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# Isothermal Relaxation

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A mathematical description of isothermal relaxation is presented. The equations are based on quite general principles, and an extension of Landau's theory of second-order transformations. Qualitative features of the experimental observations can be explained.

## I. INTRODUCTION

THE rate of phase transformations or the time-development of one phase changing into another poses an interesting problem. In its complete generality, the problem is akin to the well-known Gibbs program in statistical mechanics, and is extremely difficult. However, some phenomenological relaxation-time approach can be tried and the problem partially clarified. In this spirit, a discussion by Tempereley is pertinent.[1] He considers irreversible processes generally associated with a phase transition and defines three categories. First, the rate of transformation is essentially governed by the "free-energy barrier" between the two states, as in a supercooled gas. Secondly, there are intrinsic irreversible processes appearing at the transition, for example, eddy currents generated in attempting to change the magnetization of a ferromagnetic metal. Thirdly, in certain transitions, the relaxation time gets longer and longer as the transition point is approached.

The first problem was mathematically formulated by Kramers[2] in terms of the escape of a Brownian particle trapped in a potential well across a barrier. It is connected with the definition of a metastable state and is often discussed through a potential with two minima.[3] Here a quasithermodynamic theory has long seemed plausible. The second category is the hardest to discuss mathematically, because intrinsic irreversible processes are inevitable at the transition. The third type seems amenable again to a quasithermodynamic treatment, since near the transition point the rate processes are slow. There may be no free-energy barrier, and the transition is presumably of the second order. We are concerned with a mathematical description of this category.

Tempereley illustrates the fact of long relaxation time by a mechanical analogy. If $x$ represents a possible displacement of a mechanical system, the condition for equilibrium is $\partial V/\partial x=0$, where $V$ is the potential energy. The equilibrium is stable or unstable according as $\partial^2V/\partial x^2$ is positive or negative. If $\partial^2V/\partial x^2$ is positive but small, the system described by

$$md^2x/dt^2+x\partial^2V/\partial x^2=0$$

is just stable. The period of oscillation tends to become long as $\partial^2V/\partial x^2\to 0$. Although the thermodynamic functions possess many properties of the potential energy—for instance, they may be stationary at equilibrium—there is no statistical mechanical analog of the effective mass and the mathematical analogy is not particularly apt.

As mentioned above, the third category may be relevant to second-order transformations. It is well known that a general theory of such processes was given by Landau.[4] One would naturally look for a time-dependent extension of the theory to illustrate Tempereley's third category. This will be tried here. Recently attempts have been made, in connection with the theory of superconductivity, to derive such time-dependent equations from more basic principles. No such attempt will be made here. But we shall try to formulate the theory in a quite general manner and discuss some questions of principle involved in such a quasithermodynamic extension.

## II. EQUATIONS FOR ISOTHERMAL RELAXATION

Following Landau,[4] we introduce an order parameter $\eta$, supposed dimensionless. The ordered phases are characterized by nonvanishing values of $\eta$. In analogy with other evolution equations, such as the Schrödinger, Boltzmann, or Liouville equation, this equation will be of first order in time, that is, we have an equation for $\partial\eta/\partial t$. Such an equation, which is our starting point, was written by Landau and Khalatnikov[5] in connection with their work on liquid He II:

$$-\partial\eta/\partial t=\gamma\partial\Phi/\partial\eta\equiv\gamma H[\eta]. \quad (1)$$

Here $\gamma$ is an appropriate kinetic coefficient; its operational definition is provided by Eq. (19) below. $\Phi$ and consequently the operator $H[\eta]$ is related to the free energy of the system, since phase transformations are governed by free-energy changes. We shall take everything to be real valued only, although the order parameter can be complex in certain physical problems, such as superconductivity, and appropriate generalizations are possible. Notice that $H[\eta]$ need not be linear in $\eta$. In fact, in general, it is *nonlinear*.

To see the significance of $H[\eta]$, we note that when $\partial\eta/\partial t=0$ we have the stationary solutions, among which we have the thermodynamic solutions. Thus the de-

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[1] H. N. V. Tempereley, *Changes of State* (Cleaver-Hume Press, London, 1956), p. 31.

[2] H. Kramers, Physica **7**, 284 (1941).

[3] See, for instance, R. B. Griffiths, C. Weng, and J. S. Langer, Phys. Rev. **149**, 301 (1966).

[4] L. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1958), p. 430.

[5] L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk SSSR **96**, 469 (1954).

termination of $H[\eta]$ may be possible under some circumstances from the knowledge of thermodynamic states. Indeed,

$$\partial\Phi/\partial\eta \equiv H[\eta]=0 \qquad (2)$$

is simply the requirement that the free energy be minimized with respect to the order parameter $\eta$. We also note that under some conditions $\partial/\partial\eta$ may have to be replaced by a functional derivative.

