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Isotopic order by phonon-induced interactions

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We examine conditions for isotopic order on a chain of harmonic oscillators with two isotopic species (host, with mass m_a and impurity, with mass m_b) and find that they are the same as those for a phase transition of condensation in a one-dimensional model proposed by Fisher. In a thermodynamical equilibrium state of the system, phonon-induced interactions among impurities are computed and, under a certain approximation, are conveniently decomposed into a sum over short-range many-body potentials φ_s involving s particles inside a cluster of impurities. We show that in a range of physical values for the model parameters in which $m_b < m_a$, $\varphi_s \sim -1/s^2$ for large s.

I. INTRODUCTION

Defects associated with different stable isotopic species of a particular chemical element that composes a crystal are influential on its phonon properties.[1] These "isotopic impurities" are usually assumed to be randomly distributed among the lattice sites. This is justified on the basis that, concerning their chemical nature, all isotopic species are identical to each other so it is unlikely to find an *a priori* positional correlation among particles of a same species. As a result, in calculating thermodynamical functions of the system, the impurities are, in general, considered quenched.

Here, we review this assumption from an opposite point of view: instead of studying the effects of impurities on the phonons properties, we draw attention to the influence that the phonons might have on the equilibrium properties of impurities. In particular, we ask whether and under what conditions the phonons of the lattice can induce positional correlations among impurities. Eventually then, "isotopic order" might be established in a way that the system would present macroscopic regions entirely constituted by a single isotopic species.

We consider a chain of harmonic oscillators, all with a common force constant K between pairs of nearest-neighbor isotopes of masses m_a (host) and m_b (impurity). We assume that this system can be driven into a region of sufficiently high temperatures where the particles can freely interchange positions with each other. In this situation the phonons may be influential on determining the equilibrium configurations of impurities on the host lattice.

We also assume that whatever the dynamical processes that provide the system with these change of positions, they are very fast processes compared to the observation time. We then examine the conditions for isotopic fractionation of thermalized impurities.

This is accomplished by describing the system through a model Hamiltonian $H = H(\{b_q\},\{b_q^\dagger\},\{\sigma_n\})$, defined by Eqs. (2.8)–(2.12), which is a function of a set of phonon creation ($b_q^\dagger$) and annihilation (b_q) operators as well as it is a function of a set of classical, site-dependent, spin variables σ_n that assume values 0 or 1 depending on whether the isotopic species at site n is a host or an impurity, respectively. At inverse temperature β the grand-canonical partition function is given by

$$\Xi(\beta,\mu) = \mathrm{Tr}\left\{\exp(-\beta H)\exp\left[\beta\mu\sum_n \sigma_n\right]\right\}, \tag{1.1}$$

where the trace of an operator A is defined to be

$$\mathrm{Tr}\{A\} = \sum_{\{\sigma_n\}}\left[\sum_{\{n_q\}}\langle\{n_q\}|A|\{n_q\}\rangle\right]. \tag{1.2}$$

Here we sum over the spin configuration $\{\sigma_n\}$ and over the phonon occupation number in the q mode, $\{n_q\}$. μ is a chemical potential that controls the density of impurities.

Integration over phonon variables allows us to write Ξ as

$$\Xi(\beta,\mu) = Z_0 \sum_{\{\sigma_n\}} e^{-\beta\Delta F(\{\sigma_n\})} e^{\beta\mu\sum_n \sigma_n}, \tag{1.3}$$

where

$$\Delta F(\{\sigma_n\}) \equiv -\frac{1}{\beta}\ln\frac{\sum_{\{n_q\}}\langle\{n_q\}|e^{-\beta H}|\{n_q\}\rangle}{\sum_{\{n_q\}}\langle\{n_q\}|e^{-\beta H_0}\{n_q\}\rangle} \equiv -\frac{1}{\beta}\ln\frac{Z}{Z_0} \tag{1.4}$$

is the effective interaction among impurities.

Here, $H_0 = \sum_q \omega_q b_q^\dagger b_q$ is the part of H which is independent of the configurations $\{\sigma_n\}$ and Z_0 is a normalization constant defined to set $\Delta F(0) = 0$.

