

AN ANALYTIC METHOD IN STATISTICAL MECHANICS

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1. The Problem of Ferromagnetism.

In order to illustrate the nature of the problem, let us consider a system of N spins, each of which takes $+1$ or -1 value. If the number of the nearest neighbors of a given atom is z , then the total number of neighboring atomic pairs is $P = zN/2$. Following Bethe, we consider only the nearest neighbor interactions and ignore other interactions. We write the interactions as E_{++} , E_{+-} , and E_{--} and put

$$e^{-E_{++}/kT} = \eta_{++}, \quad e^{-E_{+-}/kT} = \eta_{+-}, \quad e^{-E_{--}/kT} = \eta_{--}. \quad (1.1)$$

In the presence of an external magnetic field H , the spin state $+$ or $-$ has the energy $-mH$ or mH respectively. Here m is the magnetic moment of the atom in the $+$ spin state. Further we put

$$\xi_{+} = e^{mH/kT}, \quad \xi_{-} = e^{-mH/kT}. \quad (1.2)$$

Consider a configuration of these N atoms. The relative weight of each configuration is given by assigning the factor ξ_{+} or ξ_{-} to each of $+$ or $-$ spins and the factor η_{++} , η_{+-} , or η_{--} to each of neighboring pairs according to the spin pair state. Namely the relative weight of each spin configuration is a monomial which is order N in ξ 's and order P in η 's. The sum-over-states (Zustandssumme) is obtained by summing up these relative weights over all possible configurations, so that it is a homogeneous function of order N with respect to ξ 's and order P with respect to η 's. If the asymptotic form of this function is found for $N \rightarrow \infty$, our problem is completely solved.

Thus the sum-over-states Ξ_N is written as

$$\Xi_N = \sum_{\text{all configurations}} \xi_{+}^{N_{+}} \xi_{-}^{N_{-}} \eta_{++}^{P_{++}} \eta_{+-}^{P_{+-}} \eta_{--}^{P_{--}} \quad (1.3)$$

$$= \sum W(N_{+}, N_{-}, P_{++}, P_{+-}, P_{--}) \xi_{+}^{N_{+}} \xi_{-}^{N_{-}} \eta_{++}^{P_{++}} \eta_{+-}^{P_{+-}} \eta_{--}^{P_{--}} \quad (1.3')$$

where N_{+} and N_{-} are the numbers of $+$ spin atoms and $-$ spin atoms respectively, and P_{++} etc. are the numbers of atomic pairs in the states $++$ etc. Note that the thermodynamic function corresponding to (1.3) is not a Helmholtz free energy but is a Gibbs free energy which is a function of the intensity variable H . The resultant magnetic moment of the whole system in a given configuration is

$$M = m(N_{+} - N_{-}). \quad (1.4)$$

A method to treat this sort of problem is to find the maximum term in the summand rather than to calculate the sum. In this method the number N_{+} or N_{-} (or M) is regarded as fixed and we calculate the weight W for a given set of P_{++} , P_{+-} , and P_{--} which are consistent with this constraint. Then it is multiplied by the Boltzmann factor to obtain the term in the summand of (1.3') and the resulting expression must be maximized by proper choice of the values of P_{++} , P_{+-} and P_{--} . Thermodynamically this procedure corresponds to calculation of the minimum of the Helmholtz free energy. The difficulty of this sort of approach lies in combinatory calculations of W , which is elementary but becomes complicated in higher approximations and is almost hopeless for rigorous treatments. Therefore, there have been devised such indirect methods as Bethe's method¹⁾ and the quasi-chemical

method of Guggenheim and Fowler²⁾ and some other intuitive methods like that of Takagi.³⁾

However, one wonders if an analytical method can be devised for calculation of the asymptotic form of the expression (3). As will be shown in the following, this is possible for a system in one-dimension. The author is not able to conclude at present if this can be extended to two or three dimensions and only hopes that the present note may give some hints for such possibilities. In one-dimensional cases, the problem is shown to be reduced to a linear difference equation. In higher dimensions this may be replaced by a non-linear partial difference equation. As will be shown later, no discontinuous critical phenomena are possible in one-dimension. It may be conjectured that the occurrence of such phenomena in higher dimensions will be essentially due to such non-linearity.

