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CLUSTER VARIATION METHOD
FOR LATTICE MODELS:
LATTICE GAS ON THE SQUARE LATTICE

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The cluster-variation method represents one of the oldest approaches to the approximative treatment of the cooperative phenomena in equilibrium statistical mechanics of lattice models. A useful combinatorial technique for constructing an approximative expression for the free energy - the subject of further minimalization has been developed by Kikuchi^{/1/}. A number of attempts to improve the efficiency of the method and to perform a classification of various approximations have been made since then. A general scheme of successive approximations converging to exact results has been given in ref.^{/3,4/} and rederived in ref.^{/5/}. Our noncombinatorial approach, in some aspects related to ref.^{/5/}, provides a method for construction of convergent series of approximations to the free energy in a more efficient way and in a simpler manner than the methods described in the previous papers. By minimizing the free energy with respect to the correlators of lattice site occupation numbers, we get a full information about the equilibrium state of the system. The method can be used for a large class of classical lattice models, but in this paper we shall mainly deal with a relatively general model of an alloy consisting of M kinds of molecules. It is described by the following Hamiltonian

$$H = \sum_{\nu=1}^M \sum_i \epsilon_{\nu}^{\nu} n_i^{\nu} + \frac{1}{2} \sum_{\nu, \lambda=1}^M \sum_{i, \ell} \kappa_{i\ell}^{\nu\lambda} n_i^{\nu} n_{\ell}^{\lambda}, \quad (1)$$

where $n_i^{\nu} = 0, 1$ is an occupation number operator describing the presence of the ν -th molecule on the i -th site. The fol-

lowing relations should be fulfilled $n_i^{\nu} n_i^{\kappa} = \delta_{\nu\kappa} n_i^{\nu}$, $\sum_{\nu=1}^M n_i^{\nu} = 1$. We also assume a finite range of the molecule-molecule interaction $\kappa_{i\ell}^{\nu\lambda}$. The lattice gas model is obtained identifying the M-th particle with the hole, i.e., putting $\epsilon^M = 0$, $\kappa_{i\ell}^{\nu M} = 0$, $\kappa_{i\ell}^{MM} = 0$.

Let the infinite lattice considered in (1) and the state of the system of molecules on the lattice be denoted by I and by the random variable Σ , respectively. Let $J \subset I$ divide the lattice I into two separate parts I_1, I_2 , ($I_1 \cup J \cup I_2 = I$), in such a way that no molecule which occupies a site from I_1 can interact via potential $\kappa_{i\ell}^{\nu\lambda}$ with a molecule which occupies a site from I_2 . When $J_1 \subset I_1$, $J_2 \subset I_2$ and Λ_1, Λ_2 and Λ are the random variable describing the states of the areas J_1, J_2 and J respectively, the conditional probability $P(\Lambda_1 \Lambda_2 | \Lambda)$ factorizes $P(\Lambda_1 \Lambda_2 | \Lambda) = P(\Lambda_1 | \Lambda) P(\Lambda_2 | \Lambda)$.

Then

$$P(\Lambda_1 \Lambda_2 \Lambda) = P(\Lambda_1 \Lambda_2 | \Lambda) P(\Lambda) = \frac{P(\Lambda_1 \Lambda) P(\Lambda_2 \Lambda)}{P(\Lambda)} \quad (2)$$

On the other hand the probability $P(\Lambda)$ is equal to the average of the operator $\hat{\Lambda} = \prod_{i \in J} m_i$, where m_i denotes the occupation number operator n_i^v of that kind of molecule which occupies the site i in the state Λ . Then the relation (2) can be rewritten as follows:

$$\langle \hat{\Lambda}_1 \hat{\Lambda} \hat{\Lambda}_2 \rangle = \frac{\langle \hat{\Lambda}_1 \hat{\Lambda} \rangle \langle \hat{\Lambda}_2 \hat{\Lambda} \rangle}{\langle \hat{\Lambda} \rangle} \quad (3)$$

If J does not separate the areas J_1, J_2 in the above-mentioned sense entirely, eqs. (2), (3) will not hold. In this case relation (3) will be used as a decoupling

$$\langle \hat{\Lambda}_1 \hat{\Lambda} \hat{\Lambda}_2 \rangle \rightarrow \frac{\langle \hat{\Lambda}_1 \hat{\Lambda} \rangle \langle \hat{\Lambda}_2 \hat{\Lambda} \rangle}{\langle \hat{\Lambda} \rangle} \quad (4)$$

It is possible to show that a series of decouplings converging to the exact equation (3) can be constructed by choosing an appropriate sequence of areas J .

