

in this section the form of the curve changed basically by an increase of the composition gradients dc/dh .

Figure 7 shows exposures of a series with stepwise increase of temperature. Here too a faint fog was formed as in the series above. At the temperatures of the exposures 7a and 7b the smooth arched section of the curve changed basically at each step by a decrease of the gradients dc/dh at the various compositions.

At the step 7b the critical temperature is passed and the concentration curve is broken close to critical composition.

Exposure 7d is taken at a temperature 17 mdeg above critical. The left part of the curve is arched basically in the same way as shown on figures 1 and 3. The upper part of the right side leading to the surface dividing the phases is nearly vertical. The reason for this may be a convection flow in the lower phase during the establishment of this phase.

End Remarks

In the beginning of this paper it was said that the effect of gravity added to the analogy which is known to exist between the binary and the one-component systems. This may be further illuminated:

1. The presence of a temperature gradient in the binary systems leads to the Soret effect. In the one-component systems a temperature gradient will lead to mass distribution curves which will constitute isobars in the temperature-density diagram. In both cases it must however be remembered that the effect of the temperature gradient in the experiments will come in addition to the effect of gravity.

It may also be mentioned that when in the one-component systems the isobars are experimentally known, and also the gradient dp/dT at the critical density, the isotherms can be constructed. A similar relationship may be expected to hold in the binary systems between the Soret effect and the effect of gravity.

2. It was said that the effect of gravity in the binary systems was a necessary consequence of the small diffusion coefficient in the critical region, caused by the fall of the molecules of the heavier

component towards the bottom of the container. In the same way the known sigmoid form of the mass distribution curves in the one-component systems can be regarded as a consequence of the fall of the molecules balanced by a diffusion upwards. This leads to the conclusion that the diffusion coefficients also of the one-component systems are very small in the critical region and will apply to an equation analogous to eq (2).

Hirschfelder [4] and Prigogine [5] have pointed out that diffusion measurements are of fundamental importance for the study of liquid mixtures on the molecular level.

By experimental determination of the equilibrium mass distributions in mixtures, preferably in fields of increased acceleration, one should have an additional method for the study of liquid mixtures—not only in the region of the critical solution points, but also for the study of liquid mixtures in general.

The reestablishment of the mixtures were observed in 1957. Professor Joseph Mayer kindly reviewed the reports from the experiments and showed that the form of the new established curves were related to the gradient of the chemical potential and consequently to the diffusion coefficient as function of the temperature and composition. I am very much in debt to Professor Mayer, who thereby gave me the clue to the problems.

I also express my thanks to Professor Odd Hassel for his interest and assistance. Furthermore, I express my thanks to Professor E. G. D. Cohen and Dr. J. M. H. Levelt Sengers, who have reviewed my paper.

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1. Introduction

The properties of alloys of magnetic substance and nonmagnetic substance are investigated experimentally and theoretically as problems of dilute magnetism. Here we consider Ising spins of $S=1/2$ as a magnetic substance and the energy of the system is assumed to be given by a sum of exchange energies between nearest neighbor Ising spins, positive or negative, corresponding to ferro- and antiferromagnetic coupling. That is, the interaction energy between nonmagnetic ions and that between nonmagnetic ions and Ising spins are neglected. This restriction can easily be removed. The calculation based on the inclusion of the interaction energy of nonmagnetic ions will be carried out in future.

The idealization of the preparation of the system can be classified into two limiting cases. We denote the spin average by $\langle \rangle_s$ and the configuration average by $\langle \rangle_c$.

The free energy of the system which was heated at infinitely high temperature and was cooled infinitely rapidly up to temperature T is given by

$$F_Q = -kT \langle \ln \langle Z \rangle_s \rangle_c. \quad (1.1)$$

In this system the true thermal equilibrium is not realized and it is a free energy of an idealized quenched system in which ions are frozen randomly at their positions.

On the other hand, if the temperature and external parameters are varied infinitely slowly and true thermal equilibrium is realized, the free energy of the system is given by

$$F_A = -kT \ln \langle Z \rangle_{s,c}. \quad (1.2)$$

Although the interaction energy of the nonmagnetic ions are to be taken into account, the system corresponds to an idealized annealed system.

The distinction between these two cases has been discussed by Brout [1], Mazo [2], and Morita [3].