$\Delta F(\{\sigma_n\})$ is the impurities contribution to the free energy of the phonon system at a given $\{\sigma_n\}$. An approximate expression for this quantity is derived here by summing Feynman diagrams of certain classes up to all orders in phonon perturbation theory. In a regime of sufficiently low impurity density, disjoint clusters of impurities are nearly noninteracting; under this condition, $\Delta F(\{\sigma_n\})$ is decomposed into a sum over energies ΔF_{l_i} of l_i clusters, defined as a sequence of l_i consecutive impurities. Besides, under a suitable resummation of the considered diagrams, each ΔF_{l_i} is expressed as a sum over defined short-range many-body potential φ_s of infinite great order, involving a sequence of s particles inside the set l_i. We found that in the range of physical values for the model parameters for which $m_b < m_a$: (i) all φ_s are negative (attractive potentials) and (ii) for large s, $|\varphi_s| \sim 1/s^2$.

The computed (effective) energy ΔF is then mapped onto a one-dimensional (1D) model proposed and solved exactly by Fisher[2] in the context of the theory of condensation of classical particles. Equivalently to 1D models with long-range interactions, Fisher has shown that in the class of short-range many-body potentials, (i) and (ii) are necessary and sufficient conditions for the system to display a phase transition at a finite temperature T_c. In his model, the energy of a l cluster is written as

$$E_l = \sum_i \varphi_2(r_i - r_{i\pm 1}) + \sum_{s=3}^{l} (l - s + 1)\varphi_s , \tag{1.5}$$

$$\sim l\Phi + \sum_i \varphi_2(r_i - r_{i\pm 1}) + W_l , \tag{1.6}$$

where a term W_l is distinguished from a bulk energy $l\Phi$. (ii) implies that W_l goes as $\ln l$ when $l \to \infty$. Hence W_l can compete with the cluster entropy S_l which is also a logarithm function of the cluster size l. This competition becomes relevant to disclose thermodynamical properties of the system provided that the bulk is depreciated relatively to these logarithm terms. This is achieved through a convenient choice of the chemical potential μ. In this case, when the energy becomes larger than the entropy at a certain temperature T_c, condensation takes place. In our model it means stabilization of large clusters of impurities, or isotopic order.

In Sec. II we describe the model. The evaluation of $\Delta F_l(\{\sigma_n\})$ which is identified here as the cluster energy E_l is presented in Sec. III. We discuss our results and approximations in Sec. IV.

II. THE MODEL

The model Hamiltonian describes a chain of N isotopic particles interacting with first neighbors via harmonic potentials. It is given by

$$H = \sum_{n=1}^{N} \left\{ \frac{m_n}{2}\dot{u}_n^2 + \frac{K}{2} u_n (u_n - u_{n-1}) \right\} , \tag{2.1}$$

where u_n and m_n are, respectively, the displacement from the equilibrium position and the mass of the particle at site n. K is a common force constant.

We consider the case of two isotopic species A (host) and B (impurity) with masses m_a and m_b, respectively. It is useful then to introduce site-dependent spinlike variables σ_n assuming values 0 or 1 and write m_n as

$$m_n = m_a + (m_b - m_a)\sigma_n \tag{2.2}$$

so, for $\sigma_n = 0(1)$, the site n is occupied by a host (impurity).

With the aid of (2.2), H is decomposed as $H = H_0 + H_1$ where H_0 is the homogeneous part describing a chain of harmonic oscillators, all with equal mass m_a:

$$H_0 = \sum_{n=1}^{N} \left\{ \frac{m_a}{2}\dot{u}_n^2 + \frac{K}{2} u_n (u_n - u_{n-1}) \right\} \tag{2.3}$$

and H_1 describes the perturbations due to the presence of impurities:

$$H_1 = \frac{m_b - m_a}{2} \sum_{n=1}^{N} \dot{u}_n^2 \sigma_n . \tag{2.4}$$

To quantize the normal modes we introduce the phonon creation $(b_q^\dagger)$ and annihilation (b_q) operators as follows:

$$u_n = \sum_q \left[\frac{1}{2Nm_a\omega_q} \right]^{1/2} (b_q + b_{-q}^\dagger) e^{iqn} \tag{2.5}$$

and

$$\dot{u}_n = i \sum_q \left[\frac{\omega_q}{2Nm_a} \right]^{1/2} (b_q - b_{-q}^\dagger) e^{iqn} \tag{2.6}$$

(we have set $\hbar$ and the lattice constant equal to the unity).

