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Diffusion Constants near the Critical Point for Time-Dependent Ising Models. III. Self-Diffusion Constant*

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Employing a time-dependent Ising model of the kind used in the preceding works of this series, we have studied the self-diffusion constant. In the local-equilibrium approximation, the self-diffusion constant is expressed in terms of certain equal-time spin correlation functions. At the critical point the self-diffusion constant is shown to have a finite value, and it is conjectured that it may have an infinite slope as a function of temperature at the critical point. The two relevant experiments are discussed.

1. INTRODUCTION

THIS work is a continuation of the two previous works on time-dependent Ising models,[1] where we have endeavored to obtain the behavior of the diffusion constant near the critical point under a simple approximation which allows us to incorporate some recent advances in Ising-model statistics.[2] The present work is concerned with the self-diffusion constant whose behavior near the critical point is radically different from that of the ordinary diffusion constant treated in I and II. The statistical-mechanical treatment of this problem was first given by Kikuchi[3] using a time-dependent Ising model. However, the approximation of his treatment is equivalent to the classical Bethe approximation, or to Kikuchi's cluster-variation approximation.[4]

In the present treatment we shall employ the local equilibrium approximation which we have used in I. Some of the properties of this approximation have been investigated in II. Although this approximation is solely concerned with the dynamics of the problem, and thus allows us to incorporate the results of accurate treatments of Ising-model statistics,[2] it has not been possible to estimate the error of this approximation in general. Nevertheless, because of the simplicity and other advantages of this treatment, we shall pursue the present approach, and then the final validity of the approach should be judged by the experiments, if not by more accurate theory.

The model employed is similar to Kikuchi's,[3] which is described in Sec. 2. In Sec. 3 we obtain the self-diffusion constant in terms of certain equal-time spin correlation functions. In Sec. 4 we shall discuss the behavior of the diffusion constant near the critical point. Although the diffusion constant itself is finite there, we shall conjecture that it may have an infinite slope as a function of the temperature, and we shall discuss the two relevant experiments. The final section is devoted to some discussion of the problem.

2. KINETIC MODEL

For studying the self-diffusion, we consider a binary alloy AB in which one of the species, A, has an isotope denoted by A^*. There are N lattice sites, each of which is occupied by A, A^*, or B. Then, the state of each lattice site, say, the jth site is completely specified by assigning the type of atom occupying that site which is denoted by a symbol S_j. S_j equals either A or A^* or B according to whether the jth site is occupied by the atom A or its isotope A^* or the atom B, respectively. Here we suppose that the isotope simply serves to label some of the A atoms and in no way affects its interactions with other atoms. Thus, an isotope A^* can, for example, be an atom A with its nuclear spin reversed.

The state of the system is described by giving the probability distribution function $p_N(\{S\}_N,t)$ of the entire system with N lattice sites.[5] Introducing the spin variable $\sigma_j=\sigma(S_j)$ which is defined in Table I and which specifies the state of the jth site when the isotope loses its identity, the equilibrium distribution function for the case with N_A A atoms, $N_{A^*}A^*$ atoms, and N_B B atoms is given by

$$p_N^e(\{S\}_N)=\frac{N_A!N_{A^*}!}{(N_A+N_{A^*})!}p_N^e(\{\sigma\}_N), \tag{2.1}$$

where use is made of the fact that in equilibrium isotopes

TABLE I. State variable S_j and its functions for binary alloy and lattice gas.

Alloy	Occupied by an atom A	Occupied by an isotope A^*	Occupied by an atom B
S_j	A	A^*	B
$\sigma_j\equiv\sigma(S_j)$	1	1	-1
$u_j\equiv u(S_j)$	0	1	0
Lattice gas	Occupied by an atom	Occupied by an isotope	Vacant

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[1] K. Kawasaki, Phys. Rev. **142**, 164 (1966); **145**, 224 (1966). Hereafter referred to as I and II.

[2] See for example C. Domb, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, Chap. I.

[3] R. Kikuchi, J. Phys. Chem. Solids **20**, 35 (1961) and the references cited therein.

[4] R. Kikuchi, Phys. Rev. **81**, 988 (1951).

