the other hand, the chemical diffusion coefficient $D_c(\theta)$ is determined by an expression which is analogous to Eq. (133) but with the factor

$$G_A a_A^2/m_a\eta = (V_0/m_a\eta)\beta^2 e^\beta \theta^{-2} \exp(-\beta/\theta) \tag{135}$$

instead of D_f in front of the figure brackets. The function (135) has a maximum at $\theta = \beta/2$. However, we should remember that the limits of the temperature interval (132) depend on the parameter g_A and, therefore, on the coverage parameter θ.

At low temperatures, the phenomenological approach developed above leads to the similar behavior of the function $D_\mu(\theta)$. Indeed, let us consider the FK chain within the temperature interval (124) for the coverage parameter θ which is close to the value $\theta_0 = 1$, i.e. $|\theta - \theta_0| \ll 1$, when interaction between the residual t-kinks is small enough so that they do not form a kink lattice. In this case the

chemical diffusion coefficient D_c is equal to D_{tk} for $\theta > \theta_0$ and $D_{\bar{t}\bar{k}}$ for $\theta < \theta_0$, and it is approximately independent on θ. (This latter statement is in agreement with numerical simulations of Gillan and Holloway.[24] However, the function $D_c(\theta)$ may slowly increase with increasing of $|\theta - \theta_0|$ due to a kink–kink repulsion of residual kinks). Because the quantity of thermally-excited kinks $\langle N_{\text{pair}} \rangle$ is approximately independent on θ while the quantity of the residual kinks $|N_w|$ linearly increases with $|\theta - \theta_0|$, the susceptibility $\chi \approx \langle N_{\text{tot}} \rangle / N$ as a function of θ should have a local minimum at $\theta = \theta_0$. Therefore, the function $D_\mu(\theta)$ will have a local minimum at $\theta = \theta_0$ too. Analogously, the function $D_\mu(\theta)$ will have local minima at each of those commensurate coverages θ_0 whose "melting" temperature $T_{\text{melt}}(\theta_0)$ is larger than T. (It is clear that between the neighboring local minima the function $D_\mu(\theta)$ has local maxima.) At high temperatures this criterion is fulfilled only for the trivial coverages $\theta_0 = 1/q$. But with decreasing of T, additional local minima of the function $D_\mu(\theta)$ will appear and they correspond to higher-order commensurate structures, and in the limit $T \to 0$ the function $D_\mu(\theta)$ should have minima at each rational value of the coverage parameter θ. It is clear that the values of $D_\mu(\theta)$ at those minima will tend to zero according to the Arrhenius law provided $T \to 0$. Otherwise, loval maxima of $D_\mu(\theta)$ at irrational θ will tend to infinity when $T \to 0$ provided the dimensionless elastic constant $g_A(\theta)$ of the model is larger than the Aubry threshold $g_{\text{Aubry}}(\theta)$ where the $T = 0$ GS exhibits the existence of the "sliding mode". In the opposite case, i.e. when $g_A(\theta) < g_{\text{Aubry}}(\theta)$, the value of $D_\mu(\theta)$ at local minima will tend to zero for $T \to 0$ according to the Arrhenius law too.

The behavior of the function $D_c(\theta)$ becomes clear if we recall that the mass transport along the chain is carried out by kinks at $\theta = \theta_0 + \delta$ and by antikinks at $\theta = \theta_0 - \delta$ (where $\delta \to 0$), provided temperature T of the system is lower than "melting" temperature $T_{\text{melt}}(\theta_0)$ for the structure with a given value $\theta = \theta_0$. For anharmonic interatomic interactions such as the exponential law (5), the PN barrier for the kinks (local contractions of the chain) are lower than those for antikinks (local extensions of the chain). Thus, when the coverage parameter θ increases passing through the value θ_0, the activation energy for the chemical diffusion decreases jumplikely. Therefore, the dependence given by $D_c(\theta)$ should have jumps similar to the inverse Devil's staircase: the value of D_c should rise sharply each time whenever the coverage parameter θ exceeds the value θ_0 that characterizes the structure which commensurates with the substrate and has the "melting" temperature larger than T. It may be predicted also that both the diffusion activation energy and (owing to decrease of the free path length of kinks) the preexponential factor in the formula for $D_c(\theta)$ decrease simultaneously with increasing θ (the so-called compensation effect). It is clear that the jump in $D_c(\theta)$ at a given $\theta = \theta_0$, as well as a local minimum for $D_\mu(\theta)$, exists only if $T < T_{\text{melt}}(\theta_0)$; when temperature increases to be above $T_{\text{melt}}(\theta_0)$, the jump disappears. Thus, the structure of the inverse Devil's staircase for $D_c(\theta)$ (and an irregular structure for $D_\mu(\theta)$) will be smoothed with increasing temperature since only those peculiarities which correspond to the simple commensurate structures ($\theta_0 = 1, \frac{1}{2}$, etc.) will "survive".