Let us suppose that N atoms make an array on a line. Constructing this system by adding one atom after another, we ask how the sum-over-states Ξ_N changes with increasing N . By finding this law we try to determine the asymptotic form of Ξ_N .

We write the sum-over-state as Ξ_N^+ (or Ξ_N^-) when it is taken over all configurations of atoms 1, 2, ..., $N-1$ with the constraint that the N -th atom is in the + (or -) state. Then it is clear that this function satisfies a difference equation as shown below.

$$\begin{aligned}\Xi_{N+1}^+ &= \xi_+ (\eta_{++} \Xi_N^+ + \eta_{+-} \Xi_N^-), \\ \Xi_{N+1}^- &= \xi_- (\eta_{-+} \Xi_N^+ + \eta_{--} \Xi_N^-).\end{aligned}\quad (1.5)$$

Regarding Ξ^+ and Ξ^- as a two-component vector and defining

$$\begin{bmatrix} \xi_+ & 0 \\ 0 & \xi_- \end{bmatrix} = Q^{-1}\quad (1.6)$$

$$\begin{bmatrix} \eta_{++} & \eta_{+-} \\ \eta_{-+} & \eta_{--} \end{bmatrix} = R\quad (1.7)$$

we write Eq. (1.5) as

$$Q \vec{\Xi}_{N+1} = R \vec{\Xi}_N.\quad (1.8)$$

Namely, $\vec{\Xi}_{N+1}$ is generated from $\vec{\Xi}_N$ by a given transformation. The meaning of Eq. (1.5) will be clear if Eq. (1.3) is written as

$$\Xi_N = \sum_{i_1=\pm 1} \dots \sum_{i_N=\pm 1} \exp\left[-\frac{1}{kT} \sum_{n=1}^N E(i_n) - \frac{1}{kT} \sum_{n=1}^N E(i_{n-1}, i_n)\right].$$

In order to solve Eq. (1.8) we put

$$\vec{\Xi}_N = \lambda^N \psi\quad (1.9)$$

and obtain the eigenvalue problem

$$R \psi = \lambda Q \psi.\quad (1.10)$$

Since Eq. (1.8) is linear, its solution for an arbitrary initial condition is expanded in terms of the eigen-functions of (1.10). Namely, if the solutions of Eq. (1.10) are denoted by $\lambda_1, \psi_1; \lambda_2, \psi_2$ we have

$$\vec{\Xi}_N = c_1 \lambda_1^N \psi_1 + c_2 \lambda_2^N \psi_2\quad (1.11)$$

where the coefficients are determined by the initial conditions

$$\begin{aligned}\vec{\Xi}_1 &= (\xi_+, \xi_-) \\ \vec{\Xi}_2 &= (\eta_{++} \xi_+^2 + \eta_{+-} \xi_+ \xi_-, \eta_{-+} \xi_- \xi_+ + \eta_{--} \xi_-^2),\end{aligned}$$

but this is not needed in the following arguments.

The sum-over-states relaxed the constraint on the N -th atom is

$$\Xi_N = \Xi_N^+ + \Xi_N^-$$

and the Gibbs free energy is

$$G = -kT \log \Xi_N.$$

For $N \rightarrow \infty$, there remains in the expression (1.11) the term with the larger λ , the other being asymptotically ignored;

$$\Xi_N \sim C \lambda_1^N$$

and consequently

$$G = -kT \log C \lambda_1^N \simeq -NkT \log \lambda_1 \quad (1.12)$$

That is to say, we need only the largest eigenvalue for calculation of the Gibbs free energy. A complete solution of the problem is not necessary.

In terms of the chemical potential, the Gibbs free energy is expressed as

$$G = N\mu.$$

Equation (1.12) gives

$$\mu = -kT \log \lambda_1.$$

In other words, the absolute activity, $\exp(\mu/kT)$ is given as the largest eigenvalue of a transformation which characterize the system.

