Analytical solution of a one-dimensional lattice gas model with an infinite number of multiatom interactions

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We consider a one-dimensional lattice gas model in which the atoms interact via an infinite number of cluster interactions within contiguous atomic chains plus the next-nearest-neighbor pairwise interaction. All interactions are of arbitrary strength. An analytical expression for the size distribution of atomic chain lengths is obtained in the framework of the canonical ensemble formalism. Application of the exact solution to the problems of self-assembly and self-organization is briefly discussed.

I. INTRODUCTION

In recent years there has been growing interest in studies of monatomic chains obtained in the processes of heteroepitaxial growth [1–3] at various substrates. A major goal of these studies is to obtain the so-called quantum wires for potential use in microelectronic applications. In these experiments one usually aims at obtaining wires of infinite length for subsequent use in the studies of the Luttinger liquid [3]. In practice, however, one frequently encounters the monatomic wires of finite length. These may be useful in more practical applications, such as the microelectronic circuitry [4]. Such finite one-dimensional (1D) clusters were observed, e.g., in Refs. [5,6]. Current theoretical interest is in magnetic properties of finite monatomic clusters [7] in view of their potential use in magnetic memory devices. The latter application, however, will require the development of the techniques of mass production of such objects. In this context it would be interesting to study the possibility of their self-assembly and self-organization similar to analogous processes in 2D heteroepitaxial systems [8,9].

In the present paper we consider an analytic solution for the cluster size distribution in the framework of a 1D lattice gas model with an arbitrary number of cluster interactions within contiguous atomic chains plus the next-nearest-neighbor (NNN) pair interaction. Such model can be justified in the framework of the Frenkel-Kontorova model of strained epitaxy [12] but also can be useful in other cases, e.g., in *ab initio* approaches, where the cluster interactions appear because of the many-body nature of the electron interactions, which cannot be reduced to the pair interatomic potential.

II. THE MODEL

Let us consider a lattice gas model (LGM) defined by the function $E(l)$ describing the dependence of the energy of 1D atomic clusters (or chains) on their length l. Such a model was already used for the description of the self-assembly phenomena in Ref. [10]. We note, however, that in two dimensions this approach can be only phenomenological because the cluster size does not characterize a 2D structure uniquely. In contrast, in one-dimensions the cluster is defined unambiguously by its length and the function $E(l)$ is also

uniquely defined provided the clusters do not interact.

To apply standard tools of statistical physics, we need to find the Hamiltonian corresponding to our model. To this end we consider the following trial expression:

$$H = \sum_{i;l=2}^{\infty} V_l n_i n_{i+1} \ldots n_{i+(l-1)}, \qquad (1)$$

where V_l are the numerical coefficients to be fitted to reproduce the chain energies $E(l)$ and n_i are the occupation numbers taking values 0 or 1 depending on whether site i is empty or is occupied by an atom. Assuming that we have already fitted $V_{l-1}, V_{l-2}, \ldots, V_2$ to the energies $E(l-1) \equiv E_{l-1}, E_{l-2}, \ldots, E_2$, let us consider the chain of length l. From Eq. (1) one finds

$$E(l) = E(l-1) + V_l + V_{l-1} + V_{l-2} + \cdots + V_2, \qquad (2)$$

where the V terms on the right-hand side (rhs) account for the interactions of the newly added atom with the rest. Similarly,

$$E(l-1) = E(l-2) + V_{l-1} + V_{l-2} + \cdots + V_2. \qquad (3)$$

Subtracting Eq. (3) from Eq. (2) we get

$$E(l) - E(l-1) = E(l-1) + V_l - E(l-2), \qquad (4)$$

from where it follows that the Hamiltonian of our model is Eq. (1) with the coefficients given by the recursion relation

$$V_l = E_l - 2E_{l-1} + E_{l-2} \qquad (5)$$

initialized by $E_0 = E_1 = 0$. For the system to be well defined in the thermodynamic limit, the chain energy E_l cannot grow quicker than linearly when $l \to \infty$. This means that the the cluster interactions V_l tend to zero at large l because according to Eq. (5) they are equal to the discrete second derivative of E_l with respect to l.