For the sake of simplicity we shall develop our method at first for a two-dimensional square lattice with the nearest-neighbour interaction between molecules. In this case the most advantageous choice of the area J is an infinite line dividing the lattice into two halves as shown by empty circles in Fig. 1. The areas J_1, J_2 are denoted by the full dot and by the semi-infinite area of full squares bellow J , respectively. Denoting the states in the new defined areas J_1, J_2, J by random variables $\Lambda_1, \Lambda_2, \Lambda$, we can again use eq. (2). We see that for our choice of J_1, J_2, J the area $J \cup J_2$ has the same form as $J \cup J_1 \cup J_2$. Thus eq. (2) may be again applied to $P(\Lambda_2 \Lambda)$, etc. It is clear that the probability of the state Σ of the whole lattice can be written down as

$$P(\Sigma) = \prod_{i \in I} \frac{P(\Lambda_{i1} \Lambda_i)}{P(\Lambda_i)} = \prod_{i \in I} \frac{P(\Lambda'_i)}{P(\Lambda_i)},$$

where $\Lambda'_i = \Lambda_{i1} \Lambda_i$ is a state of the area $J'_i = J_{i1} \cup J_i$ and J_{i1} runs over all lattice sites. Now the entropy s of the system may be expressed by means of the quasi-one-dimensional probabilities (correlators)

$$\begin{aligned} s &= -k \ln P(\Sigma) = -k \sum_I (\ln P(\Lambda'_i) - \ln P(\Lambda_i)) \\ &= -kN (\ln P(\Lambda') - \ln P(\Lambda)) \end{aligned} \quad (5)$$

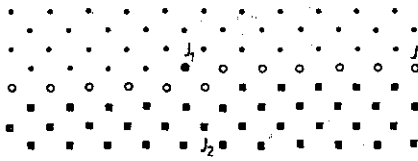


Fig. 1

(As we are interested only in translationally invariant systems, we shall further omit the lattice index in all the symbols).

In order to find an approximate solution for the entropy s , we introduce besides the infinite area J' , finite areas with L lattice sites in both upper and lower row. We denote them by

J'_{2L} and the random variables, defined on them, by

$\Lambda'_{2L} \equiv \Lambda' \left(\begin{smallmatrix} u \\ l \end{smallmatrix} L \right)$, where u_L, l_L are vectors on the upper and lower row of J'_{2L} , respectively; $u_{Li} = \nu$ ($l_{Li} = \nu$) when the site i_u (i_l) is occupied by ν -th molecule. (Labeling of the sites of J'_{2L} is shown in Fig. 2). The finite random variable corresponding to Λ is defined as a linear combination $\Lambda_{2L} = \sum_{\nu=1}^M \Lambda' \left(\nu, \begin{smallmatrix} u \\ l \end{smallmatrix} L \right)$.

Defining Λ_r on $J_r = J' - J'_{2L}$ in such a way that $\Lambda'_{2L} \Lambda_r = \Lambda'$ and $\Lambda_{2L} \Lambda_r = \Lambda$ (Λ_r is a random variable of the "rest" of J'), we see that

$$\frac{P(\Lambda)}{P(\Lambda)} = \frac{P(\Lambda_r | \Lambda'_{2L})}{P(\Lambda_r | \Lambda_{2L})} \frac{P(\Lambda'_{2L})}{P(\Lambda_{2L})} = \frac{P(\Lambda'_{2L})}{P(\Lambda_{2L})} \frac{\langle \hat{\Lambda}'_{2L} \rangle}{\langle \hat{\Lambda}_{2L} \rangle} \quad (6)$$

is a good approximation when L is large enough, except for the close vicinity of critical points. For $L \rightarrow \infty$ the relation (6) is exact.