ω_q is the dispersion relation for the free phonons described by H_0, with periodic boundary conditions, i.e.,

$$\omega_q = \sqrt{2K(1 - \cos q)/m_a} ,$$
$$q \in \left\{ -\pi, \frac{-(N-2)\pi}{N}, \ldots, \frac{-2\pi}{N}, 0, \frac{2\pi}{N}, \ldots, \pi \right\} . \tag{2.7}$$

With (2.5) and (2.6), H_0 and H_1 are rewritten as

$$H_0 = \sum_q \omega_q b_q^\dagger b_q , \tag{2.8}$$

$$H_1 = \frac{\alpha}{N} \sum_{q,q'} \tilde{\sigma}_{q-q'} (\omega_q \omega_{q'})^{1/2} B_q^\dagger B_{q'} , \tag{2.9}$$

where

$$B_q = (b_q - b_{-q}^\dagger) , \tag{2.10}$$

$$\alpha = \frac{1}{4} \left[\frac{m_b}{m_a} - 1 \right] , \tag{2.11}$$

is the coupling constant and

$$\tilde{\sigma}_{q-q'} \equiv \sum_n \sigma_n e^{i(q-q')n} . \tag{2.12}$$

III. EFFECTIVE ENERGY FOR IMPURITIES

A. Perturbation theory

At fixed temperature T and configuration $\{\sigma_n\}$ the difference $\Delta F(\{\sigma_n\})$ between the free energy of the full system described by H and the free energy of the system described by H_0 (or equivalently, the effective energy of impurities) is obtained via integration over the phonons variables:

$$-\beta\Delta F(\{\sigma_n\}) = \ln \frac{\sum_{\{n_q\}} \langle\{n_q\}| e^{-\beta H_0} U[(\beta,0);\{\sigma_n\}] |\{n_q\}\rangle}{\sum_{\{n_q\}} \langle\{n_q\}| e^{-\beta H_0} |\{n_q\}\rangle} , \tag{3.1}$$

where

$$U[(\beta,0);\{\sigma_n\}] = \exp\left\{ -\int_0^\beta e^{-\tau H_0} H_1 e^{\tau H_0} d\tau \right\}$$

and $\tau = it$ is the Euclidean time variable.

If the argument of the logarithm above is expanded according to the usual perturbation theory for phonons,[3,4] expression (3.1) simplifies to

$$-\beta\Delta F(\{\sigma_n\}) = \sum_{p=1}^{\infty} \frac{(-\alpha)^p}{p} \left[\frac{\beta}{N}\right]^p \times \sum_{q_1,q_2,\ldots,q_p} \tilde{\sigma}_{q_1-q_2} \cdots \tilde{\sigma}_{q_p-q_1} \times \sum_{\bar{\nu}} G(q_1,\bar{\nu}) \cdots G(q_p,\bar{\nu}) , \tag{3.2}$$

where

$$G(q,\bar{\nu}) = \omega_q G_0(q,\bar{\nu}) , \tag{3.3}$$

G_0 is the free-phonon temperature Green's function

$$G_0(q,\bar{\nu}) = \frac{1}{\beta}\int_0^\beta e^{-i\bar{\nu}\tau} \langle \mathcal{T}[B_q(\tau) B_q^\dagger(0)] \rangle d\tau = \frac{2\omega_q}{\beta(\omega_q^2 + \bar{\nu}^2)} \tag{3.4}$$

and $\bar{\nu}$ are the Matsubara's frequencies

$$\bar{\nu} = \frac{2\pi\nu}{\beta} \quad \text{for } \nu = 0, \pm 1, \pm 2, \ldots . \tag{3.5}$$

B. Random-walk representation

To the following evaluation of ΔF, it shall be more convenient to rewrite expression (3.2) in the direct space. Using definition (2.12) it becomes

$$-\beta\Delta F(\{\sigma_n\}) = \sum_{p=1}^{\infty} \frac{(-2\alpha)^p}{p} \sum_{i_1,i_2,\ldots,i_p \in \{1,\ldots N\}} \sigma_{i_1} \cdots \sigma_{i_p} \sum_{\bar{\nu}} F_{i_1 i_2}(\bar{\nu}) \cdots F_{i_p i_1}(\bar{\nu}) , \tag{3.6}$$

where

$$F_{ij} = \frac{1}{N} \sum_q e^{iq(i-j)} \frac{\omega_q^2}{\omega_q^2 + \bar{\nu}^2} . \tag{3.7}$$

In the limit of $N \to \infty$ the sum above can be replaced by the integral

$$F_{ij} = \frac{1}{2\pi} \int_{-\infty}^{\infty} dq\, e^{+iq(i-j)} \frac{\omega_q^2}{\omega_q^2 + \bar{\nu}^2} , \tag{3.8}$$

which can be evaluated by residues on the complex v plane where $v \equiv \tan(q/2)$. The result is

$$F_{ij} = \delta_{i,j} - x \left[\frac{1-x}{1+x}\right]^{|i-j|} , \tag{3.9}$$

where

$$x = x(\bar{\nu}) = \left[\frac{\bar{\nu}^2}{\bar{\nu}^2 + c^2}\right]^{1/2} \tag{3.10}$$

and

$$c^2 = \frac{4K}{m_a} . \tag{3.11}$$

It is useful at this point to think of F_{ij} as an arrow connecting the site i to j. Each term on the right-hand side of (3.6) can be represented by closed walks visiting impurities sites only, as illustrated in Fig. 1.

