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Structural Relaxations, Phonons, and Ising Models

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Lattice models such as Ising or Potts models are very often successfully applied to order–disorder phenomena in solids (e.g., for alloys) or on surfaces (e.g., for physisorption). In this contribution it is shown how to derive such models from a microscopic Hamiltonian in the framework of classical statistical mechanics. Both structural relaxations and thermal fluctuations can be incorporated within the (temperature-dependent) parameters of the lattice model.

KEY WORDS: Ising model; lattice relaxation; phonon; order–disorder transition.

1. INTRODUCTION

The popularity of lattice models (such as Ising or Potts models) does not need to be emphasized. It originates from the fact that these simple models provide a qualitative description of a great variety of phenomena (ferromagnetism, order–disorder transitions, adsorption, spin glasses,...), providing valuable insight into the general importance of dimensionality, surfaces, and impurities. They also constitute an ideal playground for the quest of rigorous results.

However, a number of studies(1–4) where coupling parameters were determined on a microscopic basis have demonstrated that lattice models can be very successful for *quantitative* predictions. These impressive successes raise the question of the extent to which the lattice models can faithfully represent the underlying microscopic theories. Intuitively, one of the obvious differences between lattice models and "reality" is that atoms are never located on a perfect lattice. On the one hand, there are always

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thermal fluctuations around equilibrium positions. On the other hand, even when atoms are in an equilibrium position, they often do not form a perfect lattice. Consider two classic examples of order–disorder transitions: adsorption and substitutional alloys. In the first case, an atom adsorbed on a surface (e.g., He on graphite) has preferential sites disposed on a regular lattice defined by the underlying substrate. But if another atom adsorbed on the surface comes close to this atom, their mutual interaction will tend to move them a little bit off the underlying lattice. Also, the mere presence of an atom on the surface will tend to modify slightly the positions of the atoms of the substrate. These phenomena are called local relaxation. In the case of substitutional alloys, the situation is even more complicated, because on top of local relaxations a change of the mean lattice constant occurs as a function of composition, a phenomenon called global relaxation.

At first view, it seems hopeless to try to describe such phenomena by lattice models. Our goal is to show that this a misconception, and that these relaxation phenomena can perfectly be taken into account, as long as it is possible to associate to each lattice configuration a metastable state of the physical system. Even the contribution of phonons to the partition function can be included, if lattice models with temperature-dependent couplings are envisaged. This last point has been recognized before; see, e.g., refs. 1 and 2. However, our approach is more systematic.

More precisely, we want to show how it is possible to derive in a natural way a lattice model from the classical partition function using a simple hypothesis on the metastable states of the system together with a harmonic expansion about these states (which is justified asymptotically). This shows the *microscopic* origin of the coupling parameters, and puts calculations with lattice models on a better footing by indicating in which limit and under what general hypothesis they can be justified. Note the difference with the studies of refs. 1–4 and similar ones, where an Ising model is *postulated* as a starting point, and the problem is then to determine its coupling parameters on a microscopic basis.

The two physical systems that we will use as illustrations (adsorption and substitutional alloys) give rise to Ising models, but our analysis could just as well be applied to systems where other types of lattice models are required, like Potts models.

The rest of this article is structured in the following way. In Section 2, we consider a one-dimensional model and use it as an illustration for the general procedure leading from the classical partition function to an Ising model. All the calculations can be performed analytically, and the physical origin of the various parameters entering the couplngs of the Ising model can be discussed transparently. This example demonstrates explicitly that a lattice model does not require atoms to be located at the sites of a perfect lattice. In the next two sections, we generalize these ideas. In Section 3, we show the importance of metastable states for the classical partition function at low temperatures. As shown in Section 4, under suitable hypotheses the resulting sum over all the metastable states can be expressed as the sum over all configurations of a lattice model. Section 5 concludes the paper with a summary of the main differences between our results and more intuitive views of lattice models. We also discuss possible generalizations.