Using (5), the expression for the free energy in approximation (6) is the following:

$$F = \langle H \rangle - TS \doteq \langle H \rangle + kTN \left(\sum_{\Lambda'_{2L}} \langle \hat{\Lambda}'_{2L} \rangle \ln \langle \hat{\Lambda}'_{2L} \rangle \right) \quad (7)$$

$$- \sum_{\Lambda_{2L}} \langle \hat{\Lambda}_{2L} \rangle \ln \langle \hat{\Lambda}_{2L} \rangle .$$

The thermal equilibrium values of the correlators $\langle \hat{\Lambda}'_{2L} \rangle$ correspond to the minimum of the free energy (7) satisfying simultaneously the following constraints:

(i) Normalization $\sum_{\Lambda'_{2L}} \langle \hat{\Lambda}'_{2L} \rangle = 1$ (8)

(ii) $\langle \hat{\Lambda}' \left(\begin{smallmatrix} u \\ l \end{smallmatrix} L \right) \rangle = \langle \hat{\Lambda}' \left(\begin{smallmatrix} l \\ u \end{smallmatrix} L \right) \rangle$ (9)

(iii) Translational symmetry

$$\sum_{\nu, \lambda=1}^M \langle \hat{\Lambda}^{\nu, \lambda}(\underline{\ell}_{L-1}^u) \rangle = \sum_{\nu, \lambda=1}^M \langle \hat{\Lambda}^{\nu, \lambda}(\underline{\ell}_{L-1}^{u, \nu}) \rangle \quad (10)$$

Fig.2.

(iv) Mirror image symmetry of the upper row

$$\sum_{\underline{\ell}_L} \langle \hat{\Lambda}^{\nu, \lambda}(\underline{\ell}_L^u) \rangle = \sum_{\underline{\ell}_L} \langle \hat{\Lambda}^{\nu, \lambda}(\underline{\ell}_L^u) \rangle \quad (11)$$

v) Equivalency of double correlators on the pairs of sites $(1_u, 1_\ell)$ and $(1_u, 2_\ell)$

$$\sum_{\underline{\ell}_{L-1}, \underline{\ell}_{L-2}} \langle \hat{\Lambda}^{\nu, \lambda}(\underline{\ell}_{L-1}^u, \underline{\ell}_{L-2}^u) \rangle = \sum_{\underline{\ell}_{L-1}, \underline{\ell}_{L-1}} \langle \hat{\Lambda}^{\nu, \lambda}(\underline{\ell}_{L-1}^u, \underline{\ell}_{L-1}^u) \rangle \quad (12)$$

for $\nu, \lambda = 1, \dots, M-1$. All other symmetries can be obtained by superposition of the above-mentioned ones. The constraints (8-12) represent $K = (N^{2L} - N^{L/2}) / 2 + N^{2L-2} + (N-1)^2 + 1$ linear algebraic equations, which reduce substantially the number of unknown correlators. The remaining $M^{2L}K$ correlators have to be calculated by minimizing the free energy F by means of numerical methods or by solving the same number of nonlinear algebraic equations which might be obtained using the method of Lagrange multipliers.

In the lowest approximation of our approach the quantity should be put equal to 2. Now the constraints iv and v coincide and the expression for K needs to be slightly modified. For $N = 2$ (Ising model $s = 1/2$) $K = 9$. In order to obtain even more simple approximations, we have to use the three lowest decouplings from the sequence (4)

$$\langle m_{1_u} m_{1_\ell} m_{1_u} \rangle \rightarrow \frac{\langle m_{1_u} m_{1_\ell} \rangle \langle m_{1_\ell} m_{2_u} \rangle}{\langle m_{1_\ell} \rangle} \quad (13)$$

$$\langle m_{2_\ell} m_{1_\ell} m_{2_u} \rangle \rightarrow \frac{\langle m_{2_\ell} m_{1_\ell} \rangle \langle m_{1_\ell} m_{2_u} \rangle}{\langle m_{1_\ell} \rangle} \quad (14)$$

$$\langle m_{2\ell} m_{1_u} m_{1\ell} m_{2_u} \rangle \rightarrow \frac{\langle m_{2\ell} m_{1_u} m_{1\ell} \rangle \langle m_{1_u} m_{1\ell} m_{2_u} \rangle}{\langle m_{1_u} m_{1\ell} \rangle}. \quad (15)$$

By applying (14) and (15) to Λ'_4 and Λ_4 , we get the Kikuchi approximation (expression I.17 in ^{8/}). While that expression is valid only for $M=2$; we have obtained its straight-forward generalization for arbitrary M . The successive application of (13) to the Kikuchi approximation yields the quasichemical approximation.