From Eq. (3.9) we see that in the sum over (impurity) sites, each F_{ij} contributes either with a diagonal (local) term for $i = j$ or with an off diagonal (nonlocal) term for $i \neq j$. Of course, the total number of impurities that are visited by each walk depends on p (the order of the term in the perturbative series for the phonons) and on the number of nonlocal contributions to the corresponding product. To evaluate this sum, we have made the following approximations:

(a) The fact that $x(\bar{\nu})$ runs over discrete values such that

$$0 \le x \le 1 \tag{3.12}$$

and that for $x = 0$, $F_{ij} = \delta_{i,j}$, imply that the nondiagonal term in (3.9) is an exponentially decaying function of

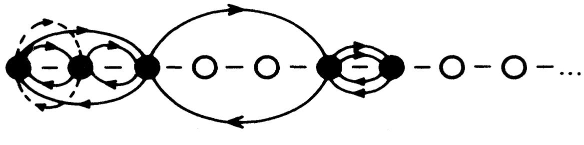

FIG. 1. Walks representation for some terms in (3.6) for a chosen configuration of impurities. ● = impurity; ○ = host. The dashed line represents a walk visiting only two particles.

$|i-j|$. [Note that for $x\neq 0, (1-x)/(1+x)<1$]. This suggests us to include only contributions of F_{ij} for which

$$|i-j|=0 \text{ or } 1 \tag{3.13}$$

and to neglect the remaining terms.

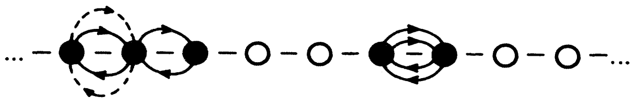

FIG. 2. Walks connecting adjacent impurities at each cluster.

In terms of walks, this approximation means that only adjacent impurities can be connected at time through a single F_{ij} step. An important consequence of this is that the walks under consideration cannot cross to different clusters of impurities, where by "cluster" we mean a sequence of consecutive impurities. In other words, under (3.13) *the clusters do not interact* with each other via phonon-induced interactions, provided they are separated from each other by more than one unity lattice space. Hence, from all walks depicted in Fig. 1, we account only for the ones shown in Fig. 2. Consequently, we have

$$\Delta F(\{\sigma_n\}) \simeq \sum_r \Delta F_{l^{(r)}} , \tag{3.14}$$

where $\Delta F_{l^{(r)}}$ is the effective energy of an isolated cluster (indexed by r) of size $l^{(r)}$. It will then be sufficient to focus only on the evaluation of $\Delta F_{l^{(r)}}$ given by [for the sake of simplicity, we drop the index (r) of $l^{(r)}$]

$$-\beta\Delta F_l \simeq \sum_{p=1}^{\infty} \frac{(-2\alpha)^p}{p} \sum_{i_1,i_2,\ldots,i_p\in l} \sum_{\bar{\nu}} (1-x)^p \tilde{F}_{i_1 i_2}(\bar{\nu}) \cdots \tilde{F}_{i_p i_1}(\bar{\nu}) \tag{3.15}$$

with

$$\tilde{F}_{ij}(\bar{\nu}) = \delta_{i,j} - y\delta_{i,j\pm 1} \tag{3.16}$$

for

$$y = y(\bar{\nu}) = \left[\frac{x(\bar{\nu})}{1+x(\bar{\nu})} \right] . \tag{3.17}$$

(b) The second approximation we shall make, now on the sum over the l-cluster sites, is suggested by the fact that

$$0 \le y \le \tfrac{1}{2} . \tag{3.18}$$

To the subsequent evaluation of that sum, we will account only for the leading contributions that come from *direct walks*, i.e., closed walks visiting a fixed number of sites inside l but passing through each of them at most twice.

With this, from all walks in Fig. 2 we consider only the ones depicted in Fig. 3.

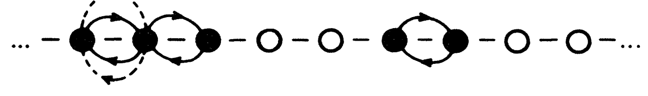

FIG. 3. Direct walks.