The strength of magnetization is obtained from G by

$$\partial G / \partial H = -M. \quad (1.13)$$

This relation is found also from (1.2) and (1.3) in the following way. The magnetization in a given configuration is given by Eq. (1.4), so that the thermodynamic average is

$$\begin{aligned}M &= \frac{\sum m(N_+ - N_-) \xi_+^{N_+} \xi_-^{N_-} \eta_{++}^{P_{++}} \eta_{+-}^{P_{+-}} \eta_{--}^{P_{--}}}{\sum \xi_+^{N_+} \xi_-^{N_-} \eta_{++}^{P_{++}} \eta_{+-}^{P_{+-}} \eta_{--}^{P_{--}}} \\ &= m \left(\xi_+ \frac{\partial}{\partial \xi_+} - \xi_- \frac{\partial}{\partial \xi_-} \right) \log \Xi_N = -\frac{\partial G}{\partial H}.\end{aligned} \quad (1.14)$$

Let us now calculate the eigenvalues solving the equation

$$\begin{vmatrix} \xi_+ \eta_{++} - \lambda & \xi_+ \eta_{+-} \\ \xi_- \eta_{-+} & \xi_- \eta_{--} - \lambda \end{vmatrix} = 0.$$

The largest eigenvalue λ_1 is found to be

$$\lambda_1 = \frac{1}{2} [\xi_+ \eta_{++} + \xi_- \eta_{--} + \sqrt{(\xi_+ \eta_{++} - \xi_- \eta_{--})^2 + 4\xi_+ \xi_- \eta_{+-}^2}]. \quad (1.15)$$

and the magnetization M is given by

$$M = Nm \frac{\xi_+ \eta_{++} - \xi_- \eta_{--}}{\sqrt{(\xi_+ \eta_{++} - \xi_- \eta_{--})^2 + 4\xi_+ \xi_- \eta_{+-}^2}} \quad (1.16)$$

In the above, η_{++} and η_{--} are generally different. But for spin systems we can put

$$\eta_{++} = \eta_{--} = \alpha, \quad \eta_{+-} / \eta_{++} = \beta \quad (1.17)$$

and simplify Eq. (1.16) to

$$M = Nm \frac{\sinh mH/kT}{\sqrt{\sinh^2 mH/kT + \beta^2}} \quad (1.18)$$

The energy and the entropy are easily calculated, but they are omitted here.

2. The Alloy Problem.

We consider now an alloy consisting of two kinds of atoms denoted by + and -. For an alloy, the numbers N_+ and N_- are prescribed so that the sum-over-states, Z , with this constraint is the coefficient of $\xi_+^{N_+} \xi_-^{N_-}$ in the polynomial (1.3'). This is expressed in terms of a contour integral as is familiar in the Darwin-Fowler method. It is convenient to write

$$\xi_+ = e^\zeta \quad \text{and} \quad \xi_- = e^{-\zeta} \quad (2.1)$$

and

$$Z = \frac{1}{2\pi i} \int_{\zeta^* - \pi i}^{\zeta^* + \pi i} \Xi_N e^{(N_+ - N_-)\zeta} d\zeta \quad (2.2)$$

This integral is evaluated by the steepest descent method choosing an appropriate parameter ζ^* . Using Ξ_N as was obtained in the previous section, namely

$$\Xi_N = C \lambda^N,$$

ζ^* is determined by the condition

$$N \frac{\partial}{\partial \zeta^*} \log \lambda(\zeta^*) = N_+ - N_- \quad (2.3)$$

Asymptotically, Z is given by

$$\log Z = N \log \lambda(\zeta^*) \quad (2.4)$$

and the free energy by

$$F = -NkT \log \lambda(\zeta^*). \quad (2.5)$$

Here the parameter ζ^* is a function of $(N_+ - N_-)/N$ and the temperature T . From this, every thermodynamic quantity is derived. Equation (2.3) is identical with that for the magnetization M . The parameter ζ corresponds to mH/kT , but it has no physical meaning in the alloy problem. It serves as the selector. By putting

$$\eta_{++} = \eta_{--} = \alpha, \quad \eta_{+-}/\eta_{++} = \beta, \quad (N_+ - N_-)/N = \nu$$

the parameter ζ^* can be easily eliminated from Eqs. (2.3) and (2.5) to result

$$F = -NkT \log \alpha \frac{\sqrt{1 + (\beta^2 - 1)\nu^2} + \beta}{\sqrt{1 - \nu^2}} \quad (2.6)$$