[5] The notation used has the meaning similar to that in I and II. $\{S\}_N$, for example, denotes the set $S_1, S_2,\cdots,S_N$.

are randomly distributed among the sites occupied by atoms A and A^*, and $p_N{}^e(\{\sigma\}_N)$ is the equilibrium distribution function in the absence of isotopes. When $(N_A+N_{A^*})/N_B$ equals the critical mixing ratio, $p_{N5}(\{\sigma\}_N)$ has the following form

$$p_N{}^e(\{\sigma\}_N)=Z^{-1}\exp\{K\sum_{\langle jl\rangle}\sigma_j\sigma_l\}, \tag{2.2}$$

where

$$K\equiv(k_BT)^{-1}[2^{-1}\epsilon_{AB}-4^{-1}(\epsilon_{AA}+\epsilon_{BB})] \tag{2.3}$$

with the familiar notation for ϵ_{AA}, ϵ_{BB}, and ϵ_{AB}. If $(N_A+N_{A^*})/N_B$ deviates from the critical mixing ratio, a term similar to the Zeeman term is added to $K\sum_{\langle jl\rangle}\sigma_j\sigma_l$.

For our kinetic model, we shall consider the two kinds of exchange mechanisms involving atoms on the nearest-neighbor sites:

(i) AB exchange. An A atom or its isotope exchanges sites with one of its nearest-neighbor B atoms. The transition probability for this process is the same as that obtained in I from the consideration of the principle of detailed balancing. Namely, using the same notation as in I, [see I (2.1)[6]]

$$W_{12}(\{\sigma\}_{(12)})=\tfrac{1}{2}\alpha\prod_j(1+\gamma\sigma_2\sigma_j)\prod_l(1+\gamma\sigma_1\sigma_l), \tag{2.4}$$

where

$$\gamma\equiv\tanh K \tag{2.5}$$

and j (or l) runs over the nearest-neighbor sites of 1 (or 2) except 2 (or 1), and α is taken to be a positive constant.

(ii) AA^* exchange. An Atom A exchanges its site with one of the nearest-neighbor isotopes. Since no energy change is involved in this process, the simplest choice for the transition probability is just a constant which we denote by w.

Having specified the transition probabilities, we are now ready to write down the master equation for the problem, which is

$$\frac{d}{dt}p_N(\{S\}_N,t)=-\sum_{\langle jl\rangle}X_{jl}(\{S\}_{(jl)})p_N(\{S\}_N,t)+\sum_{\langle jl\rangle}X_{jl}(\{S\}_{(jl)}{}^{jl})p_N(\{S\}_N{}^{jl},t), \tag{2.6}$$

where X_{jl} is the total transition probability given by

$$X_{jl}(\{S\}_{(jl)})\equiv W_{jl}(\{\sigma\}_{(jl)})\times\tfrac{1}{2}(1-\sigma_j\sigma_l)+w\tfrac{1}{2}(1+\sigma_j)\tfrac{1}{2}(1+\sigma_l) \tag{2.7}$$

and the sum $\langle jl\rangle$ is over all the pairs of the nearest-neighbor sites. The superscript jl designates the states in which S_j and S_l are interchanged.

Finally, we note that the present model applies also to the lattice gas where we replace a B atom by a vacancy and ϵ_{AA} denotes the interaction of the two particles on the nearest-neighbor site, and $\epsilon_{BB}=\epsilon_{AB}=0$.

3. SELF-DIFFUSION CONSTANT

The self-diffusion process for the present model is studied by considering the situation in which the spatial gradient exists only in the relative concentration of isotopes. Thus we can assume that when the isotopes lose their identities, the system is in the state of complete thermal equilibrium. This requires that

$$\sum_{\text{i.d.}}p_N(\{S\}_N,t)=p_N{}^e(\{\sigma\}_N), \tag{3.1}$$

where i.d. means the sum over all possible isotope distributions with $\{\sigma\}_N$ specified. This requirement is consistent with the master equation (2.6) because after the sum $\sum_{\text{i.d.}}$, (2.6) reduces to the master Eq. I (2.11) which has $p_N{}^e(\{\sigma\}_N)$ as a solution.