In the above model atoms interact only when they belong to the same contiguous chain, so that separate chains are not coupled to each other. To make the model more realistic we allow for the interchain coupling by adding to Hamiltonian (1) the next-nearest-neighbor (NNN) pair interaction term

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$$H = V_{NNN} \sum_i n_i n_{i+2} + \sum_{i;l=2}^{\infty} V_l n_i n_{i+1} \ldots n_{i+(l-1)}. \quad (6)$$

III. THE CANONICAL ENSEMBLE SOLUTION

We consider a 1D lattice with a fixed number of atoms N, which can occupy $I > N$ lattice sites. Our major goal in this paper is to find the equilibrium distribution of the atomic chain sizes at finite temperature T in the model defined by Hamiltonian (6). But, first we will consider the above problem using a simpler Hamiltonian (1), i.e., by neglecting the NNN interaction, which will be accounted for later. We will seek the canonical ensemble solution of our problem by generalizing the approach of Ref. [13]. In this approach one first have to compute the energy of the system in terms of cluster variables m_l—the number of clusters of length l and their energy $E(l)$. Because the $l \to \infty$ limit is not completely trivial, we calculate the configurational energy by assuming that all V_l with $l > L$ are equal to zero. In this case the total energy can be calculated as

$$\mathcal{E} = \sum_{l=1}^{L-2} E_l m_l + E'_L N_> - m_> \sum_{l=2}^{L} (l-1)V_l, \quad (7)$$

where $E'_L = \sum_{l=2}^{L} V_l$ is the first (discrete) derivative of E_l, $m_>$ is the total number of clusters of length exceeding $L-2$ below which we will call the big clusters, and $N_> = (N - \sum_{l=1}^{L-2} l m_l)$ is the number of atoms contained in the big clusters. The last two terms on the rhs of Eq. (7) can be verified by first checking their correctness for $m_> = 1$ and then noting that cutting a big cluster into two amounts to cutting $l-1$ couplings of type V_l. To complete the calculation of the total free energy $F_{tot} = E_{tot} - TS$, it remains to compute the entropy S. The number of atomic configurations can be expressed through the cluster variables as

$$\Omega_{at} = \frac{m_{tot}!}{m_1! m_2! \cdots m_>!} \binom{N_> - (L-2)m_> - 1}{m_> - 1}. \quad (8)$$

In this equality the first multiplier on the rhs counts all inequivalent permutations between the clusters with all big clusters being considered as equivalent, while the second factor accounts for the number of ways to divide $N_>$ atoms into $m_>$ big clusters including their permutations. We find this factor by observing that the division of $N_>$ atoms into clusters of sizes exceeding $L-2$ is equivalent to dividing $n = N_> - (L-2)m_>$ atoms into $k = m_>$ clusters. The latter quantity was calculated in Ref. [13] to be equal to the binomial coefficient

$$C_{k-1}^{n-1} = \binom{n-1}{k-1},$$

provided $n \geq k \geq 1$. Otherwise it is equal to zero. The meaning of this formula is simple. In a contiguous chain of n atoms there is $n-1$ places to cut the chain into pieces. k pieces can be obtained with $k-1$ cuts. Hence, the number of the possible cuts of n atoms into k pieces is equal exactly to

the above combinatorial coefficient. To complete the calculation of the total number of configurations we have to multiply Ω_{at} by the corresponding factor responsible for the configurations of vacant sites [13]. But before doing this we modify Eq. (7) by accounting for the omitted NNN pair interaction. To this end we note that as long as the contiguous chains are concerned, V_{NNN} interaction amounts simply to renormalization of V_3. Additionally this term introduces the interchain coupling between the chains separated by a single vacant site (a vacancy). Therefore, the term $V_{NNN} k_1$, where k_1 is the number of vacancies, should be added to the rhs of Eq. (7) (here and above we do not pay attention to the boundary conditions [13] because in this paper we are interested only in the thermodynamic limit). So when counting the configurations of empty sites we should separate the configurations with different numbers of vacancies. This is achieved by using Eq. (8) with the total number of empty sites $I - N$ instead of N, the big clusters in this case should exceed $L - 2 = 1$. Denoting the total number of clusters as k from Eq. (7) we get

$$\Omega_{vac} = \frac{k!}{k_1!(k-k_1)!} \binom{I-N-k-1}{k-k_1-1}. \quad (9)$$

Our final expression for S is obtained from Eqs. (8) and (9) with the use of the Stirling formula as