2. ISING MODEL FOR A ONE-DIMENSIONAL ALLOY

We start with the case of a very simple one-dimensional model. The method used in this section is certainly not the most direct one for this particular model, but it serves to illustrate the ideas that will be applied to more complicated situations afterward.

Consider a system of N atoms in one dimension. These atoms can be of two different types, with N_A particles of type A, N_B particles of type B, $x = N_A/N$ being the proportion of A atoms. They interact only with their nearest neighbors through a pair potential $V_{\mu\nu}(r)$, μ and ν being the types of the atoms and r their distance. We will suppose that the potentials $V_{\mu\nu}(r)$ are repulsive at short distance, attractive at large distance, and have one minimum at $r = l_{\mu\nu}$, but no other local minima. Expanding around this minimum gives

$$V_{\mu\nu}(r) = E_{\mu\nu} + \tfrac{1}{2}K_{\mu\nu}(r - l_{\mu\nu})^2 + \mathcal{O}((r - l_{\mu\nu})^3) \tag{1}$$

the constants $E_{\mu\nu}$ and $K_{\mu\nu}$ characterizing the energy and the stiffness of a bond linking an atom of type μ and one of type ν.

We want to calculate the partition function in the canonical ensemble

$$Z_N(T, x) = \frac{1}{\lambda_A^{N_A}\lambda_B^{N_B}}\frac{1}{N_A!\,N_B!}\int d^N x\, e^{-\beta U(x_1, \dots, x_N)} \tag{2}$$

where

$$U(x_1, \dots, x_N) = \sum_{i=1}^{N-1} V_{\nu_i, \nu_{i+1}}(x_{i+1} - x_i) \tag{3}$$

is the potential energy, ν_i the type of atom i, x_i its position, $\lambda_\mu = (2\pi\beta\hbar^2/m_\mu)^{1/2}$ is the thermal de Broglie wavelength, and m_μ stands for the mass of an atom of type μ.

To this aim, we use the result that if a function $h(\mathbf{x})$ has a minimum at $\mathbf{x}_0$ within a domain $B \subset \mathbf{R}^N$, then a harmonic expansion about this point gives

$$\int_B d^N x \, e^{-\beta h(\mathbf{x})} \sim \frac{(2\pi/\beta)^{N/2} \, e^{-\beta h(\mathbf{x}_0)}}{[\det(\partial^2 h/\partial x_i \, \partial x_j)(\mathbf{x}_0)]^{1/2}}, \qquad \beta \to \infty \tag{4}$$

A precise formulation of this result is to be sought in asymptotic analysis as a multidimensional generalization of Laplace's method. For our purposes in this paper, it suffices to require that B is compact and $h(\mathbf{x})$ a regular enough function with no other local minimum in B than $\mathbf{x}_0$. (For precise hypotheses and a proof, see refs. 5 and 6.) If several local minima are present inside the domain B, then one can divide it into subdomains containing each only one local minimum, and apply Eq. (4) to each of them in turn. This results in a sum over all the local minima of $h(\mathbf{x})$ in B,

$$\int_B d^N x \, e^{-\beta h(\mathbf{x})} \sim \sum_{\mathbf{x}_0 \in B} \frac{(2\pi/\beta)^{N/2} \, e^{-\beta h(\mathbf{x}_0)}}{[\det(\partial^2 h/\partial x_i \, \partial x_j)(\mathbf{x}_0)]^{1/2}}, \qquad \beta \to \infty \tag{5}$$

We will use this as an approximation to the classical partition function. In statistical field theory, this type of result forms the basis of the so-called semiclassical methods.