For the problem of self-diffusion, we shall introduce a state function at the jth site $u_j=u(S_j)$ which takes the value unity when the site is occupied by the isotope and vanishes otherwise, and consider the average value of this function defined by,

$$\bar{u}_j(t)\equiv\sum_{\{S\}_N}u(S_j)p_N(\{S\}_N,t). \tag{3.2}$$

Use of the master Eq. (2.6) then yields for the time rate of change of $\bar{u}_j$ the following;

$$\frac{d}{dt}\bar{u}_j(t)=-\sum_l^{\langle jl\rangle}\sum_{\{S\}_N}(u_j-u_l)\times X_{jl}(\{S\}_{(jl)})p_N(\{S\}_N,t), \tag{3.3}$$

where the sum l is over the nearest-neighbor sites of j. Since the right-hand side of this equation cannot in general be expressed solely in terms of $\bar{u}$'s, it is necessary to introduce a fundamental approximation here as in I. We shall again introduce the local-equilibrium approximation in which $p_N(\{S\}_N,t)$ is replaced by its value in local-equilibrium state with given $\bar{u}$'s. We have found that the equivalent and simpler procedure is to use the following ansatz for $p_N(\{S\}_N,t)$:

$$\sum_{\text{i.d.}}u_jp_N(\{S\}_N,t)=\frac{1+\sigma_j}{2}c\frac{\bar{u}_j(t)}{u_e}p_N{}^e(\{\sigma\}_N), \tag{3.4}$$

where c is the ratio of isotopes to the total number of A and A^* atoms and u_e is the equilibrium average of u_j (here we have excluded the case of antiferromagnetic interaction below the transition temperature where u_e differs from site to site). Namely,

$$u_e\equiv\tfrac{1}{2}(1+m)c, \tag{3.5}$$

$$m\equiv\langle\sigma_j\rangle, \tag{3.6}$$

where the angular bracket $\langle\ \rangle$ always designates the average over the equilibrium ensemble. Equation (3.4)

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[6] We refer to the equations in I in this manner.

follows from the intuitive consideration that the average of u_j for a specified $\{\sigma\}_N$, $\sum_{\text{i.d.}} u_j p_N(\{S\}_N,t)/p_N^e(\{\sigma\}_N)$, is equal to the product of the probability that the site is occuped by A or A^*, and the probability that, when it is occupied by A or A^*, it is A^*. This consideration ignores the correlation between the distribution of A, B atoms and the isotope distribution, and therefore cannot be exact. The equivalence of this ansatz and the local equilibrium approximation is demonstrated in the Appendix.

Substitution of (3.4) into (3.3) yields

$$\frac{d}{dt}\bar{u}_j(t) = -a^{-2}D_s \sum_{l}^{\langle jl\rangle} [\bar{u}_j(t)-\bar{u}_l(t)], \tag{3.7}$$

where a is the lattice constant (we assume a simple cubic lattice), and

$$D_s \equiv \frac{ca^2}{u_e}\langle \tfrac{1}{2}(1+\sigma_j)X_{jl}(\{S\}_{(jl)})\rangle. \tag{3.8}$$

If we introduce the number density of isotopes $u(\mathbf{r})$ by

$$u(\mathbf{r}_j) \equiv \bar{u}_j/a^3 \tag{3.9}$$

and, supposing that $u(\mathbf{r})$ is a slowly-varying function of $\mathbf{r}$, make use of the expansion

$$a^{-3}(\bar{u}_l-\bar{u}_j) \cong (\mathbf{r}_l-\mathbf{r}_j)\cdot\nabla u(\mathbf{r}_j) + \tfrac{1}{2}(\mathbf{r}_l-\mathbf{r}_j)(\mathbf{r}_l-\mathbf{r}_j):\nabla\nabla u(\mathbf{r}_j)+\cdots, \tag{3.10}$$

(3.7) becomes

$$\frac{\partial}{\partial t}u(\mathbf{r}) = D_s\nabla^2 u(\mathbf{r}), \tag{3.11}$$

which is the diffusion equation for isotopes with the self-diffusion constant D_s.