$$\begin{aligned}
\frac{S}{k_B I} = &\, 2c \ln c - \sum_{l=1}^{L-2} c_l \ln c_l - v \ln v - 2(c-v) \\
&\times \ln(c-v) + (1-\theta-c)\ln(1-\theta-c) \\
&- (1-\theta-2c+v)\ln(1-\theta-2c+v) \\
&- 2c_> \ln c_> + [\theta_> - (L-2)c_>]\ln[\theta_> - (L-2)c_>] \\
&- [\theta_> - (L-1)c_>]\ln[\theta_> - (L-1)c_>], \quad (10)
\end{aligned}$$

where $\theta = N/I$ is the total coverage, $c_l = m_l/I$ is the concentration of clusters of length l, $c = \sum_l c_l$ is the total cluster concentration, $v = k_1/I$ is the vacancy concentration, $\theta_> = \theta - \sum_{l=1}^{L-1} l c_l = N_>/I$. This expression for reduced entropy together with the reduced energy obtained from Eq. (7) are sufficient to obtain the reduced free energy as a function of the unknown quantities $\{c_l\}$, $c_>$, and v. Minimizing it with respect to these variables we arrive in the limit $L \to \infty$ at the following set of equations:

$$c_l = \frac{c^2(1-\theta-2c+v)^2}{(c-v)^2(1-\theta-c)} \exp\left(\frac{\mu l - E_l}{k_B T}\right), \quad (11)$$

$$(c-v)^2 = v(1-\theta-2c+v)\exp\left(\frac{V_{NNN}}{k_B T}\right). \quad (12)$$

To find the above limit it is necessary to know the asymptotic behavior of c_l at large l. The limit was taken by assuming the exponential behavior $c_l \propto \exp(-\lambda l)$, which is consistent with the resulting equation (11). We note that Eq. (12) is of the second order in v, so one can exclude this variable from the first equation to obtain a closed equation for $\{c_l\}$. From the

above set, however, it is easier to see that if the NNN interaction is negative, then $v \to c$ as $T \to 0$, i.e., the vacancy concentration becomes equal to the concentration of clusters, which means that the system becomes ordered: the clusters self-organize into chains separated by monovacancies. This is further confirmed by the fact that the entropy, Eq. (10), tends to zero at zero temperature provided $V_{NNN} < 0$ and the clusters are size calibrated. Indeed, in the limit $L \to \infty$ only the first two lines of Eq. (10) survive:

$$\frac{s}{k_B} = 2c \ln c - \sum_{l=1}^{\infty} c_l \ln c_l - v \ln v - 2(c-v)\ln(c-v)$$

$$+ (1-\theta-c)\ln(1-\theta-c) - (1-\theta-2c+v)$$

$$\times \ln(1-\theta-2c+v), \qquad (13)$$

where $s = S/I$ is the entropy per site.

In connection with this expression it is worth noting that Eqs. (11) and (12) can formally be obtained in the thermodynamic limit from the variation with respect to c_l of the expression for the free energy density,

$$f = \sum_{l=1}^{\infty} c_l E_l - k_B T s - \mu \left(\sum_{l=1}^{\infty} l c_l - \theta \right),$$

where μ is the Lagrange multiplier. This derivation, however, may cause doubts in the case of clusters of sizes $l = O(N)$ when the terms $l c_l = m_l O(N)/N$ in the above equation acquire discrete values and so are not suitable for the variational treatment. The derivation presented above is more rigorous and besides can be modified to be applicable to finite systems [13,16].

At $T = 0$ and $c = v$ the entropy density (13) takes the form

$$\frac{s}{k_B} = c \ln c - \sum_{l=1}^{L-2} c_l \ln c_l. \qquad (14)$$

Thus, if the clusters at $T = 0$ are size calibrated, i.e., if for some value of $l = l_0$, $c_{l_0} = c$, while $c_l = 0$ for all other l, then from the above equation it follows that $s = 0$. For $V_{NNN} \geq 0$ the entropy is positive even at $T = 0$, meaning disordered state. The issue of size calibration will be considered in more detail in Sec. V.