The procedure for calculation of thermal equilibrium properties of the alloy on the square lattice as described above can be immediately used for an arbitrary lattice. We need only to choose a line with one stop separating molecules in both created halfspaces and to add one or more sites "above" the line in such a way that the "upper" edge of the new area would be a shifted "lower" edge of the area, i.e., the original line. The obtained areas can be again reduced using the approximations (6, 13-15). The most advantageous direction of the line is that with the lowest density of sites as shown in Figs. 1,2 for the square lattice. The method may be also used effectively for irregular lattices with dislocations.

In three dimensions a separating plane replaces the line of two-dimensional case. In one dimension no approximations are necessary and the expression for the free energy (7) is exact. Here $\langle \hat{\Lambda}'_{2L} \rangle$ and $\langle \hat{\Lambda}_{2L} \rangle$ become the double site and the single site correlators, respectively.

For models with the range of interaction longer than the lattice constant, the separating areas J with the width equal to the range of interaction are necessary. The Hamiltonian H can generally be a sum of arbitrary functions of a finite number of n'_i . In the models where a superstructure appears, the lattice should be divided into the sublattices, that improves the resulting correlators substantially.

We have applied our method to the model of an alloy, i.e., the Ising model with an arbitrary spin, but it can be used in a number of other classical models, e.g., dimers, simple anharmonic lattices, etc.

The approximations in our approach involve smaller clusters than in the previous paper, e.g., for $L=2$ 13 independent variables occur in ^{8/}, while in our approach only 7 independent correlators are to be calculated. The formulation of the problem in terms of correlators of occupation numbers and an unambiguous system of decoupling makes it possible to construct easily the free energy of a general class of classical models in an arbitrary approximation.

APPENDIX

In order to illustrate our method we shall apply it to the lattice gas with one kind of molecule in $L=2$ approximation.

Now, n_i^1 is the occupation number operator of the molecule, $n_i^2 = 1 - n_i^1$ is the occupation number operator and the Hamiltonian (1) involves only the summation over the lattice indices

$$H = \epsilon \sum_i n_i^1 + \frac{1}{2} \sum_{i \neq \ell} \kappa_{i\ell} n_i^1 n_\ell^1.$$

For the sake of simplicity we introduce the following notation

$$\langle \hat{\Lambda}' \left(\begin{smallmatrix} 1, 1 \\ 1, 1 \end{smallmatrix} \right) \rangle \equiv z_1, \quad \gamma_1 = 1; \quad \langle \hat{\Lambda}' \left(\begin{smallmatrix} 1, 1 \\ 1, 2 \end{smallmatrix} \right) \rangle \equiv z_2, \quad \gamma_2 = 2;$$

$$\langle \hat{\Lambda}' \left(\begin{smallmatrix} 1, 2 \\ 1, 2 \end{smallmatrix} \right) \rangle \equiv z_3, \quad \gamma_3 = 1; \quad \langle \hat{\Lambda}' \left(\begin{smallmatrix} 2, 1 \\ 1, 1 \end{smallmatrix} \right) \rangle \equiv z_4, \quad \gamma_4 = 2;$$

$$\langle \hat{\Lambda}' \left(\begin{smallmatrix} 2, 1 \\ 1, 2 \end{smallmatrix} \right) \rangle \equiv z_5, \quad \gamma_5 = 2; \quad \langle \hat{\Lambda}' \left(\begin{smallmatrix} 2, 2 \\ 1, 1 \end{smallmatrix} \right) \rangle \equiv z_6, \quad \gamma_6 = 2;$$