C. Walks classification

Under the above approximations we wish to classify the terms appearing in the products in (3.15) according to s, defined to be the number of sites visited by a single walk. This is achieved by collecting in all orders p of the phonon perturbation theory, all walks that visit any s particles for fixed s.

The multiplicity arising from this arrangement has various sources: (i) all positions that a sequence of s adjacent particles can assume in the l cluster. This gives a factor of $(l-s+1)$. (ii) the number of possible sites from which a walk can be initialized (and ended) and its direction. This gives a factor of $2(s-1)$. (iii) the number of ways that a given walk can be "decorated" by local terms in each order p. By a local term we mean the diagonal element of F_{ij} which can be inserted into any site in the direct walk. All of such "decorations" shall be included. From this resummation, it follows that

$$\begin{aligned} -\beta\Delta F_l = 2 \sum_{s=2}^{l} (l-s+1)(s-1) \\ \times {\sum_{\bar{\nu}}}' \sum_{p=2(s-1)}^{\infty} \frac{(-2\alpha)^p}{p} L_{p-2(s-1)}^{2(s-1)} \\ \times (1-x)^p y^{2(s-1)} + S_1 , \end{aligned} \tag{3.19}$$

where the prime to the summation symbol means that $\nu=0$ is excluded.

Here, the sum over s replaces the sum over sites in (3.15), as long as only direct walks are accounted for. S_1 comes from the occurrences of only diagonal terms (decorations) in all products,

$$S_1 = l \sum_{p=1}^{\infty} \frac{(-2\alpha)^p}{p} \sum_{\bar{\nu}} (1-x)^p = -l \sum_{\bar{\nu}} \ln[1+2\alpha(1-x)] . \tag{3.20}$$

The coefficients L_r^{γ} account for all possible ways of having $\gamma+1$ sites decorated with r decorations. These are given by

$$L_r^{\gamma} = \left[\begin{matrix} \gamma+r \\ r \end{matrix} \right] , \tag{3.21}$$

which satisfy the recurrence relation

$$L_{r+1}^{\gamma+1} = L_{r+1}^{\gamma} + L_r^{\gamma+1} \tag{3.22}$$

with initial values $L_0^{\gamma}=1$ and $L_r^0=1$. Hence, L_r^{γ} are identified with the *Laguerre polynomials* $L_r^{\gamma}(\xi)$ at $\xi=0$.

Now, the following sum

$$X \equiv \sum_{p=2(s-1)}^{\infty} \frac{(-2\alpha)^p}{p} L_{p-2(s-1)}^{2(s-1)} (1-x)^p = \sum_{p=0,1,2,\ldots} L_p^{2(s-1)} \frac{\bar{x}^{p+2(s-1)}}{p+2(s-1)} , \tag{3.23}$$

where

$$\bar{x} = -2\alpha(1-x) \tag{3.24}$$

can be written as an integral over the generating function of Laguerre polynomials[5]

$$X = \int_0^{\bar{x}} dx' \, x'^{2s-3} \sum_{p=0}^{\infty} L_p^{2(s-1)} x'^p = \int_0^{\bar{x}} dx' \left[\frac{x'}{1-x'} \right]^{2s} \frac{(1-x')}{x'^3} . \tag{3.25}$$

Changing the variable: $u \equiv x'/(1-x')$ gives immediately

$$X = \frac{1}{2(s-1)} \left[\frac{\bar{x}}{1-\bar{x}} \right]^{2(s-1)} . \tag{3.26}$$

Substituting this result into (3.19), and accounting also for definitions (3.17) and (3.24), gives

$$-\beta \Delta F_l = \sum_{s=2}^{l} (l-s+1) \times \sum_{\bar{\nu}}{}' \left[\frac{2\alpha x(1-x)}{(1+x)[(1+2\alpha)-2\alpha x]} \right]^{2(s-1)} + S_1 . \tag{3.27}$$

D. Comparison with Fisher's model

Comparing (1.5), which gives the energy of a l cluster in the Fisher's model,[2] with the corresponding expression (3.27) for the present model, we are lead to identify (phonon-induced) many-body interaction potentials φ_s as

$$-\beta\varphi_s = \sum_{\bar{\nu}}{}' \left[\frac{x(1-x)}{(1+x)[\Lambda - x]} \right]^{2(s-1)} \quad s=2,3,\ldots , \tag{3.28}$$

where we define

$$\Lambda = \frac{1+2\alpha}{2\alpha} = \frac{m_b + m_a}{m_b - m_a} . \tag{3.29}$$

To use Fisher's criteria on the existence of a phase transition of condensation, it remains to show that $\varphi_s \sim -1/s^2$ for large s.