In order to apply Eq. (5) to the partition function (2), we must first determine the local minima of $U(x_1,..., x_N)$, or in other words the metastable configurations. With our choice for the potentials $V_{\mu\nu}(r)$, the system has 2^N metastable configurations, since to any choice of $\nu_1,..., \nu_N$ corresponds a metastable state with $x_{i+1} - x_i = l_{\nu_i, \nu_{i+1}}$. This state has an energy

$$E(\nu_1,..., \nu_N) = \sum_{i=1}^{N-1} E_{\nu_i, \nu_{i+1}} \tag{6}$$

and a matrix of second derivatives given by

$$\mathscr{D} = \begin{pmatrix} \lambda_{1,2} & -\lambda_{1,2} & 0 & & \cdots & & 0 \\ -\lambda_{1,2} & \lambda_{1,2}+\lambda_{2,3} & -\lambda_{2,3} & 0 & \cdots & & 0 \\ \vdots & \vdots & \vdots & \ddots & & & \vdots \\ 0 & & & & -\lambda_{N-2,N-1} & \lambda_{N-2,N-1}+\lambda_{N-1,N} & -\lambda_{N-1,N} \\ 0 & & \cdots & & 0 & -\lambda_{N-1,N} & \lambda_{N-1,N} \end{pmatrix} \tag{7}$$

with $\lambda_{i,i+1} = K_{\nu_i, \nu_{i+1}}$ $(i = 1, 2,..., N-1)$.

The determinant of this matrix is zero, since the vector (1, 1,..., 1) is always an eigenvector, with zero as corresponding eigenvalue. To be able to apply formula (5), we must first eliminate this translational mode; practically, this amounts to working on a subspace of all the possible displacements, orthogonal to the subspace generated by the (1, 1,..., 1) vector. On this subspace, the determinant of $\mathscr{D}$ is given by the product of the other eigenvalues of $\mathscr{D}$, which can be shown to be equal to

$$D(\nu_1, \ldots, \nu_N) \equiv \det \mathscr{D} = N \prod_{i=1}^{N-1} K_{\nu_i, \nu_{i+1}} \tag{8}$$

The application of formula (5) implies then that in the harmonic approximation the partition function $Z_N(T, x)$ is given by

$$\begin{aligned} Z_N(T, x) \sim \frac{1}{\lambda_A^{N_A} \lambda_B^{N_B}} \left(\frac{2\pi}{\beta}\right)^{N/2} \sum_{\nu_1 = A, B} \cdots \sum_{\nu_N = A, B} \exp\left(-\beta \sum_{i=1}^{N-1} E_{\nu_i, \nu_{i+1}}\right) \\ \times \exp\left(-\frac{1}{2} \sum_{i=1}^{N-1} \ln K_{\nu_i, \nu_{i+1}}\right) \end{aligned} \tag{9}$$

(We have neglected a term $\ln N$ which would anyway disappear in the thermodynamic limit.) Since we are working at fixed concentration, only the configurations with the correct number of A and B atoms should be retained in the preceding sum.

It is now straightforward to represent this result in terms of Ising variables σ_i ($i = 1, 2, \ldots, N$) defined as

$$\sigma_i = \begin{cases} +1 & \text{if the atom } i \text{ is of type A} \\ -1 & \text{if it is of type B} \end{cases} \tag{10}$$

One easily shows that the energy of a metastable configuration can be written as

$$U[\{\sigma_i\}] \equiv \sum_{i=1}^{N-1} E_{\nu_i, \nu_{i+1}} = NE_0^U + h^U \sum_{i=1}^{N} \sigma_i + J^U \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} \tag{11}$$

with

$$\begin{aligned} E_0^U &= (E_{AA} + 2E_{AB} + E_{BB})/4 \\ h^U &= (E_{AA} - E_{BB})/2 \\ J^U &= (E_{AA} - 2E_{AB} + E_{BB})/4 \end{aligned} \tag{12}$$

and similarly for $\ln D$,

$$\tfrac{1}{2} \ln D[\{\sigma_i\}] \equiv \tfrac{1}{2} \sum_{i=1}^{N-1} \ln K_{\nu_i, \nu_{i+1}} = NE_0^D + h^D \sum_{i=1}^{N} \sigma_i + J^D \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} \tag{13}$$

with

$$\begin{aligned} E_0^D &= (\ln K_{\mathrm{AA}} + 2\ln K_{\mathrm{AB}} + \ln K_{\mathrm{BB}})/8 \\ h^D &= (\ln K_{\mathrm{AA}} - \ln K_{\mathrm{BB}})/4 \\ J^D &= (\ln K_{\mathrm{AA}} - 2\ln K_{\mathrm{AB}} + \ln K_{\mathrm{BB}})/8 \end{aligned} \tag{14}$$

up to boundary terms which are negligible in the thermodynamic limit as far as bulk properties are concerned.