Quenched random dilute magnetism has been investigated by Behringer [4], Sato, Arrott and Kikuchi [5], Brout [1], Rushbrooke and Morgan [6], Elliott and Heap [7], and Abe [8]. In experiments ideal randomness in Brout's sense is not realized an actual "randomness" depends on the history of the preparation of samples. Experimental situation lies, more or less, between two idealized limiting cases. Hence it seems worthwhile to compare physical properties of those two systems for exactly solvable cases.

On the other hand, Syozi [9] investigated a two-dimensional decorated lattice model of dilute magnetism, where Ising spins locate on lattice points of regular two-dimensional lattice, and nonmagnetic atoms or Ising spins locate on middle points between nearest neighbor lattice points (fig. 1). He obtained exactly thermal properties of two-dimensional lattices by reducing its partition function to Onsager's partition function. We can get thermal and magnetic properties of the one-dimensional Syozi's model since the original Ising model of a one-dimensional system is known in a magnetic field. We will also compare properties of Syozi's model with above mentioned two cases.

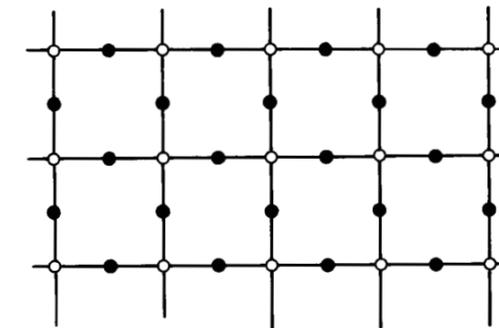


FIGURE 1. Syozi's decorated lattice model of dilute Ising model. ○ Ising spins. ● Ising spins or nonmagnetic atoms.

2. Annealed System: Formulation by Generating Function Method

In this and next sections, it will be shown that the problem of the annealed system is formulated by introducing a generating function in case of Ising spins, and that in the case of a one-dimensional problem evaluation of the generating function is reduced to an eigenvalue problem [10]. Moreover that eigenvalue equation is solved exactly and the free energy, the energy and the susceptibility are obtained.

A crystal lattice whose lattice point is named $i=1, 2, \dots, N$ is considered. On each lattice point there is either an Ising spin of $S=1/2$ or a nonmagnetic atom. If $\mu_i=1, 0$ or -1 is the state of each lattice point, the total energy of this system is given by

$$E = -\frac{J}{2} \sum_{\langle ij \rangle} \mu_i \mu_j - m\mathcal{H} \sum_i \mu_i \quad (2.1)$$

Here m is magnetic moment ($=\frac{1}{2} g\mu_B$, g : g factor, μ_B : Bohr magneton) of spin, \mathcal{H} is external magnetic field. $J > 0$ corresponds to ferromagnetic interaction and $J < 0$ antiferromagnetic interaction. $\sum_{\langle ij \rangle}$

denotes summations over all pairs of neighboring lattice points. The second term is Zeeman energy. $\mu=1$ or -1 corresponds to Ising spin (up or down) and $\mu=0$ to a nonmagnetic atom, respectively. Instead of considering the problem of the system in which concentration of Ising spins is given by p (that of nonmagnetic atoms by $1-p$), the generating function Z with parameter D is calculated.

$$Z = \sum_{\mu_i = \pm 1, 0} e^{K \sum_{\langle ij \rangle} \mu_i \mu_j + C \sum_i \mu_i + D \sum_i \mu_i^2}, \quad (2.2)$$

where

$$K = \frac{J}{2kT}, \quad C = \frac{m\mathcal{H}}{kT}.$$

Since $\mu_i^2=1$ for spin states and 0 for nonmagnetic atoms,

$$\frac{1}{N} \frac{\partial \ln Z}{\partial D} = \langle \mu_i^2 \rangle = p = p(K, D, C). \quad (2.3)$$

By solving D from (2.3) as a function of p and C ,

$$D = D(K, p, C) \quad (2.4)$$

can be derived. D corresponds to chemical potential of spins divided by kT in an alloy of nonmagnetic atoms and spins. When (2.4) is substituted into

$$E = -\frac{J}{2} \left(\frac{\partial \ln Z}{\partial K} \right) = E(K, C, D) \quad (2.5)$$

and

$$M = m \left(\frac{\partial \ln Z}{\partial C} \right)_{K, D} = \bar{M}(K, C, D), \quad (2.6)$$

energy E and magnetization M can be expressed as functions of K , p , and C . This problem is equivalent to the Ising model of $S=1$ with anisotropy.