The function inside the summation sign above depends on the parameter Λ. Of course, we shall expect different behaviors of φ_s with respect to s for different ranges of Λ. Here, in particular, we examine the region where $\Lambda < 0$ or, equivalently, $m_b < m_a$.

The method used here to evaluate the right-hand side of (3.28) is presented in the Appendix. The result is that, for large s

$$\varphi_s \sim \frac{-c}{4\pi(2-\Lambda)^2} \frac{1}{s^2} , \tag{3.30}$$

which implies that

$$E_l \sim \frac{c}{4\pi(2-\Lambda)^2} \ln l . \tag{3.31}$$

The cluster's energy E_l can thus compete with its entropy $S_l = \ln l$. When the l-cluster free energy $F_l = E_l - \beta^{-1} S_l$, for large l, is positive, the system exhibits condensation. This happens at inverse temperature β_c, where

$$\beta_c = \frac{4\pi}{c} (2-\Lambda)^2 . \tag{3.32}$$

E. Bulk contributions

As already mentioned, bulk contributions to the total energy of the cluster have to be compensated by a chemical potential μ controlling the density of impurities. Moreover, it is an essential condition for the thermodynamical stability of the model that these contributions be finite. It is convenient then to write down these energy terms.

According to the Fisher's analysis [see expression (1.6)], a bulk contribution $l\Phi_1$ to the total energy of the l cluster is

$$l\Phi_1 = l \sum_{s=2}^{\infty} (-\varphi_s) . \tag{3.33}$$

For φ_s given by (3.30), it becomes

$$l\Phi_1 \simeq \frac{lc}{4\pi(2-\Lambda)^2} \sum_{s=2}^{\infty} \frac{1}{s^2} = \left[\frac{\pi^2}{6} - 1 \right] \frac{lc}{4\pi(2-\Lambda)^2} . \tag{3.34}$$

In our model, there is an additional bulk term $l\Phi_2$ as defined by (3.20). In fact,

$$l\beta\Phi_2 \equiv S_1 = -l\beta \sum_{\bar{\nu}} \frac{1}{\beta} \ln \frac{\Lambda - x(\bar{\nu})}{\Lambda - 1} . \tag{3.35}$$

The sum above converges since $\ln[\Lambda - x(\bar{\nu})]/(\Lambda-1)$ behaves as $1/\nu^2$ for $|\nu| \to \infty$.

Then, the total bulk contribution Φ,

$$l\Phi = l(\Phi_1 + \Phi_2) \tag{3.36}$$

is finite, as expected.

IV. DISCUSSION

In this paper, we study the thermodynamical equilibrium state of a one-dimensional model describing a chain of two isotopic species, interacting via harmonic potentials. Species with mass m_a is considered to be the host, while species with mass m_b is the impurity. Assuming that there is a mechanism by which these two species can interchange positions in the lattice (the nature of this mechanism being immaterial here), we ask whether phonon-induced interactions are sufficient to produce isotopic fractionation.

Induced interactions (or effective energy) among impurities are obtained by integrating out the phonon degrees of freedom. Under certain approximations, we perform a suitable resummation of the phonon perturbative series, in such a way that the cluster energy is written as a sum over defined many-body potentials φ_s. This allows us to recognize isotopic order as a phase transition of condensation, according to the analysis carried out by Fisher.[2]

The necessary and sufficient condition for the system to display such a phase transition is that

$$\varphi_s \sim \frac{-1}{s^2} \tag{4.1}$$

for large s. Here we restrict our analysis to a particular range of the model parameters for which $m_b < m_a$, and show that in this region, φ_s satisfies (4.1).

Approximations that have been made in deriving expression (3.30), restrict the number of diagrams (walks) in the series expansion (3.6). By these approximations, (i) interactions among different clusters are neglected and to each cluster, (ii) only "direct path" diagrams are considered. Note, however, that all "decorations" to these leading terms due to local terms, have been considered and the calculations were performed exactly.

The first of these approximations is supported on the basis that the density of impurities, which is controlled by the chemical potential μ, can be made sufficiently small to a point where chances of having two or more clusters very close to one another are correspondingly small. Notice also that μ should be appropriately tuned to compensate bulk contributions. Concerning approximation (ii), the neglected diagrams are believed to be perturbatively small and their sum (after a complex combinatorial calculation) is expected to give $O(1/s^3)$ contributions to the s-body potentials φ_s. Such contributions are asymptotically irrelevant for the energy-entropy competition.