IV. THE ISING MODEL

To check Eqs. (11) and (12) we will apply them to the known exactly solvable problem—the 1D Ising model. As is known, it is equivalent to the lattice gas model with pair interatomic interaction. This can be easily shown (see Ref. [14] Ch. II) by substituting $n_i = (1-\sigma_i)/2$ ($\sigma_i = \pm 1$, the Ising spin variable) into the LGM Hamiltonian

$$H = \frac{1}{2} \sum_{ij} V_{ij} n_i n_j = \frac{1}{8} \sum_{ij} V_{ij}(1-\sigma_i)(1-\sigma_j)$$

$$= \frac{1}{2} \sum_{ij} \left(\frac{V_{ij}}{4} \right) \sigma_i \sigma_j + \sum_{j} \left(\frac{V_{ij}}{4} \right)(1-2\sigma_j). \qquad (15)$$

Thus, the Ising model with NN interaction can be solved in the canonical ensemble formalism with the use of our formulas. In this section we will obtain the appropriate formulas in closed analytical form. Also, we will compare our results obtained in the canonical ensemble with more familiar results obtained in the grand canonical formalism via the transfer matrix method. The latter solution can be found, e.g., in Ch. V of Ref. [14], where the 1D Ising model Hamiltonian was considered, which in our notation can be written as [cf. Eq. (15)]

$$H_{IM} = \left(\frac{V_{NN}}{4} \right) \sum_i \sigma_i \sigma_{i+1} - \frac{1}{2} h \sum_i (\sigma_i + \sigma_{i+1}). \qquad (16)$$

The reduced free energy calculated in the grand canonical ensemble was found to be

$$\frac{F_{GC}}{N k_B T} = -\ln(e^{-K/4} \cosh \bar{h} + \sqrt{e^{-K/2} \sinh^2 \bar{h} + e^{K/2}}), \qquad (17)$$

where $K = V_{NN}/k_B T$ and $\bar{h} = h/k_B T$ is the external field (divided by $k_B T$), which fixes the magnetization M. The latter is connected to the coverage θ by the relation

$$\theta = (1-M)/2 \qquad (18)$$

and can be calculated as

$$M = \partial F_{GC}/\partial \bar{h}. \qquad (19)$$

To obtain the canonical ensemble free energy we have to perform the Legendre transform [see Eq. (16)]

$$\frac{F_C}{N k_B T} = F_{GC} + \bar{h} \frac{\partial F_{GC}}{\partial \bar{h}}, \qquad (20)$$

where the partial derivative is calculated from Eq. (19) as

$$M = \frac{e^{-K/4} \sinh \bar{h}(1 + e^{-K/4} \cosh \bar{h}/\sqrt{e^{-K/2} \sinh^2 \bar{h} + e^{K/2}})}{e^{-K/4} \cosh \bar{h} + \sqrt{e^{-K/2} \sinh^2 \bar{h} + e^{K/2}}}. \qquad (21)$$

Finally, to obtain the LGM free energy F in the canonical ensemble formalism we have to add the statistical average of the last term on the rhs of Eq. (15):

$$\frac{F}{N k_B T} = \frac{F_C}{N k_B T} + \left(\frac{K}{4} \right)(1-2M). \qquad (22)$$

In our formalism the free energy F for the NN LGM can be calculated as follows. According to Eq. (12), in the case $V_{NNN} = 0$,

$$v = c^2/(1-\theta). \qquad (23)$$

Substituting this into Eq. (11) we get, in the case of the Ising model,

$$c_l = (1-\theta-c)\exp[\bar{\mu} + (\bar{\mu} - K)(l-1)], \qquad (24)$$

where $\bar{\mu} = \mu/k_B T$. From Eq. (24) we easily find

$$c = \sum_{l=1}^{\infty} c_l = (1-\theta-c)e^{\bar{\mu}}/(1-e^{\bar{\mu}-K}),$$

$$\theta = \sum_{l=1}^{\infty} l c_l = c + c^2 e^{-K}/(1-e^{\bar{\mu}-K}). \qquad (25)$$

These two equations are sufficient to express the unknown quantities c and $\bar{\mu}$ through the coverage θ and the interaction parameter K—the independent variables in the canonical ensemble. From Eq. (25) we have after some algebra

$$\bar{\mu} = -\ln\left[\frac{1}{2\theta} - x + \sqrt{\left(\frac{1}{2\theta} - x\right)^2 + x(1-x)}\right],$$

$$c = \frac{1}{2x}[1 - \sqrt{1 - 4\theta(1-\theta)x}],$$

where $x = 1 - e^{-K}$. These formulas can be used to obtain analytic expressions for all quantities of interest.