The internal energy is given by

$$E = [E_{++} \eta_{++} \frac{\partial}{\partial \eta_{++}} + E_{+-} \eta_{+-} \frac{\partial}{\partial \eta_{+-}} + E_{--} \eta_{--} \frac{\partial}{\partial \eta_{--}}] \log Z \quad (2.7)$$

where

$$\eta_{++} \frac{\partial}{\partial \eta_{++}} \log Z = \overline{P_{++}} \quad \text{etc.}$$

are the average numbers of the nearest atom pairs. The expression (2.7) is of course identical with the thermodynamic relation

$$E = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right).$$

If we put

$$\beta = e^{-W/kT},$$

the anomalous part of the internal energy due to the ordering of atoms in the alloy is

$$E = NW\beta \frac{\beta\nu^2 + \sqrt{1 + (\beta^2 - 1)\nu^2}}{(\beta + \sqrt{1 + (\beta^2 - 1)\nu^2}) \sqrt{1 + (\beta^2 - 1)\nu^2}}$$

In particular, when $N_+ = N_-$ ($\nu = 0$), it is

$$E = NW\beta / (1 + \beta)$$

3. General Discussions. Proof of Non-existence of Phase Change in One-Dimensions.

We consider an array of atoms on a line. Each atom is in one of the possible states, which are designated by $i = 1, 2, \dots, r$. The states can either be discrete or continuous. The interaction energy of neighboring i -atom and k -atom is assumed to be $E_{ik} = E_{ki}$. We introduce the selector ξ_i for an i -atom. If there is an energy E_i associated with the state i , this is identified with the Boltzmann factor $\exp(-E_i/kT)$. In this way, for each configuration of atoms the statistical weight is given by assigning the factor ξ_i to each atom in the state i and the factor $\eta_{ik} = \exp(-E_{ik}/kT)$ to each pair of atoms in the states i and k , so that the weight is a monomial of the order N with respect to ξ 's and of the order P with respect to η 's. The sum-over-states is then a homogeneous function of the same orders.

For a one-dimensional array of atoms, the relation defining the change of the sum-over-states with respect to the change of N is the same as the previous example discussed in the section 1. If we write $\Xi_{N,i}$ for the sum-over-states with the constraint that the N -th atom is specified in the state i and regard (

$\Xi_{N,1} \dots \Xi_{N,i} \dots \Xi_{N,r}$) as a vector, it holds that

$$\vec{\Xi}_{N+1} = Q^{-1} R \vec{\Xi}_N, \quad (3.1)$$

where

$$Q^{-1} = \begin{bmatrix} \xi_1 & 0 & \dots & 0 \\ 0 & \xi_2 & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & 0 & \dots & \xi_r \end{bmatrix} \quad (3.2)$$

$$R = \begin{bmatrix} \eta_{11} & \dots & \eta_{1r} \\ \eta_{21} & \dots & \\ \dots & \dots & \\ \eta_{r1} & \dots & \eta_{rr} \end{bmatrix} \quad (3.3)$$

Note that the elements of Q and R can never be negative. The general solution of Eq. (3.1) is expanded as

$$\vec{\Xi}_N = \sum_{\alpha} C_{\alpha} \lambda_{\alpha}^N \psi^{(\alpha)} \quad (3.4)$$

in terms of the eigenvalues and eigenfunctions of

$$R\psi = \lambda Q\psi. \quad (3.5)$$

The expansion coefficients are determined by the initial conditions but the asymptotic behavior is solely determined by the term which corresponds to the largest eigenvalue. We may put

$$\vec{\Xi}_N \sim C \lambda^N \psi \quad (3.6)$$

and have the Gibbs free energy

$$G = -NkT \log \lambda, \quad (3.7)$$

where λ is the largest root of the equation

$$\det | R - \lambda Q | = 0. \quad (3.8)$$

If the system shows a discontinuous phase change, there must be a crossing of two roots of Eq. (3.8) at the corresponding temperature and pressure. However, such a crossing never occurs except some special cases as we will see in the following.

The largest eigenvalue of Eq. (3.4) is determined by the maximization,

$$\lambda = \frac{\psi R \psi}{\psi Q \psi} = \frac{\sum R_{ik} \psi_i \psi_k}{\sum Q_{ij} \psi_i^2} = \text{Max}. \quad (3.9)$$