Corresponding to the two mechanisms of particle exchange, the self-diffusion constant consists of the two parts

$$D_s = D_{s1}+D_{s2}, \tag{3.12}$$

where

$$D_{s1} \equiv \frac{ca^2}{u_e}\langle \tfrac{1}{2}(1+\sigma_1)\tfrac{1}{2}(1-\sigma_1\sigma_2)W_{12}(\{\sigma\}_{(12)})\rangle, \tag{3.13}$$

$$D_{s2} \equiv \frac{ca^2 w}{u_e}\langle \tfrac{1}{2}(1+\sigma_1)\tfrac{1}{2}(1+\sigma_2)\rangle, \tag{3.14}$$

and the sites 1, 2 are the nearest-neighbor sites. If $\sigma_1=-\sigma_2$ only for which (3.13) gives nonvanishing contributions, W_{12} can be rewritten as [see I(3.9)]

$$W_{12}(\{\sigma\}_{(12)}) = g\exp(-\mathcal{K}_0), \tag{3.15}$$

where

$$g \equiv \tfrac{1}{2}\alpha e^{-K}[\cosh K]^{-2(z-1)}, \tag{3.16}$$

and $\mathcal{K}_0$ is defined by I(2.4) and represents the interaction energy of the site 1, 2 and their first nearest neighbors apart from a factor $-(k_BT)^{-1}$. Thus, if we substitute (3.15) into (3.13), it reduces to an average of $\frac{1}{2}(1+\sigma_1)\frac{1}{2}(1-\sigma_1\sigma_2)$ over the equilibrium ensemble of the system in which the "spins" σ_1 and σ_2 are removed from the system. Namely, (3.10) becomes, using (3.5),

$$D_{s1} = \tfrac{1}{2}a^2 g\langle e^{-\mathcal{K}_0}\rangle/(1+m). \tag{3.17}$$

If we define the spin pair correlation ϕ_{jl} by I(3.5), (3.14) reduces to

$$D_{s2} = \tfrac{1}{2}a^2 w[1+m+\phi_{12}/(1+m)]. \tag{3.18}$$

In the above derivation, we have excluded the case of antiferromagnetic interaction below its transition temperature. We shall now discuss this case briefly. The only difference is that, since we have here two sublattices, $\langle u_j\rangle$ is not the same for all j and $u(\mathbf{r}_j)$ is no longer a slowly varying function of $\mathbf{r}_j$. Thus the ansatz (3.4) is now replaced by

$$\sum_{\text{i.d.}} u_j p_N(\{S\}_N,t) = \tfrac{1}{2}(1+\sigma_j)c\frac{\bar{u}_j(t)}{u_j^e}p_N^e(\{\sigma\}_N), \tag{3.19}$$

where

$$u_j^e \equiv c(1+m_j)/2, \tag{3.20}$$

and m_j depends on the sublattice to which the jth state belongs. Substituting this into (3.3), we obtain

$$\frac{d}{dt}\bar{u}_j(t) = -\sum_{l}^{\langle jl\rangle}[F_j\bar{u}_j(t)-F_l\bar{u}_l(t)], \tag{3.21}$$

where

$$F_j \equiv \frac{c}{u_j^e}\langle \tfrac{1}{2}(1+\sigma_j)X_{jl}(\{S\}_{(jl)})\rangle. \tag{3.22}$$

This quantity takes two values F_1 or F_2 according to whether the jth site belongs to the first or to the second sublattice, respectively. Although $u(\mathbf{r})$ changes rapidly as $\mathbf{r}$ moves from one sublattice to another, it can still be regarded as two smooth functions of $\mathbf{r}$ if $\mathbf{r}$ is allowed to move only on either one of the sublattices. Thus we can put

$$\begin{aligned} a^{-3}\bar{u}_j &\equiv u_1(\mathbf{r}_f) \quad \text{if} \quad \mathbf{r}_j=\mathbf{r}_f \text{ is on the first sublattice} \\ &\equiv u_2(\mathbf{r}_g) \quad \text{if} \quad \mathbf{r}_j=\mathbf{r}_g \text{ is on the second sublattice,} \end{aligned} \tag{3.23}$$

where $u_1(\mathbf{r})$ and $u_2(\mathbf{r})$ are the slowly varying functions of $\mathbf{r}$. Then (3.21) becomes,