It follows that in the limit of low temperatures ($\beta \to \infty$) the partition function $Z_N(T, x)$ is equivalent to that of an Ising model with temperature-dependent couplings. Explicitly,

$$\begin{aligned} Z_N(T, x) \sim \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_N = \pm 1} \exp\Bigg\{ -\beta \Bigg[E_0(T) + h(T) \\ \times \sum_{i=1}^{N} \sigma_i + J(T) \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} \Bigg] \Bigg\} \end{aligned} \tag{15}$$

as $\beta \to \infty$, where

$$E_0(T) = E_0^U + k_{\mathrm{B}} T \log\left(\frac{\hbar\bar{\omega}}{k_{\mathrm{B}} T}\right), \qquad \text{with} \quad \bar{\omega} = \left(\frac{K_{\mathrm{AA}} K_{\mathrm{AB}}^2 K_{\mathrm{BB}}}{m_{\mathrm{A}}^2 m_B^2}\right)^{1/8} \tag{16}$$

$$h(T) = h^U + k_{\mathrm{B}} T [h^D + \tfrac{1}{4} \log(m_{\mathrm{B}}/m_{\mathrm{A}})] \tag{17}$$

$$J(T) = J^U + k_{\mathrm{B}} T J^D \tag{18}$$

The temperature-dependent terms represent the contribution of the harmonic fluctuations around the metastable states. The importance of this contribution increases with temperature.

This simple example shows that a lattice model does not require atoms to be fixed at the sites of a regular lattice. Rather, the distances between atoms depend on the metastable state that is being considered, while the spin variables appear quite naturally as a convenient way of labeling the metastable states of the system. Summing over all spin configurations is then equivalent to summing over all these states. Note also that even if the average interatomic distances change with the overall composition, the spin couplings themselves remain fixed!

We notice that even the term $\ln D[\{\sigma_i\}]$ originating from the harmonic fluctuations gives rise only to nearest neighbor couplings. (This would not be true for other functions like $D[\{\sigma_i\}]$.) This is surprising, as one would expect elastic forces to induce longer-range couplings. One is tempted to consider this as an artifact of the one-dimensional case. However, the result (8) can be generalized to higher dimensions. For a square lattice comprising N_x columns and N_y rows, again with couplings between nearest neighbors and free boundary conditions, the generalization of (8) reads

$$\det \mathscr{D}_{2\mathrm{D}} = N_x^{N_y} N_y^{N_x} \prod_{\langle i,j \rangle} K_{\nu_i,\nu_j} \tag{19}$$

(where $\prod_{\langle i,j \rangle}$ means the product over all pairs of nearest neighbors, each pair being counted only once). Similarly, for a cubic lattice one gets

$$\det \mathscr{D}_{3\mathrm{D}} = N_x^{N_y N_z} N_y^{N_x N_z} N_z^{N_x N_y} \prod_{\langle i,j \rangle} K_{\nu_i,\nu_j} \tag{20}$$

Therefore, we notice that integrating out harmonic fluctuations is not enough to generate long-range interactions, even in two and three dimensions. We have also tried models with couplings up to second nearest neighbors. Although we have not found general expressions like (19) and (20), our results for small systems again indicate that no long-range couplings are generated.