In the canonical ensemble case the free energy is

$$\frac{F}{Nk_B T} = \bar{\mu}\theta - (1-\theta)\ln\left(1 + \frac{e^{\bar{\mu}}}{1-e^{\bar{\mu}-K}}\right). \qquad (26)$$

As we see, it is quite different from Eq. (22). We were unable to compare the two solutions analytically and used the numerical procedure. By fixing $\bar{h}$ and K we computed M with the use of Eq. (21) and $F/Nk_B T$ from Eq. (22). Then θ was calculated according to Eq. (18) and $F/Nk_B T$ was computed from Eq. (26). Both values coincided within 13–15 significant digits depending on how singular the values of $F/Nk_B T$ are at the chosen values of $\bar{h}$ and K.

Thus, we have solved the 1D NN LGM in the canonical ensemble approach and expressed all quantities of interest in terms of the atomic density (or coverage) θ, which is more natural and easier to measure quantity than the chemical potential variable of the grand canonical formalism.

V. THE SIZE CALIBRATION

According to Ref. [10], the system exhibits the size calibration of the atomic clusters if the energy density per atom $E(l)/l$ has a minimum. The size calibration is easiest to see in the case $V_{NNN} = 0$ when the distribution Eq. (11) takes the form

$$c_l = (1-\theta-c)\exp\beta(\mu l - E_l).$$

Except for the excluded volume prefactor this expression coincides with the formula proposed in Ref. [10] where a detailed discussion of the size calibration issue is given and which fully applies to our case, provided the pair attraction V_{NN} is not too strong. In Ref. [12] we have shown that in the framework of the Frenkel-Kontorova model the effective chain energy (in fact, the free energy; see Ref. [12] for details) has the form
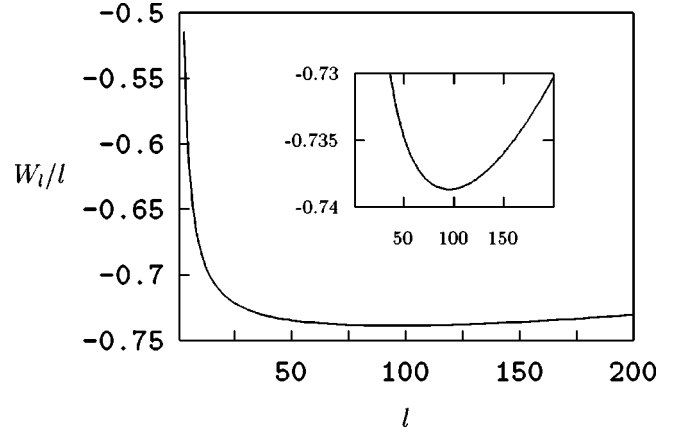

FIG. 1. The length dependence of the reduced chain energy with the relaxation energy corresponding to $\alpha = 10^{-5}$ and $V_{NN} = -0.25$ in units of $k_p f^2$ (see the text). The inset shows the location of the minimum.

$$E_l = V_{NN}(l-1) - \sum_{\text{chains}} (W_l - TS_l), \qquad (27)$$

where the last two terms represent the relaxation free energy. The length dependence of the relaxation energy W_l is governed by the dimensionless parameter $\alpha = k_s/k_p$, where the spring constants k_s and k_p are the second derivatives of the potentials that bind the atom to the substrate (k_s) and of the pair interatomic interaction (k_p), respectively. In the illustrative calculations below, the energy unit was chosen to be equal to the energy of the unrelaxed misfit strain $k_p f^2$, where the interatomic spring constant k_p was defined earlier and f is the misfit as defined in Ref. [12]. The relaxation entropy S_l is practically linear in l and so according to Eq. (5) essentially contributes only into the NN interaction.