9. Conclusions

In conclusion, using the phenomenological approach based on the approximation of the ideal kink gas and hierarchy of the "melted" kink lattices, we have analysed the diffusion coefficients of the anharmonic FK chain as functions of the coverage parameter θ and temperature T. In particular, we have shown that the chemical diffusion coefficient $D_c(\theta)$ as a function of θ has a form similar to the inverse Devil's staircase, i.e. we have demonstrated that the function $D_c(\theta)$ should exhibit jumps at those rational values of the coverage parameter θ where, at a given value of T, the corresponding commensurate structure has a short-range order that allows the system dynamics to be described in terms of the well-defined kink excitations. In the same time, the chain conductivity $\sigma(\theta) \propto \theta D_\mu(\theta)$ should display local minima at the same rational values of the coverage parameter θ. The quantity of such singularities, i.e. the quantity of the jumps for $D_c(\theta)$ and the minima for $D_\mu(\theta)$, should increase with decreasing of T.

The predicted behavior of the diffusion coefficients D_c and D_μ are expected to be observed in those physical objects which may be described with the help of the anharmonic FK model, such as one-dimensional conductors and adsorbed layers. For example, the experimentally measured dc conductivity of one-dimensional conductors exhibits a local maximum between $\theta = 0.75$ and $\theta = 0.80$, i.e. $D_\mu(\theta)$ has local minima at $\theta_1 = \frac{1}{2}$ and $\theta_2 = 1$, and a local maximum between those values. According to our predictions, at lower temperatures the function $D_\mu(\theta)$ will have, additionally to the minima at θ_1 and θ_2, a local minimum at $\theta_3 = \frac{2}{3}$. Then, with futher decreasing of temperature, an additional minimum appears at $\theta_4 = \frac{3}{4}$, and so on.

Referring to adsorbed layers, we should mention a sharp increase of the chemical diffusion coefficient for Ag atoms adsorbed on a stepped (vicinal) Ge surface when the concentration of atoms increases to above the value corresponding to the commensurate (4×2) structure of adsorbed atoms. Unfortunately, we do not know at the moment the detailed results of investigations for the surface diffusion on furrowed surfaces, although preliminary experimental results of Vedula *et al.*[53] are in a good qualitative agreement with the predictions of the present analysis.

At last, we would like to mention briefly possible generalizations of the model. First, in more realistic physical models the periodic substrate potential may have a more complicated than sinusoidal shape. If the shape of the potential $V_{sub}(x)$ allows the existence of different types of kinks, the low-temperature activation energy which determines the diffusion coefficients will be given by a contribution of the kinks corresponding to the largest value of the PN barrier. Second, in real physical objects we have not one single isolated chain but, instead, a system of weakly coupled parallel FK chains. The interaction between the chains leads to interaction between kinks in the chains and, therefore, to a modification of the diffusion coefficients. Third, in the model we have investigated in the present work, atoms were allowed to move along one-dimensional "channels" only. But with increasing of interatomic

repulsion, for example, by means of increasing of θ, compression forces in the atomic chain may become so strong that the atoms may escape from a channel, and the atoms will also move in the transversal direction. In such a case, we should use the FK model with a transversal degree of freedom.[54] Finally, it would be also important to investigate two- (and three-) dimensional FK models as well as to take into account a possible role of impurities in the effects described above.

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Appendix A

Renormalization procedure

In this Appendix we discuss how we can "map" a complex commensurate structure C for the "primary" FK model to a new (more simple) structure C_k for the "secondary" FK model.

Let us suppose that we know the parameters of a single kink such as its mass, m_k, the PN barrier, $\epsilon_{\rm PN}$, the kink interaction energy, $v_{\rm int}$, which are defined for a simple commensurate structure C_0 with the coverage parameter $\theta_0 = s_0/q_0$. The structure C_0 can be presented by N_0 atoms distributed on the length $L_0 = M_0 a_s$, where N_0 and M_0 satisfy the condition $N_0 q_0 = M_0 s_0$. Then, let us add (or substract) ΔN atoms so that a new commensurate structure C has $N = N_0 + \Delta N$ atoms on the same length L_0, but the coverage parameter this time is changed to be $\theta = s/q$ with the condition $Nq = M_0 s$. Each additional atom (for $\theta > \theta_0$) or vacancy (for $\theta < \theta_0$) corresponds to q_0 kinks or antikinks. Thus, the structure C may be considered as a regular lattice of kinks with the spatial period

$$R_0 = \frac{L_0}{|N - N_0| q_0} = \frac{a_s}{|\theta - \theta_0| q_0} \,. \tag{136}$$