3. Annealed System—Continued. Eigenvalue Problem in the Case of One-Dimensional System

The formulation in 2 leads to an eigenvalue problem in the case of one dimensional system. Generating function Z is given by

$$Z = \text{Tr} V^N, \quad (3.1)$$

$$V = V_3^{1/2} V_2^{1/2} V_1 V_2^{1/2} V_3^{1/2}, \quad (3.2)$$

under a periodic boundary condition. Here

$$V_1 = \begin{pmatrix} e^K & 1 & e^{-K} \\ 1 & 1 & 1 \\ e^{-K} & 1 & e^K \end{pmatrix}, \quad V_2 = \begin{pmatrix} e^C & & \\ & 1 & \\ & & e^{-C} \end{pmatrix},$$

$$V_3 = \begin{pmatrix} e^D & & \\ & 1 & \\ & & e^D \end{pmatrix}. \quad (3.3)$$

If the maximum eigenvalue of $V = V_3^{1/2} V_2^{1/2} V_1 V_2^{1/2} V_3^{1/2}$ is λ_{\max} , Z can be expressed in terms of λ_{\max} in the limit of $N \rightarrow \infty$

$$\lim_{N \rightarrow \infty} Z^{1/N} = \lambda_{\max}. \quad (3.4)$$

The explicit expression for $\lambda_{\max}(K, C, p)$ which is a solution of a cubic equation is much too complicated to be differentiated analytically. It is sufficient, however, to derive λ_{\max} exactly only up to the second order in powers of C since we are interested mainly in the energy and the susceptibility at zero field. From the symmetry of this matrix, the eigenvalue at $C=0$ and the coefficient of C^2 in the expansion of λ_{\max} can be obtained simply by solving a quadratic equation. V can be written as a sum of even function and odd function of C .

$$V = \begin{pmatrix} k^2 d^2 \text{ch } C, & \alpha \text{ch } \frac{C}{2}, & k^{-2} d^2 \\ d \text{ch } \frac{C}{2}, & 1, & d \text{ch } \frac{C}{2} \\ k^{-2} d^2, & \alpha \text{ch } \frac{C}{2}, & k^2 d^2 \text{ch } C \end{pmatrix} + \begin{pmatrix} k^2 d^2 \text{sh } C, & d \text{sh } \frac{C}{2}, & 0 \\ d \text{sh } \frac{C}{2}, & 0, & -d \text{sh } \frac{C}{2} \\ 0, & -d \text{sh } \frac{C}{2}, & -k^2 d^2 \text{sh } C \end{pmatrix} \quad (3.5)$$

where

$$e^K = k^2, \quad e^D = d^2.$$

By using similarity transformation matrices

$$S_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 1 \\ 0 & \sqrt{2} & 0 \\ 1 & 0 & -1 \end{pmatrix} = S_1^{-1} \quad (3.6)$$

and

$$S_2 = \begin{pmatrix} \sin \theta, & \cos \theta, & 0 \\ \cos \theta, & -\sin \theta, & 0 \\ 0, & 0, & 1 \end{pmatrix} = S_2^{-1}, \quad (3.7)$$

we have

$$S_2^{-1} S_1^{-1} V S_1 S_2 = H^{(0)} + H^{(1)}$$

$$= \begin{pmatrix} H_{11}^{(0)} & 0 & 0 \\ 0 & H_{22}^{(0)} & 0 \\ 0 & 0 & H_{33}^{(0)} \end{pmatrix} + \begin{pmatrix} 0 & 0 & H_{13}^{(1)} \\ 0 & 0 & H_{23}^{(1)} \\ H_{31}^{(1)} & H_{32}^{(1)} & 0 \end{pmatrix}, \quad (3.8)$$

where θ is determined in such a way that $H_{13}^{(1)}$ vanishes. $H^{(0)}$ is an even function of C and $H^{(1)}$ an odd function.

In order to obtain λ_{\max} in case of $C \approx 0$, $H^{(0)}$ is regarded as an unperturbed term and $H^{(1)}$ as a perturbation. From second order perturbation theory (first order perturbation term vanishes)

$$\lambda_{\max} = H_{11}^{(0)} + \frac{(H_{13}^{(1)})^2}{H_{11}^{(0)} - H_{33}^{(0)}}. \quad (3.9)$$

Taking $C \approx 0$ into consideration, $H_{11}^{(0)}$, $H_{33}^{(0)}$, and $H_{13}^{(1)}$ are expanded with respect to C ,

$$H_{11}^{(0)} = \lambda^{00} + C^2 \lambda^{01} + O(C^4), \quad (3.10)$$

$$\frac{(H_{13}^{(1)})^2}{H_{11}^{(0)} - H_{33}^{(0)}} = C^2 \lambda^{11} + O(C^4). \quad (3.11)$$

The term of $O(C^2)$ does not appear from the third and higher order terms of the perturbation.