$$\begin{aligned} \frac{\partial}{\partial t}u_1(\mathbf{r}_f) &= -\sum_{g'}^{\langle fg'\rangle}[F_1u_1(\mathbf{r}_f)-F_2u_2(\mathbf{r}_{g'})], \\ \frac{\partial}{\partial t}u_2(\mathbf{r}_g) &= -\sum_{f'}^{\langle gf'\rangle}[F_2u_2(\mathbf{r}_g)-F_1u_1(\mathbf{r}_{f'})], \end{aligned} \tag{3.24}$$

where the sums of g' and f' are over the nearest neighbors of f and g, respectively. For $u_1(\mathbf{r})$ and $u_2(\mathbf{r})$ we can make use of expansions such as given by (3.10), and (3.24) finally reduces to

$$\begin{aligned}\frac{\partial}{\partial t}u_1(\mathbf{r})&=-6[F_1u_1(\mathbf{r})-F_2u_2(\mathbf{r})]+F_2a^2\nabla^2u_2(\mathbf{r}),\\ \frac{\partial}{\partial t}u_2(\mathbf{r})&=-6[F_2u_2(\mathbf{r})-F_1u_1(\mathbf{r})]+F_1a^2\nabla^2u_1(\mathbf{r}).\end{aligned}\tag{3.25}$$

This set of equations can be solved by setting

$$u_i(\mathbf{r})=A_i e^{-\lambda t}\, e^{i\mathbf{k}\cdot\mathbf{r}}+\langle u_i(\mathbf{r})\rangle,\quad i=1,2.\tag{3.26}$$

The condition of obtaining a nontrivial solution then determines λ;

$$\begin{vmatrix}\lambda-6F_1 & (6-a^2k^2)F_2\\ (6-a^2k^2)F_1 & \lambda-6F_2\end{vmatrix}=0.\tag{3.27}$$

For small ak, this has the following two solutions:

$$\begin{aligned}\lambda_1&=D_sk^2,\\ \lambda_2&=6(F_1+F_2)-D_sk^2,\end{aligned}\tag{3.28}$$

where

$$D_s\equiv 2a^2F_1F_2/(F_1+F_2).\tag{3.29}$$

A general solution of (3.25) is then written down as

$$u_i(\mathbf{r})=A_i\, e^{-t\lambda_1}+B_i\, e^{-t\lambda_2}+\langle u_i(\mathbf{r})\rangle,\quad i=1,2.\tag{3.30}$$

Since, for small k, $\lambda_1 \ll \lambda_2$, this shows that for the time t such that $\lambda_1^{-1}\gg t\gg\lambda_2^{-1}$ $u_i(\mathbf{r})$ obeys a simple diffusion equation with the diffusion constant D_s given by (3.29). F_j given by (3.22) can be transformed in the same manner as we obtained (3.17) and (3.18), and we find that

$$\begin{aligned}F_1=\tfrac{1}{2}g(1+m_1)^{-1}\langle e^{-\mathcal{K}_0}\rangle\\ +\tfrac{1}{2}w[1+m_2+(1+m_1)^{-1}\phi_{12}]\end{aligned}\tag{3.31}$$

with F_2 given by interchanging m_1 and m_2 in (3.31). Using this result together with (3.29), we obtain

$$D_s=D_{s1}+D_{s2},\tag{3.32}$$

$$D_{s1}=\tfrac{1}{2}a^2g\langle e^{-\mathcal{K}_0}\rangle,\tag{3.33}$$

$$D_{s2}=\tfrac{1}{2}a^2w(1-m^2+\phi_{12}),\tag{3.34}$$

where we have used the fact that $m_1=-m_2=m$. Since $\langle e^{-\mathcal{K}_0}\rangle$ and ϕ_{12} do not depend on the sign of m, D_s is also independent of the sign of m as one expects for antiferromagnetic interactions. This is not the case for ferromagnetic interactions.

Equations (3.12), (3.17), (3.18), (3.32), (3.33), and (3.34) give the expressions for the self-diffusion constants for systems with ferro- and antiferromagnetic interactions. It is seen that in the local equilibrium approximation, diffusion constants are simply given as sums of the diffusion constants arising from different diffusion mechanisms.