Considering now the kinks as effective quasiparticles ("atoms") subjected into the PN potential $V_{\rm PN}(X) \approx \frac{1}{2}\epsilon_{\rm PN}[1 - \cos(2\pi X/a_0)]$ with the period $a_0 = q_0 a_s$ and interacting via the potential $v_{\rm int}(|X_1 - X_2|)$, the structure C of the primary FK chain can be treated as a new ("secondary") FK chain of kinks instead of atoms with the coverage parameter $\theta_k = a_0/R_0 = q_0^2|\theta - \theta_0|$. Then, it may be proved that a kink of the primary structure C is equivalent to a kink of the secondary structure C_k. Thus, choosing an appropriate simple reference structure C_0 such that $|\theta - \theta_0| \ll \theta_0$, we may significantly simplify calculations of kink parameters for the complex structure C. It is clear that such a renormalization procedure may be

repeated by a required number of times if necessary. The details of the procedure are summarized in Table 9.

The renormalization procedure $C \to C_k$ was firstly proposed by Joos *et al.*[55] (see also Ref. 16). Note, however, that shapes of the "substrate" potential $V_{\rm PN}(X)$ and the "atomic" interaction law $v_{\rm int}(X)$ for the secondary FK model may deviate very much from those defined for the primary FK model. Besides, the parameters m_k^*, $\epsilon_{\rm PN}^*$, and $\epsilon_{\rm pair}^*$ of the kink lattice do not exactly coincide with the analogous values defined for an isolated kink because interaction between kinks leads to narrowing of the kink's width, $d \to d^* = kd < d$. The parameter k ($k < 1$) is known as the modulus in the analytical periodic solution for the kink lattice; in particular, in the limit when the SG equation is valid this parameter is determined by the equation $2k\mathrm{K}(k) = R/a_0\sqrt{g_a}$, where $\mathrm{K}(k)$ is the complete elliptic integral of the first kind. The values m_k^*, $\epsilon_{\rm PN}^*$, etc. may be approximately calculated using the same formulas as for an isolated kink with the renormalized interaction constant $g_a^* = k^2 g_a$ instead of g_a. Because $g_a^* < g_a$, we obtain naturally that $m_a^* > m_k$, $\epsilon_{\rm PN}^* > \epsilon_{\rm PN}$, and $\epsilon_{\rm pair}^* < \epsilon_{\rm pair}$.

Table 1. Comparison of the "primary" and "secondary" FK models when the reference structure C_0 is characterized by the coverage parameter $\theta_0 = s_0/q_0$ and the period $a_0 = q_0 a_s^{(0)}$, so that the dimensionless elastic constant and anharmonicity parameter are equal to $g_a^{(0)} = [a_s^{(0)}]^2 V_{\rm int}''(a_0)/2\pi^2\epsilon_s^{(0)}$ and $\tilde{\beta}^{(0)} = -a_s^{(0)} V_{\rm int}'''(a_0)/V_{\rm int}''(a_0)$, respectively.

parameter	"primary" FK chain	"secondary" FK chain
mass	$m_a^{(0)} = m_a$	$m_a^{(1)} = m_k^*$
coordinate	$x_l^{(0)} = x_l$	$x_l^{(1)} = X_l$
interaction potential	$V_{\rm int}^{(0)} = V_{\rm int}(x_{l+1} - x_l)$	$V_{\rm int}^{(1)} = v_{\rm int}(X_{l+1} - X_l)$
substrate potential	$V_{\rm sub}^{(0)} = V_{\rm sub}(x)$	$V_{\rm sub}^{(1)} = V_{\rm PN}(X)$
period	$a_s^{(0)} = a_s$	$a_s^{(1)} = a_0 = q_0 a_s^{(0)}$
height	$\epsilon_s^{(0)} = \epsilon_s$	$\epsilon_s^{(1)} = \epsilon_{\rm PN}^*$
coverage	$\theta^{(0)} = \theta = s/q$	$\theta^{(1)} = \theta_k = s_k/q_k$
order	$s^{(0)} = s$	$s^{(1)} = s_k = q_0\lvert sq_0 - s_0 q\rvert$
period	$q^{(0)} = q$	$q^{(1)} = q_k = q^{(0)}$
	$a^{(0)} = a = qa_s$	$a^{(1)} = a_k = qa_0 = qq_0 a_s$
mean distance	$a_{\rm A}^{(0)} = a_{\rm A} = a/s$	$a_{\rm A}^{(1)} = R_0 = a_k/s_k$

Appendix B.