Thus the maximum eigenvalue of (3.2) is obtained exactly up to order of C^2 .

When $\mathcal{H} = 0$, the relation between p and D is represented by

$$e^{-D} = d^{-2} = \frac{p(p-1)(k^2+k^{-2})}{(k^2+k^{-2}-4)p(p-1)-1-(2p-1)\sqrt{2(2-k^2-k^{-2})p(p-1)+1}}. \quad (3.12)$$

The energy E and the susceptibility χ in case of $\mathcal{H} = 0$ is expressed in terms of d^{-2} .

$$\frac{E}{NJ} = -\frac{1}{4} \frac{k+k^{-1}}{k-k^{-1}}$$

$$\times \left[1 + \frac{k^2-4+k^{-2}-d^{-2}}{\sqrt{(k^2+k^{-2}-d^{-2})^2+8d^{-2}}} \right]. \quad (3.13)$$

$$\frac{kT\chi}{Nm^2} = \frac{2(\lambda^{01} + \lambda^{11})}{\lambda^{00}} = \frac{1}{k^2 + k^{-2} + d^{-2} + \sqrt{(k^2 + k^{-2} - d^{-2})^2 + 8d^{-2}}} \left[\frac{k^4 + 1 - d^{-2}(k^2 - 2)}{\sqrt{(k^2 + k^{-2} - d^{-2})^2 + 8d^{-2}}} + k^2 \right] + \frac{4k^4 + 2d^{-2} + \frac{4\left\{(k^2 + k^{-2} - d^{-2})\left(k^4 \frac{d^{-2}}{2}\right) + 4d^{-2}k^2\right\}}{\sqrt{(k^2 + k^{-2} - d^{-2})^2 + 8d^{-2}}}}{3k^{-2} - k^2 + d^{-2} + \sqrt{(k^2 + k^{-2} - d^{-2})^2 + 8d^{-2}}} \quad (3.14)$$

d^{-2} in (3.13) and (3.14) is regarded as given by (3.12) in terms of p . Substituting $p=1$ into (3.13) and (3.14), well-known results on the Ising model

$$\frac{E}{NJ} = -\frac{1}{2} \text{th} K, \quad \frac{kT\chi}{Nm^2} = e^{2K} \quad (3.15)$$

are reproduced.

4. Quenched System

Next we consider the quenched system in one-dimension. The partition function for a given configuration of nonmagnetic atoms is given by

$$\langle Z \rangle_s = \sum \exp \left\{ K \sum_{\langle ij \rangle} \mu_i \mu_j + C \sum \mu_i \right\} \quad (4.1)$$

$$= \text{ch}^M K \text{ch}^{N_s} C \sum_{\mu=\pm 1} \prod (1 + \mu_i \mu_j \text{th} K) \prod (1 + \mu_k \text{th} C) \\ = \text{ch}^M K \text{ch}^{N_s} C \sum_{\mu=\pm 1} \left(1 + \sum_{\langle ij \rangle} \mu_i \mu_j \text{th} K + \sum_{\langle ij \rangle} \sum_{\langle i'j' \rangle} \mu_i \mu_j \mu_{i'} \mu_{j'} \text{th}^2 K + \dots \right) \\ \times (1 + \sum \mu_k \text{th} C + \sum \sum \mu_k \mu_{k'} \text{th}^2 C + \dots) \quad (4.2)$$

Here $\mu = \pm 1$, in contrast to the annealed system. N_s is the number of Ising spins. M is the number of bonds connecting Ising spins. The summation $\sum_{\langle ij \rangle}$ in (4.1) is carried out for only Ising spin pairs.