In our calculations we chose $\alpha = 10^{-5}$ to be quite small in order to visualize all qualitative details of the self-assembly behavior. Physically this would correspond to very weak binding to the substrate. In the above energy units V_{NN} was chosen to be equal to -0.25 so that there was a minimum in $E(l)/l$ at $l \approx 100$ (see Fig. 1). The calculation of the size distribution for this case is shown in Fig. 2. It qualitatively agrees with the Monte Carlo simulations of Ref. [11] (cf. Fig. 2 of that reference). The most notable feature of the above calculations is the change of the position of the maximum of the cluster size distribution with lowering temperature—the feature is not clearly understood from the theory of Ref. [10]. Although the entropic contribution into E_l is rather small due to the small temperatures considered, the shallowness of the minimum in $E(l)/l$ makes it possible that the above shift of the maximum is due to the shift in the position of the minimum in $E_l = W_l - TS_l$ with lowering temperature. To check this possibility we repeated the calculations with E_l replaced by temperature-independent part W_l. The results of this calculation is shown in Fig. 3. The only qualitative difference with Fig. 2 is that the bimodal distribution is never observed in the case of T-independent case. Presumably, this is due to the 1D character of our model, because in 2D case where
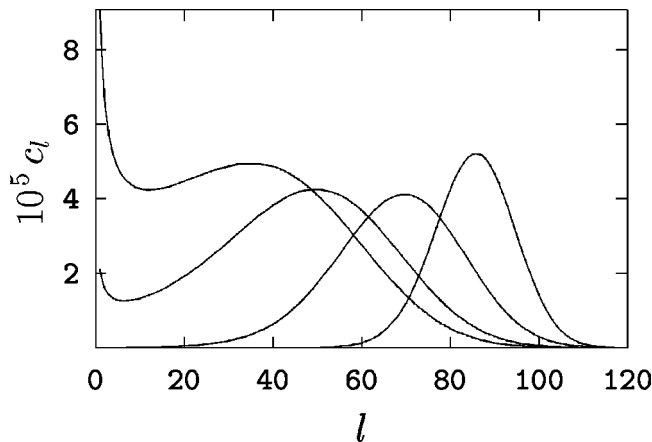
FIG. 2. Equilibrium distribution of atomic chain lengths at the coverage $\theta=0.1$ corresponding to (from left to right) $1/k_BT=20$, 22, 30, and 60 (in units of $k_p f^2$). The pair interaction $V_{NN}=-0.25$ and $\alpha=10^{-5}$ (for explanation of notation see the text).

T-independent interactions were also used we found a strongly bimodal distribution [15].

VI. CONCLUSION

In this paper we considered an analytical solution of a 1D lattice gas model with an arbitrary number of cluster interatomic interactions within contiguous atomic chains. We illustrated the model by applying it to the description of the equilibrium distribution of atomic clusters in strained epitaxy in the thermodynamic limit. However, the model can also be used in other cases when the multiatom interactions are of the above type, as well as can be applied to finite systems, like those discussed in Refs. [13,16]. Our analytical solution confirms the observation made in Ref. [11] in the framework of a phenomenological approach that the maximum in the *equilibrium* distribution of the cluster sizes moves to higher
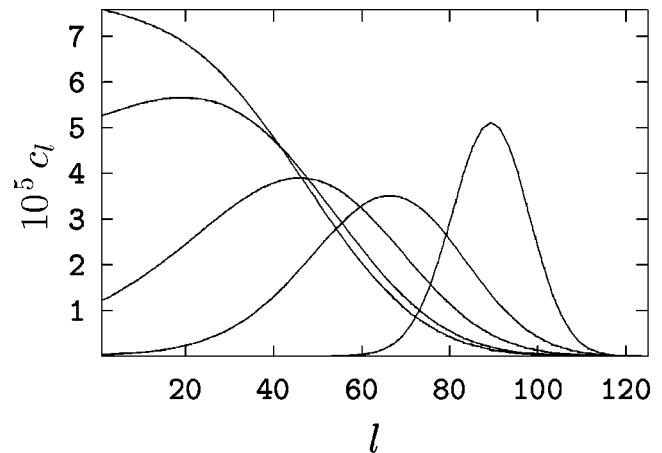

FIG. 3. The same as in Fig. 2 except that the entropic part of E_l is set to zero and the temperatures are (from left to right) $1/k_BT = 12.5$, 13, 15, 20, and 60.

values with lowering temperature. This can lead to an interesting kinetic phenomenon consisting in the saturated ripening when the system is quenched to lower temperature.

Note added. After this work was completed it was brought to our attention [17] that the class of Hamiltonians considered in the present paper in the case $\tilde{V}_{NNN}=0$ [our Eq. (1)] contains the Hamiltonian of the Muñoz-Eaton model of the protein folding [18]. The latter was exactly solved in Ref. [19]. The method of solution is very different from our approach and the comparison of results is not straighforward. The connection between the two approaches is currently being investigated.

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