This seems at first to contradict results obtained for compressible Ising models,$^{(7,8)}$ where the integration over the harmonic fluctuations generates spin couplings decaying like $1/r^d$.[2] The difference stems from the fact that in the compressible case the expansion is not around local minima, but around fixed atomic positions for all configurations. Therefore, the expansion of the energy starts with a term linear in the fluctuations. The integration of this linear term gives rise to spin couplings mediated by the elastic Green's function, which decays like $1/r^d$. (This is easy to check for the one-dimensional model. Instead of considering fluctuations around metastable states where $x_{i+1} - x_i = l_{\nu_i,\nu_{i+1}}$, one can consider fluctuations around a state for which $x_{i+1} - x_i = l$, where l is a fixed distance. Performing the integration, one obtains again an Ising model, this time with long-range couplings and multispin interactions.) For our purposes, the use of the asymptotic result (5) requires that we expand around local minima.

As to the qualitative effects of the harmonic fluctuations, note that if the terms $E_0(T)$ and $h(T)$ are important for thermodynamic quantities like the specific heat, the ordering itself is controlled solely by the spin coupling $J(T)$. One can examine separately its two components. The temperature-independent term originating from the energies of the bonds is antiferromagnetic ($J^U > 0$) if

$$E_{\mathrm{AB}} < (E_{\mathrm{AA}} + E_{\mathrm{BB}})/2 \tag{21}$$

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[2] We thank a referee for raising this point.

i.e., if the energy of an A–B bond is smaller than the (arithmetic) average of the energies of A–A and B–B bonds. On the other hand, the temperature-dependent term originating from the harmonic fluctuations is antiferromagnetic ($J^D > 0$) if

$$K_{AB} < (K_{AA} K_{BB})^{1/2} \tag{22}$$

i.e., if the force constant (the stiffness) of an A–B bond is smaller than the *geometric* average of the force constants of A–A and B–B bonds.

So we see that the system will as usual tend to favor bonds that are as low in energy as possible, but the additional effect of the harmonic fluctuations will be to favor bonds as *loose* as possible.

A simple argument predicts that the two components of the spin coupling $J(T)$ generally have opposite signs. Suppose that the term originating from the energies of the bonds is antiferromagnetic ($J^U > 0$). This means that the energy of an A–B bond is lower than the average energy of A–A and B–B bonds. But a bond lower in energy is usually tighter and henceforth more rigid. Therefore we expect that $K_{AB}^2 > K_{AA} K_{BB}$, which implies that the term originating from the harmonic fluctuations is ferromagnetic ($J^D < 0$).

3. GENERAL CASE: REDUCTION TO METASTABLE STATES

The model presented in the preceding section is illustrative because the calculations can be carried out analytically. We discuss now the general case.

Consider a classical system of N identical particles. The classical partition function in the canonical ensemble (including the correct Boltzmann counting term) is given by

$$Z_N(V, T) = \frac{1}{N!\, h^{3N}} \int d^{3N}p \, d^{3N}q \, e^{-\beta \mathscr{H}(p,q)} \tag{23}$$

Usually, the particles are restricted to a certain volume V of space whose volume is adjusted to give the correct density. This is necessary to describe gases where the atoms must be confined, but here we want to describe bound atoms, either in solids or as surface adsorbates. In this case, confinement is not necessary since the atoms do not escape from the sample (at least not at important rates). Therefore we lift the usual restriction on the volume of integration in Eq. (23) and replace it by some other constraint to be specified later. We denote this condition by $\int' d^{3N}q$.

We assume a Hamiltonian $\mathscr{H}(p, q)$ of the form

$$\mathscr{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + U(\{\mathbf{q}_i\}) \tag{24}$$

where $U(\{\mathbf{q}_i\})$ is the interaction energy of the N atoms in the configuration $\{\mathbf{q}_i\}$ and m is their mass. We suppose that there are no external fields, and that therefore the energy $U(\{\mathbf{q}_i\})$ is invariant under overall translations or rotations.

The integration on the momentum variables is trivial, and we get

$$Z_N(T) = \frac{1}{\lambda^{3N} N!} \int' d^{3N}q \, e^{-\beta U(\{\mathbf{q}_i\})} \tag{25}$$

where the thermal wavelength is $\lambda = (2\pi\beta\hbar^2/m)^{1/2}$.