In this respect, we can say that, among all diagrams contributing to phonon-induced interactions, we have extracted and performed an exact calculation of those relevant for a mapping onto Fisher's model. Our treatment is, nevertheless, not rigorous in the sense that we have not addressed here questions concerning stability of this picture against perturbations.

The range where condition $m_b < m_a$ is satisfied includes the set of values for which the pair (m_a, m_b) has a correspondence with masses of two natural isotopes. In principle then, one should be able to observe long-range order in a 1D crystal with respect to its isotopic components. For realistic cases where differences in isotopic masses are very small, Λ is very large. A rough estimation of T_c in this case can be obtained by substituting for example, $m_a = 10$ a.m.u., $m_b = 9$ a.m.u. and $K = 4$ eV/Å^2 (for covalent bonds) for the parameters appearing in (3.32). With these we get $T_c \approx 60$ K. Although thermally excited hopping to vacancies or interstitials in 1D (or quasi-1D) systems is expected to be the dominant mechanism for rearranging the constituting ions, it is interesting to note that at low temperatures, quantum-mechanical tunneling might also be important for providing positioning exchange among different isotopic species. Note also that measurements of thermal conductivity, for example, can be performed to check experimentally the theoretical results obtained here. Calculations of this quantity in the ordered phase are in progress.

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APPENDIX

Here we evaluate the sum over the Matsubara's frequencies in the expression (3.28) for φ_s

$$-\beta\varphi_s = \sum_{\bar{\nu}}{}' \left[\frac{x}{\Lambda - x}\,\frac{1-x}{1+x} \right]^{2(s-1)} , \tag{A1}$$

where $x(\nu) = [\bar{\nu}^2/(\bar{\nu}^2 + c^2)]^{1/2}$ and $\bar{\nu} = (2\pi/\beta)\nu$, for $\nu = 0, \pm 1, \pm 2, \ldots$.

As usual (see, e.g., Ref. 6) it is convenient to make the analytical continuation

$$i\bar{\nu} = z$$

to introduce a contour integral representation for the sum above in the complex z plane.

Note that if we put $z = \omega + i\delta$ with $|\omega| < c$, and take the two limits: $\delta \to 0_+$ and $\delta \to 0_-$, the corresponding limit values of $x(z)$ become

$$x_\pm(\omega) \equiv \lim_{\delta \to 0_\pm} x(\omega + i\delta) = \mp i\sqrt{\omega^2/(c^2 - \omega^2)} \equiv \mp i x(\omega)\ . \tag{A2}$$

Consequently,

$$\lim_{\delta \to 0_\pm} \left[\frac{x(\omega+i\delta)}{\Lambda - x(\omega+i\delta)}\,\frac{1 - x(\omega+i\delta)}{1 + x(\omega+i\delta)} \right]^{2(s-1)} = \left[\frac{\mp i x(\omega)}{\Lambda \pm i x(\omega)}\,\frac{1 \pm i x(\omega)}{1 \mp i x(\omega)} \right]^{2(s-1)} \tag{A3}$$

meaning that the analytical continuation of the function $\{[x/(\Lambda - x)][(1-x)/(1+x)]\}^{2(s-1)}$ has two Riemann sheets (labeled in the following $+$ and $-$), intercepting each other at the real axis between $[-c, c]$.

Since the sum is symmetric with respect to positive or negative values for ν, it is convenient to evaluate it from contributions of the residues at the upper side of the imaginary axis. For this, we introduce the function

$$f(z) = \frac{1}{2i}\,\frac{z/|z| + i x(z)/|x(z)|}{e^{\beta z} - 1} \tag{A4}$$

whose poles are at $z_+ = 2\pi i \nu/\beta$, for $\nu = 1, 2, \ldots$. Here, $x(z) = [z^2/(z^2 - c^2)]^{1/2}$.

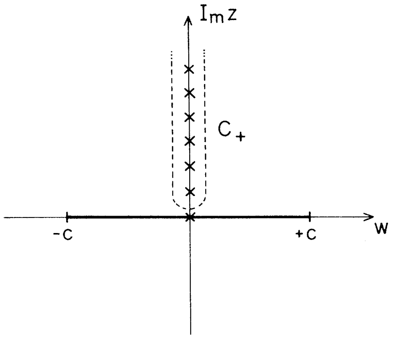

FIG. 4. Contour in the complex z plane.