4. THE BEHAVIOR OF THE DIFFUSION CONSTANTS NEAR THE CRITICAL POINT

Equations (3.17), (3.18), (3.33), and (3.34) immediately tell us that, since both D_{s1} and D_{s2} are expressed in terms of averages of finite quantities which involve only a finite number of sites, all the diffusion constants remain finite at the transition point. This does not, however, exclude singularities of the derivatives of the diffusion constants with respect to the temperature. We shall first study this problem for D_{s2} given by (3.18) and (3.34). Besides the obvious singularity coming through dm/dT or dm^2/dT, ϕ_{12} also contains a singularity, as one can see in the following: for $T>T_c$.

$$\begin{aligned}\frac{d\phi_{12}}{dT}&=-\frac{K}{T}\sum_{\langle jl\rangle}\langle\sigma_1\sigma_2(\sigma_j\sigma_l-\langle\sigma_j\sigma_l\rangle)\rangle\\ &=\frac{-2}{NzKk_B{}^2T^3}\langle(E_s-\langle E_s\rangle)^2\rangle\\ &=-\frac{2}{NzKk_BT}C_s,\end{aligned}\tag{4.1}$$

where E_s is the total energy and C_s the specific heat of the system when our system is regarded as an equivalent spin system, and z the number of nearest neighbors. Thus, just above the transition point dD_{s2}/dT can be negatively (positively) infinite for ferro- (antiferro-) magnetic interactions.

We now turn to the discussion of D_{s1}, (3.17) and (3.33). Apart from m in the denominator of (3.17), the singularity of D_{s1}, if any, must be contained in the quantity $\langle e^{-\mathcal{K}_0}\rangle$. This quantity involves the correlations of maximum $2z$ spins, and reliable estimate of the nature of singularity appears to be difficult. Nevertheless we can make a definite statement and also make some conjecture regarding the nature of the singularity of S_{s1}.

First, let us note that the diffusion constant D calculated in I [I(3.15) and I(3.11)] can be put in the following form (here we must again exclude the case of antiferromagnetic interactions below the transition temperature):

$$D\chi=a^2g\langle e^{-\mathcal{K}_0}\rangle.\tag{4.2}$$

This, combined with (3.17), yields the following relation between D and D_{s1}:

$$2(1+m)D_{s1}=D\chi.\tag{4.3}$$

This means that if we know that the AB-exchange mechanism dominates the diffusion process, the ratio $(1+m)D_s/D\chi$ does not contain any singularity at the transition temperature, which can be checked experimentally.

Next, we conjecture that $\langle e^{-\mathcal{K}_0}\rangle$ as a function of temperature may have a positive infinite slope at the transition temperature. Before going into this, it is interesting to observe that we can give a simple physical interpretation to the quantity $\langle e^{-\mathcal{H}_0}\rangle$ which is written more explicitly as

$$\sum_{\{\sigma\}_N} e^{(\mathcal{H}-\mathcal{H}_0)} \Big/ \sum_{\{\sigma\}_N} e^{\mathcal{H}}, \tag{4.4}$$

where $\mathcal{H}$ is, in the terminology of the equivalent Ising spin system, $-(k_BT)^{-1}$ times the total spin Hamiltonian of the system, whereas $\mathcal{H}-\mathcal{H}_0$ is $-(k_BT)^{-1}$ times the total Hamiltonian of the system in which all the interactions involving the spins σ_1 and σ_2 are cut off. Thus, (4.4) is written as

$$e^{-\Delta F_s/k_BT}, \tag{4.5}$$

where ΔF_s is the activation free energy for the removal of the spins σ_1 and σ_2 to the infinite distance. Our conjecture may then be stated that ΔF_s decreases infinitely rapidly with increasing temperature at the transition point.