Expanding the product we have

$$\langle Z \rangle_s = \text{ch}^M K \text{ch}^{N_s} C \sum_{\mu=\pm 1} \sum_m \sum_n (\mu_i \mu_j) (\mu_{i'} \mu_{j'}) \dots \\ \times (\mu_i^{(m)} \mu_j^{(m)}) \mu_k \mu_{k'} \dots \mu_l^{(n)} \text{th}^m K \text{th}^n C. \quad (4.3)$$

Carrying out the summation with respect to $\mu = \pm 1$, we have

$$\langle Z \rangle_s = 2^{N_s} \text{ch}^M K \text{ch}^{N_s} C \times \sum_m \sum_n [\text{Number of graphs} \\ \text{which have } m \text{ bonds and of which the sum of} \\ \text{the number of end points and odd junctions is} \\ n \text{ in that configuration}] \times \text{th}^m K \text{th}^n C. \quad (4.4)$$

When we take the logarithm and divide by N , only the term proportional to N in the bracket survives. Restricting our interest in $\text{th}^0 C$ and in $\text{th}^2 C$ terms in the case of one dimension, we find that the average number of graphs which have m bonds and two end points is Np^{m+1} , since the probability of finding an Ising spin at each lattice point is p . Taking the configurational average by $\langle \rangle_c$, we have

$$[n=0, m=0] = 1, \\ [n=0, m=1, 2, 3, \dots] = 0 \\ \langle [n=2, m] \rangle_c = Np^{m+1}, \\ \langle N_s \rangle_c = Np, \\ \langle M \rangle_c = Np^2.$$

Hence

$$\langle \ln \langle Z \rangle_s \rangle_c = Np^2 \ln \text{ch} K + Np \ln \text{ch} C + Np \log 2 \\ + \ln \left[1 + N \sum_m \text{th}^2 C p^{m+1} \text{th}^m K \right] \quad (4.5)$$

$$\lim_{N \rightarrow \infty} \frac{1}{N} \langle \ln \langle Z \rangle_s \rangle_c = p \log 2 + p^2 \ln \text{ch} K + p \ln \text{ch} C \\ + \sum p^{m+1} \text{th}^m K \text{th}^2 C + 0(\text{th}^4 C). \quad (4.6)$$

Thus the energy is given by only the first term of the series and the series for the susceptibility

can be summed, giving

$$E = -\frac{J}{2} \frac{\partial \langle \ln \langle Z \rangle_s \rangle_c}{\partial K} = -\frac{NJ}{2} p^2 \text{th} K, \quad (4.7)$$

$$\chi = \frac{m^2 N p}{kT} \left\{ 1 + 2 \sum p^m \text{th}^m K \right\} \\ = \frac{m^2 N p}{kT} \frac{1 + p \text{th} K}{1 - p \text{th} K}. \quad (4.8)$$

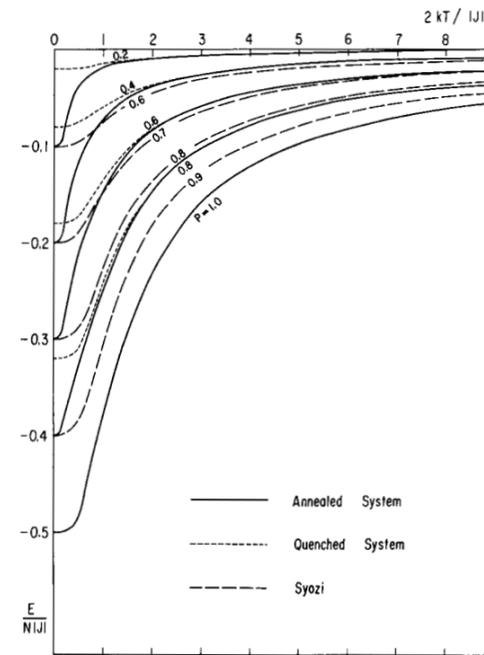


FIGURE 2. Energy in zero magnetic field. Solid line: the annealed system. Dotted line: the quenched system ($0 \leq p \leq 1$). Dashed line: Syozi's model ($\frac{1}{2} \leq p \leq 1$).

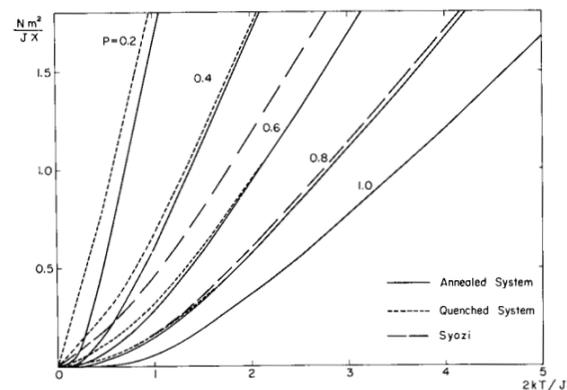


FIGURE 3. Inverse susceptibility in the ferromagnetic case. Solid line: the annealed system. Dashed line: the quenched system. Long dashed line: Syozi's model.