To apply the asymptotic result (5) to the integral on the coordinates in Eq. (25), we must consider the local minima of $U(\{\mathbf{q}_i\})$, or in other words the metastable configurations. The symmetries of $U(\{\mathbf{q}_i\})$ imply that if a microscopic configuration $\{\mathbf{q}_i\}$ is metastable, then any other configuration obtained by a rigid spatial transformation and/or relabeling of the atoms will also be metastable and of equal energy. Therefore, the set of metastable configurations can be decomposed into classes of equivalent (in the sense that they can be brought onto each other by a rigid spatial transformation and/or relabeling) microscopic configurations, which we will simply call "metastable states" in what follows.

The continuous translational and rotational symmetries prohibit the direct application of the asymptotic formula (5), which requires separate minima. But we can easily remove these degeneracies by fixing six degrees of freedom.

Thus, by adding to the integral in (23) a constraint fixing all three Cartesian coordinates of one atom, two coordinates of a second atom, and one coordinate of a third one, the degeneracies are lifted. This is the condition that we use to replace the usual confinement in a volume V. For each metastable state there are $N!$ microscopic configurations satisfying this constraint ($N!$ is the number of possible relabelings). The asymptotic formula (5) can then be applied to give

$$Z_N^{\boldsymbol{\cdot}}(T) \sim \frac{(2\pi/\beta)^{3N/2}}{\lambda^{3N}} \sum_{\substack{\text{metastable}\\ \text{states}}} \exp(-\beta U[\{\mathbf{q}_i\}_0]) \times \exp\left(-\frac{1}{2}\ln D[\{\mathbf{q}_i\}_0]\right), \qquad \beta \to \infty \tag{26}$$

where

$$D[\{\mathbf{q}_i\}_0] = \det\left(\frac{\partial^2 U(\{\mathbf{q}_i, \nu_i\}_0)}{\partial \mathbf{q}_{i,\alpha}\, \partial \mathbf{q}_{j,\beta}}\right) \tag{27}$$

In Eq. (26) logarithms of quantities with the dimension of a force constant appear. To remove this problem, we introduce an arbitrary force constant $\bar{K}$ and its associated frequency $\bar{\omega}$, with $\bar{\omega}^2 = \bar{K}/m$, so that Eq. (26) can be written as

$$Z_N(T) \sim \left(\frac{k_B T}{\hbar\bar{\omega}}\right)^{3N} \sum_{\substack{\text{metastable}\\ \text{states}}} \exp(-\beta U[\{\mathbf{q}_i\}_0]) \times \exp\left(-\frac{1}{2}\ln\left(\frac{D[\{\mathbf{q}_i\}_0]}{\bar{K}^{3N}}\right)\right), \quad \beta \to \infty \tag{28}$$

all the quantities being now dimensionless.

The preceding calculations can be easily extended to systems with several types of particles.

4. REDUCTION TO A LATTICE MODEL

The representation of Eq. (28) by a lattice model necessitates hypotheses on the structure of the metastable states. We will discuss two examples, adsorption and substitutional alloys.

In the case of adsorption, the substrate provides a regular array of preferential sites for the adsorbed atoms. Even so, the atoms in the metastable configurations will never be perfectly at these sites. On the one hand, nearby adsorbed atoms will tend to displace them a little bit, on the other hand, the substrate itself is not perfectly rigid and reacts to the presence of adsorbed atoms. Nevertheless, for each choice of occupancy of the adsorption sites, we can allow the perfect atomic configuration to "relax" to a local minimum of the energy. If the interactions are weak, we should expect the relaxed configuration to be quite close to the perfect one. In this way, we can associate with each occupancy of the adsorption sites, i.e., with each spin configuration, a metastable state. This seems perfectly reasonable, and this is the main hypothesis that we make on the structure of the metastable states.