We now enumerate the reasons for making such a conjecture. First, let us consider the derivative of $\langle e^{-\mathcal{H}_0}\rangle$ with respect to the temperature. The temperature enters in this quantity (1) through $\mathcal{H}_0$ and (2) through the equilibrium distribution function on averaging. Upon differentiation, the former gives only a finite quantity, and thus only the latter is considered. We then obtain

$$\frac{d}{dT}\langle e^{-\mathcal{H}_0}\rangle \cong -\frac{1}{T}\langle e^{-\mathcal{H}_0}(\mathcal{H}-\langle\mathcal{H}\rangle)\rangle. \tag{4.6}$$

Since

$$\mathcal{H}=K\sum_{\langle jl\rangle}\sigma_j\sigma_l \tag{4.7}$$

contains the spin variables of the sites arbitrarily distant from σ_1 and σ_2, (4.6) is a sum of spin correlations whose range can become very large near the transition point and (4.6) may become positively or negatively infinite at the transition point, if we exclude the possibility of cancellation of contributions, which appears unlikely since spins are contained in bilinear forms where only nearest-neighbor spins are combined. The sign of this quantity may be inferred, if we note that ΔF_s vanishes at the high-temperature limit whereas it reduces to a finite positive value at the absolute zero. Thus it is plausible to suppose that $-\Delta F_s$ and hence $e^{-\Delta F_s/k_BT}$ are increasing functions of the temperature. This may also be seen as follows: consider a distribution function of the form,

$$p_N(\{\sigma\}_N)=[1+a\sum_{\langle jl\rangle}(\sigma_j\sigma_l-\langle\sigma_j\sigma_l\rangle)]p_N{}^e(\{\sigma\}_N), \tag{4.8}$$

where a is a positive number. If we restrict ourselves to the case of ferromagnetic interactions, since one can easily modify the argument for the case of antiferromagnetic interactions, we see that the neighboring spins tend to align each other in this state more strongly than in equilibrium. Therefore, we may have

$$\sum_{\{\sigma\}_N} p_N(\{\sigma\}_N)e^{-\mathcal{H}_0} < \sum_{\{\sigma\}_N} p_N{}^e(\{\sigma\}_N)e^{-\mathcal{H}_0}.$$

That is,

$$\langle e^{-\mathcal{H}_0}(\mathcal{H}-\langle\mathcal{H}\rangle)\rangle<0 \tag{4.9}$$

implying that (4.6) may be positive.

Although the argument presented here is by no means rigorous, it makes plausible the supposition that the quantity $\langle e^{-\mathcal{H}_0}\rangle$ and hence $(1+m)D_{s1}$ (ferromagnetic) or D_{s1} (antiferromagnetic) have positively infinite slope at the transition point.

It is appropriate here to mention two relevant experiments. One is the measurement of the self-diffusion constant of a one-component fluid near the critical point.[7] It was found that ρD_s as a function of temperature, with ρ the density, exhibits a dip *just below* the transition point. This is consistent with our conjecture that $(1+m)D_{s1}$ has a positively infinite slope at the transition point because $1+m$ is proportional to the density for lattice gas. Since in this case diffusion is likely to occur through holes, AA^* exchange will not be important. The second relevant experiment is the measurements of self-diffusion constants of Cu or Zn isotopes in CuZn alloys which undergo order-disorder transitions.[8] The self-diffusion constants as a function of the temperature have been found to exhibit kinks near the transition point with steeper slopes below the transition point than above. However, the temperatures at which the kinks occur are found to be above the transition temperature determined by other methods and the discrepancies amount to several percent of the transition temperature. This may be understood again by supposing that the true transition point is characterized by the temperature where the self-diffusion constant has a positive infinite slope rather than a kink, although more detailed experiments are needed to confirm such a supposition.

5. CONCLUDING REMARKS

In the preceding sections we have calculated the self-diffusion constant for simple time-dependent Ising models. Near the critical point, the self-diffusion constant does not vanish although its slope may show anomalous behaviors. This is in contrast to the ordinary diffusion constant which vanishes at the critical point. This difference is due to the difference in the nature of the thermodynamic driving forces for diffusion in the respective cases. For the ordinary diffusion, the driving force is associated with the concentration gradient of AB atoms. Because of the anomalous concentration fluctuation near the transition point, the concentration gradient gives rise to very small driving forces. For the

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[7] J. D. Noble and M. Bloom, Phys. Rev. Letters **14**, 250 (1965).

[8] A. B. Kuper, D. Lazarus, J. R. Manning, and C. T. Tomizuka, Phys. Rev. **104**, 1536 (1956).

self-diffusion, the driving force is associated with the concentration of isotopes which is not affected by critical fluctuations directly, and hence the self-diffusion constant exhibits only milder anomalies at the transition point.