5. Numerical Results and Discussions

Now we compare the numerical results of three cases, an annealed system, a quenched system, and Syozi's model.

Figure 2 shows the energy in zero magnetic field. The energy of Syozi's model for p is $-(p - \frac{1}{2}) \times \text{th} K$ for $\frac{1}{2} < p < 1$. Figure 3 shows the inverse susceptibility of ferromagnetic case. Figure 4 shows the susceptibility of an antiferromagnetic case in the annealed system. Figure 5 is that for the quenched system and figure 6 shows that for Syozi's model. As the temperature goes to zero, the first tends to zero while the second and the third tends to infinity. Figure 7 shows the concentration dependence of the antiferromagnetic susceptibility of the quenched system and the annealed system.

In the above results the difference in the low temperature susceptibility between the annealed system and the quenched system in the case of antiferromagnetic interaction is most drastic. In the quenched system the susceptibility at the concentration p is obtained by the arithmetic mean of each configuration corresponding to the same

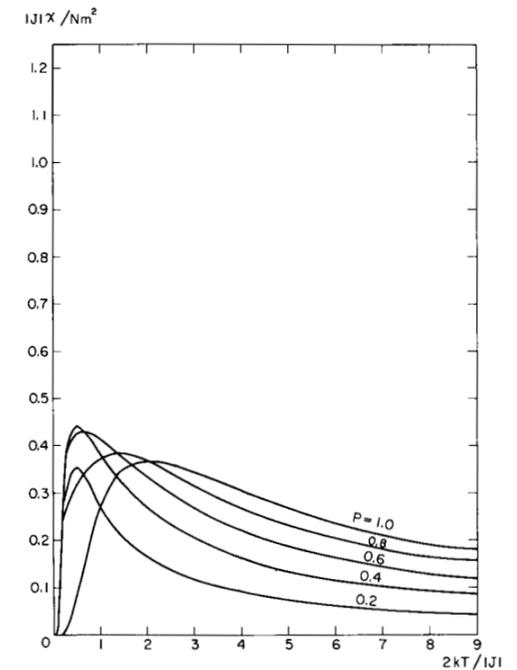


FIGURE 4. Susceptibility of an antiferromagnetic case in the annealed system.

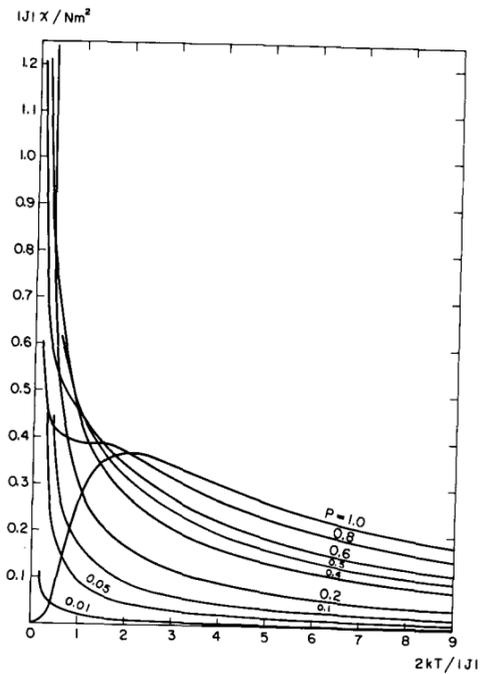


FIGURE 5. Susceptibility of an antiferromagnetic case in the quenched system.