Let the eigenfunction corresponding to this be denoted by ψ^{α} . Then we find that $\psi_i^{\alpha} > 0$. Namely ψ^{α} has no node on the set $M = \{1, 2, \dots, r\}$. If for $\psi^{\alpha} < 0$ some i 's, the expression (3.9) can be made larger by changing the sign of such components, in contradiction to the assumption that (3.9) is the maximum for ψ^{α} . Also ψ^{α} is proved to be real if R_{ik} is symmetric. Now let M_{α} be the subset of M on which $\psi^{\alpha} > 0$ and suppose that another function ψ^{β} , which is orthogonal to ψ^{α} i.e. $\psi^{\alpha} Q \psi^{\beta} = 0$, also gives the maximum value of the expression (3.9). It holds then $M_{\beta} \subset M - M_{\alpha}$. Then the function $\psi = \psi^{\alpha} + \psi^{\beta}$ makes the expression (3.9) even larger, contrary to the assumption, because

$$\frac{\sum R_{ik} \psi_i^\alpha \psi_k^\alpha}{\sum Q_{ii} \psi_i^{\alpha 2}} = \frac{\sum R_{ik} \psi_i^\beta \psi_k^\beta}{\sum Q_{ii} \psi_i^{\beta 2}}$$

$$= \frac{\sum R_{ik} (\psi_i^\alpha \psi_k^\alpha + \psi_i^\beta \psi_k^\beta)}{\sum Q_{ii} (\psi_i^{\alpha 2} + \psi_i^{\beta 2})} \leq \frac{\psi R \psi}{\psi Q \psi}$$

The equality only holds when R_{ik} 's are all zero for the intersection of M_α and M_β . Otherwise the inequality is true. Therefore the largest eigenvalue can generally never be degenerate. When a lower eigenvalue approaches the largest eigenvalue with changing parameters such as temperature and pressure, it never really crosses the larger one by a sort of resonance as is illustrated in Fig. 1. This can be easily seen for simple examples. Therefore, no discontinuous phase change can occur in one-dimensional systems.

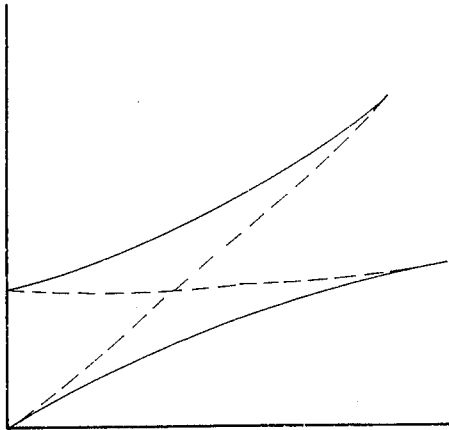


FIG. 1

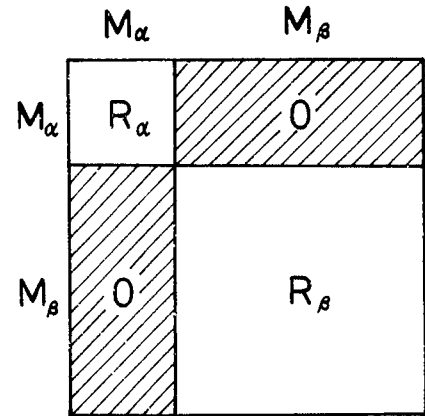


FIG. 2

Crossing without such a resonance can happen only in the cases where the matrix R has such a form as shown in Fig. 2. If the interaction energies among M_α is smaller than those among M_β , the elements of R^α are larger than those of R^β at low temperatures. Then the largest eigenvalue of R^α is larger than that of R^β . If $\dim M_\alpha < \dim M_\beta$, the order of these eigenvalues will be reversed at a certain temperature, above which R^β has the larger eigenvalue. In such a case, crossing of the eigenvalues really occur at a critical temperature, where a phase change takes place.