Another point to note in this work is that the nature of the singularity depends on the detailed mechanism for diffusion process such as AB exchange or AA^* exchange. This is in contrast to the equilibrium properties[2] whose asymptotic behaviors near the critical point seem to be determined only by gross features of the model such as the dimensionality or whether we have Heisenberg or Ising models. Finally, the additivity of the diffusion constants arising from different diffusion mechanisms in the local equilibrium approximation may be used to check the validity of this approximation experimentally.

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APPENDIX

Here we shall demonstrate the equivalence of the ansatz (3.4) and the local equilibrium approximation. The local equilibrium distribution function $p_N{}^L(\{S\}_N)$ must satisfy among others the condition (3.1),

$$\sum_{\text{i.d.}} p_N{}^L(\{S\}_N)=p_N{}^e(\{\sigma\}_N). \tag{A1}$$

Thus, $p_N{}^L$ has the following form

$$p_N{}^L(\{S\}_N)=p_N{}^e(\{S\}_N)[1+\sum_j(u_j'-f\sigma_j')h_j], \tag{A2}$$

where primed quantities imply that the equilibrium averages of the quantities have been subtracted. f is a constant determined by (A1) and h_j describes the inhomogeneous isotope distribution. Since in equilibrium isotopes are randomly distributed over the sites occupied by atoms A and A^*, we have

$$\sum_{\text{i.d.}} p_N{}^e(\{S\}_N)u_j/p_N{}^e(\{\sigma\}_N)=\tfrac{1}{2}(1+\sigma_j)c. \tag{A3}$$

Thus, substituting (A2) into (A1) and using (A3) as well as the fact that

$$\sum_{\text{i.d.}} p_N{}^e(\{S\}_N)=p_N{}^e(\{\sigma\}_N) \tag{A4}$$

we find that

$$f=\tfrac{1}{2}c. \tag{A5}$$

h_j can be obtained by calculating the average of u_j' in $p_N{}^L$ which is equal to the average of $u_j'-\frac{1}{2}\sigma_j'$ because of (A1), namely,

$$\bar{u}_j'\equiv\sum_{\{S\}_N} u_j'p_N{}^L(\{S\}_N)=\bar{u}_j'-\tfrac{1}{2}\bar{\sigma}_j'$$
$$=\sum_l\langle(u_j'-\tfrac{1}{2}\sigma_j')(u_l'-\tfrac{1}{2}\sigma_l')\rangle h_l.$$

If we use

$$\langle(u_j'-\tfrac{1}{2}\sigma_j')(u_l'-\tfrac{1}{2}\sigma_l')\rangle=\tfrac{1}{2}c(1-c)(1+m)\delta_{jl}$$

which can be easily verified by making use of the fact that isotopes are randomly distributed in equilibrium, we obtain

$$h_j=2\bar{u}_j'/[c(1-c)(1+m)], \tag{A6}$$

which together with (A5), completely determine $p_N{}^L$ in terms of $\bar{u}_j$.

Using these results let us now compute the quantity,

$$\sum_{\text{i.d.}} u_jp_N{}^L(\{S\}_N)=\sum_{\text{i.d.}} u_jp_N{}^e(\{S\}_N)$$
$$+\sum_l\sum_{\text{i.d.}} u_j(u_l'-\tfrac{1}{2}c\sigma_l')h_lp_N{}^e(\{S\}_N). \tag{A7}$$

The first term simply becomes

$$\tfrac{1}{2}(1+\sigma_j)cp_N{}^e(\{\sigma\}_N). \tag{A8}$$

In the second term, only the terms with $l=j$ contribute and one easily finds that it becomes

$$c(1-c)\tfrac{1}{2}(1+\sigma_j)h_jp_N{}^e(\{\sigma\}_N). \tag{A9}$$

With the use of (A6) and adding (A8) and (A9) and using (3.5), we finally obtain

$$\sum_{\text{i.d.}} u_jp_N{}^L(\{S\}_N)=\tfrac{1}{2}(1+\sigma_j)c\frac{\bar{u}_j}{u_e}p_N{}^e(\{\sigma\}_N) \tag{A10}$$

which is identical to the ansatz (3.4). This completes the equivalence proof of the ansatz (3.4) and the local equilibrium approximation.