$$\langle \hat{\Lambda}' \left(\begin{smallmatrix} 2, 2 \\ 1, 2 \end{smallmatrix} \right) \rangle \equiv z_7, \quad \gamma_7 = 2; \quad \langle \hat{\Lambda}' \left(\begin{smallmatrix} 2, 1 \\ 2, 1 \end{smallmatrix} \right) \rangle \equiv z_8, \quad \gamma_8 = 1;$$

$$\langle \hat{\Lambda}' \left(\begin{smallmatrix} 2, 1 \\ 2, 2 \end{smallmatrix} \right) \rangle \equiv z_9, \quad \gamma_9 = 2; \quad \langle \hat{\Lambda}' \left(\begin{smallmatrix} 2, 2 \\ 2, 2 \end{smallmatrix} \right) \rangle \equiv z_{10}, \quad \gamma_{10} = 1.$$

The number of correlators $\hat{\Lambda}' \left(\begin{smallmatrix} \nu, \kappa \\ \lambda, \nu \end{smallmatrix} \right)$ was reduced from 16 to 10 by means of the symmetry property (9); γ_i are the degeneracy factors with respect to this symmetry.

From the three symmetry conditions (10-12) only two of them are independent

$$z_2 + z_3 = z_4 + z_5 \quad z_5 + z_7 = z_8 + z_9. \quad (16)$$

The normalization condition (8) yields

$$\sum_{i=1}^{10} \gamma_i z_i = 1. \quad (17)$$

Using the new notation, the free energy (7) has the form

$$\begin{aligned} \frac{F}{N} = & \frac{1}{2} \epsilon [2z_1 + 3z_2 + z_3 + 3z_4 + 2z_5 + 2z_6 + z_7 + z_8 + z_9] \\ & + \frac{2}{3} \kappa [3z_1 + 4z_2 + z_3 + 2z_4 + 2z_5] + kT \sum_{i=1}^{10} \gamma_i Lf(z_i) \\ & - kT [Lf(z_1 + z_4) + Lf(z_2 + z_6) + Lf(z_4 + z_8) + Lf(z_5 + z_9) \\ & + Lf(z_2 + z_5) + Lf(z_3 + z_7) + Lf(z_6 + z_9) + Lf(z_7 + z_{10})]. \end{aligned}$$

$$Lf(x) = -x \ln x - x.$$

In order to write down equations for the correlators z_i , we use the method of Lagrange multipliers, where the following expression should be minimized

$$\begin{aligned} \mathcal{F} = & \frac{F}{N} + \mu \left(1 - \sum_{i=1}^{10} \gamma_i z_i\right) - \lambda (z_5 + z_7 - z_8 - z_9) \\ & - \eta (z_2 + z_3 - z_4 - z_5). \end{aligned}$$

After straightforward calculations we get a system of nonlinear equations for μ , λ , η and z_i , $i = 1, \dots, 10$.

$$z_1 q = L^2 K^6 (z_1 + z_4)$$

$$(z_2 q)^2 = E^{-1} L^3 K^8 (z_2 + z_6) (z_2 + z_5)$$

$$z_3 q = E^{-1} L K^2 (z_3 + z_7)$$

$$(z_4 q)^2 = E L^3 K^4 (z_1 + z_4) (z_4 + z_8)$$

$$(z_5 q)^2 = E M^{-1} L^2 K^4 (z_5 + z_9) (z_2 + z_5)$$

$$(z_6 q)^2 = L^2 (z_2 + z_6) (z_6 + z_9)$$

$$(z_7 q)^2 = LM^{-1} (z_3 + z_7) (z_7 + z_{10})$$

$$(z_8 q) = LM(z_4 + z_8)$$

$$(z_9 q)^2 = LM(z_5 + z_9) (z_6 + z_9)$$

$$(z_{10} q) = z_7 + z_{10}$$

$$L = e^{-\frac{\beta \epsilon}{2}}, \quad K = e^{-\frac{\beta \kappa}{3}}, \quad E = e^{-\beta \eta}, \quad M = e^{-\beta \lambda}, \quad q = e^{-\beta \mu}$$

$$\beta = 1/T,$$

which are to be solved together with the linear equations (16), (17). There are 6 linear equations among 13 equations (16, 17, 18) which can be solved easily. The remaining 7 equations have to be treated numerically.

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