It is worthwhile to add that this condition, requiring a relatively deep substrate potential and weak couplings between adsorbed atoms (order–disorder limit), is not always satisfied. In fact, in the case of a shallow substrate potential and relatively strong forces between the adsorbed atoms (displacive limit) the metastable states correspond to domains with domain walls extending over several adsorption sites. A lattice model cannot represent the metastable states in this limit; a continuum model appears more appropriate.

As an example for substitutional alloys, we consider the Cu_xAu_{1-x} family. This case is particularly simple since the lattice structure is not changing with concentration x; it always remains fcc. The copper atoms are slightly "smaller" than the gold atoms, and this means that the actual lattice is never perfectly fcc, for if at a particular site a copper atom is replaced by a gold atom, nearby atoms would be pushed away a little bit. This effect is analogous to the local relaxation effects in the case of adsorption. But here there is an additional effect: the mean lattice constant changes with composition (Vegard's law). Nevertheless, for each possible occupancy of the fcc lattice, we can allow the perfect atomic configuration to "relax," this time by allowing local displacements and changes in the lattice constants, until a local minimum of the energy is reached. Assuming that these local and global relaxations do not change "topology" of the atomic configuration, we can again associate a metastable state to each spin configuration.

Note that in both examples other types of metastable states exist. For the alloy case, structures with defects like vacancies or dislocations can also be metastable. For the simplicity of the argument, we neglect them here, but we will come back to this point in the conclusion when discussing polymorphism.

We define the functions $U[\{\sigma_i\}]$ and $\ln D[\{\sigma_i\}]$ by identifying them with the values taken by $U[\{\mathbf{q}_i\}_0]$ and $\ln D[\{\mathbf{q}_i\}_0]$ in the metastable configuration corresponding to $\{\sigma_i\}$. In view of our hypotheses, they are well defined for all lattice configurations.

If we retain only metastable configurations corresponding to spin configurations, the sum over the metastable states in Eq. (28) can be replaced by a sum over the configurations of the lattice model

$$Z_N(T) \sim \left(\frac{k_B T}{\hbar\bar{\omega}}\right)^{3N/2} \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \exp(-\beta U[\{\sigma_i\}]) \\ \times \exp\left(-\frac{1}{2}\ln\left(\frac{D[\{\sigma_i\}]}{\bar{K}^{3N}}\right)\right), \qquad \beta \to \infty \tag{29}$$

The final step is based on the following simple mathematical result.$^{(9)}$ Any function f of a set of variables $\sigma_1, \sigma_2, \ldots, \sigma_N$ restricted to the values $\{+1, -1\}$ can be expanded as

$$f(\sigma_1, \sigma_2, \ldots, \sigma_N) = \sum_\alpha f_\alpha \prod_{i\in\alpha} \sigma_i \tag{30}$$

where the sum is on all the subsets of $\{1, 2,..., N\}$. Furthermore, if the value of the function f is given for all the possible values of $\sigma_1,..., \sigma_N$, then the coefficients f_α are uniquely determined. (This result can be extended to other types of models, like Potts models.(9))

We can apply this cluster expansion to the functions $U[\{\sigma_i\}]$ and $\ln D[\{\sigma_i\}]$. Since by our hypothesis these are defined for all spin configurations, they can be expanded as in Eq. (30) with uniquely determined coefficients. Note that these coefficients are fixed once for all; they are therefore independent both of the temperature and of the concentration. This has at first some nonintuitive consequences, because the coupling parameters in a lattice model are usually considered as mean interaction energies between atoms; these energies are expected to change if the mean interatomic distances change. We have seen that in $\mathrm{Cu}_x\mathrm{Au}_{1-x}$ alloys the mean lattice constant indeed changes with composition, but the expansion coefficients that we have defined are independent of this composition! We have also shown this explicitly for the soluble one-dimensional model of Section 2, where the mean interatomic distance changes with composition, but the expansion coefficients for $U[\{\sigma_i\}]$ and $\ln D[\{\sigma_i\}]$ remain fixed.