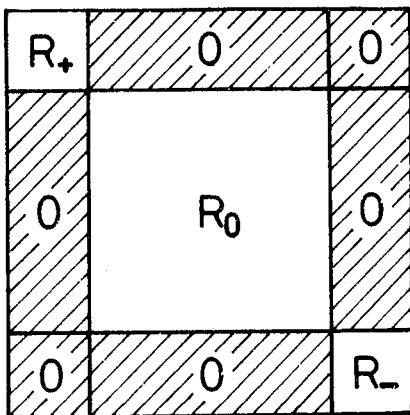


FIG. 3

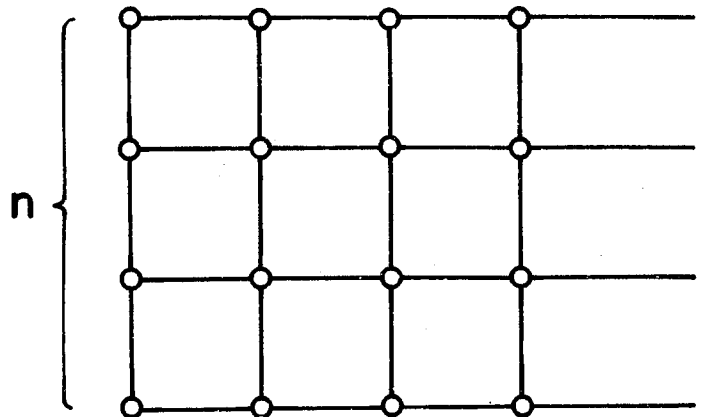


FIG. 4

We generally have $R_{ik} > 0$ in one-dimension and so no phase change. But in higher dimensions, the matrix R may have such a form as described above and accordingly a phase change can be realized. For example, consider the ferromagnetism of spins. In order to make it two-dimensional, we take a row of n spins and add it one after another as shown in Fig. 3. In this case the number of states for n spins in a row is 2^n so that R is a $2^n \times 2^n$ matrix. If $\eta_{++} = \eta_{--} > \eta_{+-}$, the matrix elements between the states of complete ordering, namely the state where n spins are all plus and that where all are minus become very small as n goes to infinity. Therefore we expect that the matrix R will have asymptotically a form like that is shown in Fig. 4, where R_+ or R_- corresponds the ordered state with plus or minus spins and R_0 corresponds to the disordered states. Matrix elements between M_+ , M_- , and M_0 become vanishingly small. (More exactly the states cannot be so distinctly separated, but is quasi-continuously grouped in such a manner.) Configurations in which spins are disordered are far more numerous than those for ordered. Namely the dimension of R_0 is far larger than those of R_+ or R_- . Hence the state M_+ or M_- will be realized at low temperatures (which of them is realized depends on the external field). On the other hand the entropy dominates at higher temperatures and the disorder will appear. This is considered as the phase change from the ferromagnetic to the paramagnetic state.

The above is only a qualitative argument for the fact that phase change is possible in two or higher dimensions while it is impossible in one-dimension. The basic physics is in accord with that which is commonly accepted.

Let us assume that the matrix Q has elements only on the diagonal which are functions of an external force X . The corresponding extensive variable x defined by

$$\frac{\partial G}{\partial X} = x = -NkT \frac{\partial \log \lambda}{\partial X}$$

Using the relations

$$\psi^\alpha Q \psi^\beta = \delta_{\alpha\beta}, \quad \psi^\alpha R \psi^\beta = \lambda_\alpha \delta_{\alpha\beta},$$

we obtain easily from (3.4) the formula

$$\frac{\partial \log \lambda_\alpha}{\partial X} = -\psi^\alpha \frac{\partial Q}{\partial X} \psi^\alpha \quad (3.10)$$

If Q is even in X , this is zero for $X = 0$. Therefore an ordering like ferromagnetism does not occur generally. For the same reason, in the statistical distribution of chain molecules, the end-to-end distance is most likely to be zero as long as the excluded volume effect is not considered. In the alloy problems, the number of constituent atoms are prescribed so that the thermodynamic functions are given by the two equations, Eq. (3.10) and

$$F = -NkT \log \lambda.$$

The situation is the same as that was discussed in section 2. For the extremum problem (3.9), Eq. (3.10) is considered as a subsidiary condition. Therefore the proof remains the same as before for the non-existence of phase change in one dimensions.

4. Concluding Remarks.

By the same method we can treat a one-dimensional system in which the neighboring atoms are interacting with a potential depending on the distance. If the interaction is considered only between the

nearest neighbors, this is the same as what was given by Dr. H. Takahashi⁴⁾ some time ago. If the next nearest neighbor interactions are also included, namely if interactions with four atoms are included for each atom in the system, the problem reduces to an eigenvalue problem for an integral equation. The author has solved this for a square well potential, but the final numerical calculation has not yet been completed.

In conclusion, the writer thanks to Dr. Takahashi for useful discussions. The non-existence theorem of phase change in one-dimension was suggested by his physical intuition, which stimulated the writer to attempt this mathematical proof.

References

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