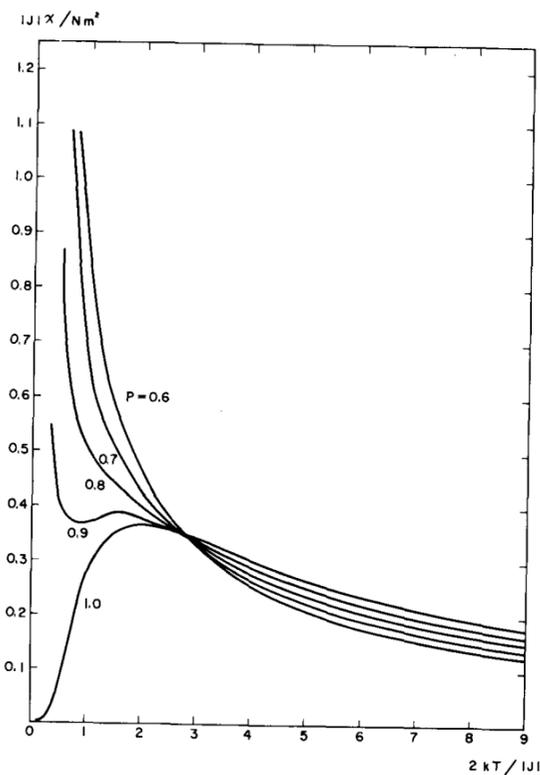


FIGURE 6. Susceptibility of an antiferromagnetic case in Syozi's model.

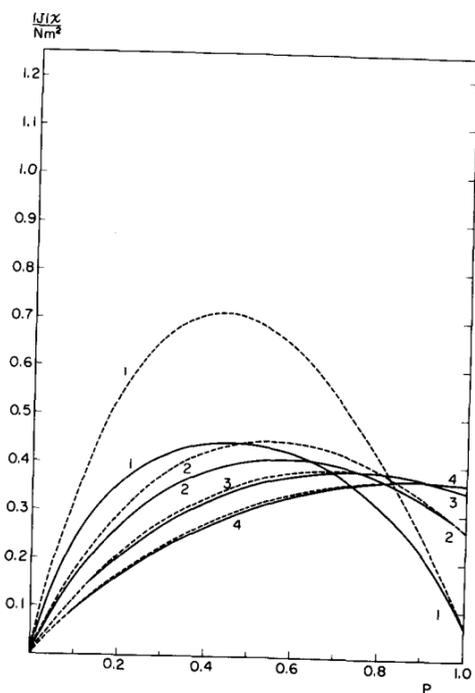


FIGURE 7. Concentration dependence of the antiferromagnetic susceptibility.

Solid line: the annealed system. Dashed line: the quenched system.
 1: $T=|J|/4k$, 2: $T=2|J|/4k$,
 3: $T=3|J|/4k$, 4: $T=4|J|/4k$.

concentration p , and the paramagnetic configuration gives the dominant contribution compared with the antiferromagnetic configuration. On the other hand, in the annealed system, the energy of the paramagnetic configuration is high compared with the antiferromagnetic configuration, and hence it dies and the susceptibility tends to zero.

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IBM 7090 in UNICON (University contribution of Japan IBM).

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The Statistical Mechanics of a Single Polymer Chain

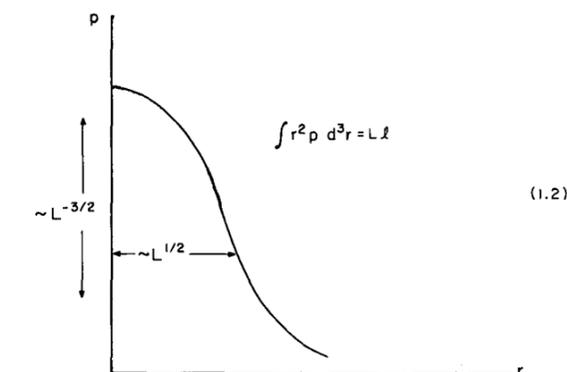
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It is clear from the papers presented at this conference that near critical points thermodynamic functions and correlation functions take on forms which reflect only a very small amount of the detailed structure of the systems considered, and are rather manifestations of the three dimensionality of space and the short range of interactions. The configurational statistics of polymers shares this feature and is therefore interesting as an indication of how the critical behavior may be generated mathematically; in fact the problem is one way of approximating to the Ising lattice as was mentioned by Professor Domb [1]. In this talk I shall develop the theory applied to polymers themselves however, and comment on their critical behavior, since whether the analysis will really be useful for bulk systems remains to be seen. A polymer without interaction will have the well-known distribution

$$p(\mathbf{r}, L) = \left(\frac{2\pi L l}{3}\right)^{-3/2} \exp\left(-\frac{3r^2}{2Ll}\right) \quad (1.1)$$

for the probability that the end points are at $\mathbf{0}, \mathbf{r}$ when the length is L . This has the form



For the case of excluded volume i.e., a repulsion between elements of the polymer, p has no simple analytic form, but salient features are shown in