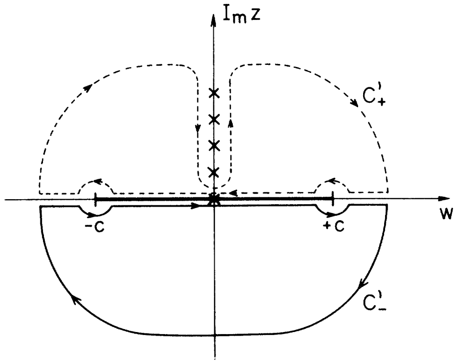

FIG. 5. Deformed contour.

With this, the sum in (4.2) is replaced by

$$-\beta\varphi_s=\frac{2\beta}{2\pi i}\oint_{C_+}dz\,f(z)\left[\frac{x(z)}{\Lambda-x(z)}\,\frac{1-x(z)}{1+x(z)}\right]^{2(s-1)}, \tag{A5}$$

where C_+ is the contour depicted in Fig. (4).

Next, we deform contour C_+ into C'_+ as shown in Fig. (5). For canceling the contributions of integrals on the real axis in the intervals $[c,\infty]$ and $[-\infty,-c]$, we add to the integral on C'_+ the contribution from the integral on C'_-. Note that in the region of parameters for which $\Lambda<0$, there are no singularities in these intervals. Also, there are no poles inside C'_-, and since the whole integrand gives no contributions at $|z|\rightarrow\infty$, the total contribution coming from integrals on C'_+ and C'_- equals to the sum over residues at the upper side of imaginary axis plus the integrals on the real axis in the interval $[-c,c]$. Accordingly, we rewrite (4.6) as

$$\varphi_s=-\frac{1}{\pi}\int_0^c d\omega\left[\frac{e^{-2(s-1)h_1}}{e^{-\beta\omega}-1}+\frac{e^{2(s-1)h_2}}{e^{\beta\omega}-1}\right], \tag{A6}$$

where

$$h_1=\ln\left[\left[\frac{ix(\omega)}{\Lambda-ix(\omega)}\,\frac{1-ix(\omega)}{1+ix(\omega)}\right]\right] \tag{A7}$$

and

$$h_2=\ln\left[\left[\frac{-ix(\omega)}{\Lambda+ix(\omega)}\,\frac{1+ix(\omega)}{1-ix(\omega)}\right]\right]. \tag{A8}$$

A convenient change of variables: $\omega=c\cos\theta$ replaces the above integral by

$$\varphi_s=\frac{-c}{2\pi}\{I_1+I_2\}, \tag{A9}$$

where

$$I_1=\int_0^{\pi/2}d\theta\sin\theta\left[\frac{\exp\{2(s-1)[2i\theta-\ln(1+i\Lambda\tan\theta)]\}}{e^{-\beta\cos\theta}-1}\right] \tag{A10}$$

and

$$I_2=\int_0^{\pi/2}d\theta\sin\theta\left[\frac{\exp\{-2(s-1)[2i\theta+\ln(1-i\Lambda\tan\theta)]\}}{e^{\beta\cos\theta}-1}\right]. \tag{A11}$$

For obtaining the asymptotic behavior of I_1 and I_2 with respect to s, we apply the method of stationary phase. Since the argument of exponentials in the integrands have no turning points in $0\leq\theta\leq\pi/2$, the contribution to each of these integrals come from the end point $\theta=0$ and is expressed by a series in powers of $1/s$.[7] The first nonzero contribution to this series is of order $1/s^2$,

$$I_1\approx\frac{-1}{\{2(s-1)[2-\Lambda]\}^2}\,\frac{1}{e^{-\beta c}-1} \tag{A12}$$

and

$$I_2\approx\frac{-1}{\{2(s-1)[2-\Lambda]\}^2}\,\frac{1}{e^{\beta c}-1} \tag{A13}$$

for $\Lambda\neq0$.

Substituting (4.13) and (4.14) into (4.10), we obtain the dominant behavior of φ_s with respect to s:

$$\varphi_s=\frac{-c}{\pi}\,\frac{1}{\{2(s-1)[2-\Lambda]\}^2}+O(1/s^3). \tag{A14}$$

In the limit of $s\rightarrow\infty$ it becomes

$$\varphi_s\approx\frac{-c}{4\pi[2-\Lambda]^2}\,\frac{1}{s^2},$$

which is result (3.30).

[1] For a review, see for example, A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova, in *Solid States Physics: Advances in Research and Applications,* edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1971), Vol. 3.

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