Susceptibility of the Toda chain

To determine the high-temperature behavior of the susceptibility $\chi(T)$, we use the fact that for $k_B T \gg \max(\epsilon_s, \epsilon_k)$, when we may neglect the substrate potential, the anharmonic FK model with the exponential interaction (5) reduces to the exactly integrable Toda lattice.[56] To calculate the value $\chi(T)$ for the Toda chain, it is more convenient to consider a "free-end" atomic chain at an external "pressure" Π. It is clear that the "free-end" atomic chain and the "fixed-density" atomic chain will have the same value of $\chi(T)$ provided both the chains are characterized by the same density $\langle n \rangle \equiv n$ of atoms in the chain.

To consider the "free-end" Toda chain, we add to Eq. (5) a linear attractive branch and we rewrite Eq. (5) in the form,

$$V_{\rm int}(x) = G_A b^2 (e^{-r} - 1 + r) , \quad r \equiv (x - a_{\min})/b . \tag{137}$$

The parameters of the potential (137) are connected with those of Eq. (5) by the relations $b = a_s/\beta$ and $G_A b^2 \exp(a_{\min}/b) = V_0 \exp(\beta)$. The parameter $a_{\min}$ in Eq. (137) is selected in such a way that the mean interatomic distance $a_A(T)$ in the "free-end" atomic chain coincides with that in the "fixed-density" atomic chain.

The Gibbs free energy of the "free-end" Toda chain is known to be

$$G(T, \Pi, N) = -k_B T N \ln \left[y \sqrt{m_a k_B T / 2\pi\hbar^2} \exp(-\Pi a_{\min}/k_B T) \right] \tag{138}$$

where

$$y(T, \Pi) = b \exp(B) \Gamma(B + b\Pi/k_B T) B^{-(B + b\Pi/k_B T)} , \tag{139}$$

$$B = G_A b^2 / k_B T , \tag{140}$$

and $\Gamma(x)$ is the Gamma function. The chain's length at the pressure Π is defined by the equation

$$L(T, \Pi, N) = \left(\frac{\partial G}{\partial \Pi} \right)_{T, N} = N a_A(T, \Pi) , \tag{141}$$

where

$$a_A(T, \Pi) = a_{\min} + \delta a(T, \Pi) , \tag{142}$$

$$\delta a(T, \Pi) = b[\ln B - \Psi(B + b\Pi/k_B T)] , \tag{143}$$

where $\Psi(x) = \frac{d}{dx} \ln \Gamma(x)$. Defining the dimensionless susceptibility $\chi(T)$ as

$$\chi = -k_B T \frac{n^2}{N} \left(\frac{\partial^2 G}{\partial \Pi^2} \right)_{T,N} , \tag{144}$$

we obtain from Eqs. (141) to (144) that $\chi(T)$ is equal to

$$\chi = -k_B T \frac{N}{L^2} \frac{\partial L}{\partial \Pi} \bigg|_{\Pi=0} = \frac{\Psi'(B)}{[\ln B - \Psi(B) + a_{\min}/b]^2} . \tag{145}$$

To investigate Eq. (145), let us introduce an "anharmonicity" energy ϵ_{anh} defined as

$$\epsilon_{anh} = G_A b^2 \approx V_0 \exp[-\beta(a_A - a_s)/a_s] . \tag{146}$$

For very high temperatures, $k_B T \gg \epsilon_{anh}$, we have $B \ll 1$ and $\Psi(B) \approx -\gamma_0 - 1/B$ (γ_0 being the Euler constant), so that

$$\chi \approx \left[1 + \left(\frac{a_{\min}}{b} \right) B + B \ln B \right]^2 \approx 1 - 2 \left(\frac{\epsilon_{anh}}{k_B T} \right) \left(\frac{a_{\min}}{b} \right) . \tag{147}$$

As may be seen from Eq. (147), this result exhibits the correct limit $\chi(T) \to 1$ as $T \to \infty$. Otherwise, for an intermediate temperature interval, $k_B T \ll \epsilon_{anh}$, where $B \gg 1$ and $\Psi(B) \approx \ln B - 1/2B - 1/12B^2$, from Eq. (145) we obtain

$$\chi \approx \left(\frac{k_B T}{G_A a_A^2} \right) \left(1 + \frac{1}{2} \frac{k_B T}{\epsilon_{anh}} \right) , \tag{148}$$

i.e. the result which corresponds to a harmonic chain.

Note also that in the limit $b \to 0$ the potential (137) reduces to a hard-core potential $V_{int}(x) = V_0 \Theta(a_{\min} - x)$ with $V_0 \to \infty$, $\Theta(x)$ being the Heaviside step function which describes interaction of hard balls of the diameter $a_{\min}$. In this latter case Eq. (145) leads to the expression[57]

$$\chi = (1 - n a_{\min})^2 . \tag{149}$$

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