Inserting the cluster expansion (30) for $U[\{\sigma_i\}]$ and $\ln D[\{\sigma_i\}]$ into the partition function, we obtain the desired result, namely that in the limit of low temperatures the partition function of the system is equivalent to that of an Ising model on a regular lattice. We have therefore established a link between Ising configurations and atomic configurations in the "real" world, and shown that, contrary to the immediate intuition, a lattice model is absolutely not incompatible with either local or global relaxation effects.

At low enough temperatures, only the term in the partition function originating from the energies of the metastable states will survive. At higher temperatures, we obtain an Ising model with temperature-dependent coupling parameters, which includes the contribution of the harmonic fluctuations around the equilibrium positions, or in other words the *phonons*. The fact that the phonon spectrum depends on the configuration is taken into account naturally.

As a final point for this section, we remark that the practical usefulness of any lattice model will depend on the number of coefficients in the cluster expansion of the functions $U[\{\sigma_i\}]$ and $\ln D[\{\sigma_i\}]$ necessary to obtain good approximations. Formally, these two functions have 2^N expansion coefficients, but in any physical situation discrete symmetries will drastically reduce the number of independent coefficients. Furthermore, it has been found empirically that good results can be obtained in many systems by considering couplings only between rather close lattice sites. This assumption of short-range couplings is the starting point of most studies using lattice models. It is important to notice that it does not mean that the underlying interactions must also be short ranged; it just means that they can be described by a small number of effective expansion coefficients. For example, such an approach has been applied to calculations of Madelung energies in a simple charge-transfer model,(10) where the underlying interaction is the Coulomb interaction. Even in this case, an Ising model with a small number of couplings has been shown to give accurate results.

5. DISCUSSION AND CONCLUSION

In our derivation of an Ising model starting from the classical partition function of N particles, we have noticed two important points. First, the Ising model (or other similar lattice models) can account for both local and global relaxations. A spin configuration represents a metastable atomic configuration, where the atoms are not located at the sites of the perfect lattice, but have been allowed to "relax" to a local minimum of the energy. Second, the Boltzmann weight for a given spin configuration depends not only on the energy of the corresponding metastable configuration, but also on the thermal fluctuations (phonons) about this configuration.

We have also argued, on the basis of a simple one-dimensional model, that the ordering, which is dictated by purely energetic considerations at low temperatures, is more and more weakened by the phonon effects as the temperature increases. Thus the critical temperatures for the order–disorder transitions would in reality be lower than what is predicted on the basis of an Ising model with couplings determined from the energies of the metastable states. We have made a crude estimate of the magnitude of this effect for the case of Cu_xAu_{1-x} alloys, and found it to be of the order of 5–10% around the transition temperature.(11) Stronger effects are expected to occur in the presence of phonon softening, in particular in the vicinity of a second-order structural phase transition.

Several generalizations of our approach are possible. It can be extended to other lattice models, like Potts models, or to systems with surfaces where relaxations are particularly important.[3] Another possible generalization is to consider metastable states with different lattice structures. In our example for substitutional alloys, we have retained only metastable configurations with atoms in fcc structure. Of course, other types of metastable states exist, with atoms on different lattices, such as bcc or cubic lattice. One could repeat the mapping to a lattice model for these states, and the sum on all metastable states in the partition function would

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[3] We are currently calculating the changes in the Ising couplings close to the (100) surface of Cu_xAu_{1-x} alloys, to study phenomena such as surface-induced disordering.

become a sum on the partition functions corresponding to each of these possible structures. For Cu_xAu_{1-x} alloys, this would not be necessary since the fcc structure is stable on the whole concentration range, which indicates that the other metastable states must have sufficiently higher energies to be negligible. But many binary alloys exhibit polymorphism, which indicates that several types of metastable states have very close energies, and must therefore all be taken into account in the partition function.

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NOTE ADDED IN PROOF

The effects of lattice vibrations on the ordering in binary alloys has recently also been studied by Garbulsky and Ceder (*Phys. Rev. B* **49**:6327 (1994)).

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