The free energy is, of course, also a function of other thermodynamic variables, in particular the temperature $T$. For equilibrium states, temperature has a well-defined operational meaning, and so Eq. (2) is well defined. On the other hand, when we substitute the operator $H[\eta]$ from (2) into Eq. (1), it is not well defined in general and requires careful analysis. If we could carry out the Gibbs program, the temperature of a system would arise as a very complicated function of dynamical variables and would reduce to the correct thermodynamical variable in the equilibrium state. Unfortunately, this is seldom possible. For rather long-lived metastable states,[6] temperature can be assigned to the system and is in fact taken to be the same as that of the surroundings. This provides a clue to a possible generalization in our case. We are concerned with long relaxation-time processes, and energy exchange of the material under investigation with the environment is rather slow. Since the environment is comparatively large and remains essentially unmodified (the assumption of long relaxation time), we can regard the temperature appearing in Eq. (1) as that of the surrounding heat bath. This definition is a natural extension of the equilibrium definition. In equilibrium, of course, the two temperatures are equal and in Eq. (2) one can regard the temperature to be of either the bath or the material.

This definition of temperature is used in the so-called isothermal relaxation processes. So our Eq. (1) may be regarded as formally providing a mathematical description of such processes.

The introduction of the heat bath for defining the temperature immediately raises the question of uniqueness of the determination of $H[\eta]$ from the equilibrium conditions. The problem cannot be answered in its entirety without a more fundamental approach. We shall attempt to make it plausible that for isothermal processes the problem is not very serious.

In order to do this, we shall utilize an idea introduced by Bragg and Williams[7] in their work on the attainment of equilibrium of an alloy and regard temperature itself as a variable in time. However, we shall use a considerably simplified version of their procedure. Since the rate processes are assumed to be slow, we suppose that the system can be thought of as passing through successive equilibrium stages, each stage characterized by a temperature $T$. Initially the system is at a temperature $T_i$ attained by keeping it in contact with a heat bath at that temperature; it is then brought in contact with another heat bath at a temperature $T_f$. $T_i$ and $T_f$ both lie in the neighborhood of the transition temperature $T_c$. Following Bragg and Williams, the temperature of the body changes according to an equation

$$dT/dt=-(T-T_f)/\tau. \qquad (3)$$

Here $\tau$ is a phenomenological temperature relaxation time and depends on the coupling between the bath and the material under investigation, as well as on the state of the material, i.e., on $\eta$. Therefore, (1) and (3) become coupled equations when we use $T$ of Eq. (3) as the temperature in (1). However, in the vicinity of the critical temperature the value of $\eta$ even in the ordered state is small and, in the spirit of the Landau theory, the dependence of $\tau$ on $\eta$ can be neglected. It is then possible to solve (3) independently of (1). We obtain

$$T=T_ie^{-t/\tau}+T_f(1-e^{-t/\tau}). \qquad (4)$$

Introducing this $T$ in Eq. (1), the resulting equation can be solved under some circumstances (see the Appendix). However, for isothermal relaxation processes two limiting situations are seen to be of importance. First, the rate of temperature change is so fast compared with other physically interesting rates ("quenching") that the limit $\tau\rightarrow 0$ in Eq. (4) is relevant. This gives

$$T\approx T_f. \qquad (5)$$

Secondly, the rate of temperature change is extremely slow ("annealing") in comparison with other rates, and we may take the limit $\tau\rightarrow\infty$ in Eq. (4). This yields

$$T\approx T_i. \qquad (5')$$

Equations (5) and (5′) are the conditions for isothermal relaxation. In these limiting cases the actual value of $\tau$ is unimportant, and the coupling of the material and the bath formally disappears. One should add that the assertion rests on the assumption that the effect of the surroundings is felt in the temperature variable alone. In any case all the rates are assumed to be slow.

Finally, the sign of the left-hand side of Eq. (1) is not determined by (2). It is fixed by the physical requirement that above the transition temperature the perturbations decay toward the normal state.

## III. A SIMPLE EXAMPLE

We start with the case treated by Landau and Lifshitz.[4] The total free energy as a function of $\eta$ regarded as independent of spatial coordinates is written as

$$\Phi(\eta)=\Phi_N+a\eta^2+b\eta^4. \qquad (6)$$

$\Phi_N$ is the free energy of the normal or disordered state.

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[6] For second-order transformations, metastability is impossible, although the time for actual rearrangement of atoms may be long. See Ref. 4.

[7] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. (London) **96,** 699 (1934).

The properties of the coefficients $a$ and $b$ of interest to us are

$$a(T_c)=0, \tag{7}$$

$$a(T)\gtrless 0 \quad \text{for} \quad T\gtrless T_c; \tag{8}$$

and in the neighborhood of the critical temperature $T_c$

$$a(T)=a_0(T-T_c), \qquad a_0>0, \tag{9}$$

$$b(T_c)>0, \tag{10}$$

and by continuity

$$b>0 \tag{11}$$

in the vicinity of $T_c$. Note that the assumptions that $a$ and $b$ are well-behaved in the temperature range considered may be quite restrictive for actual physical applications.[8] In (8), (9), and (11) the temperature $T$ may be $T_i$ or $T_f$, depending on the situation.

The minimization condition is

$$d\Phi/d\eta\equiv 2a\eta+4b\eta^3=0. \tag{12}$$

Above the critical temperature, the only solution is $\eta=0$. Below the critical temperature, besides $\eta=0$, there is a new solution,

$$\eta_0{}^2=-a/2b. \tag{13}$$

$\eta_0$ is real, because $a$ is negative below $T_c$. Equation (13) gives $\Phi(\eta)=\Phi_N-(a^2/4b)$, which is lower than the free energy with $\eta=0$.

Corresponding to Eq. (1) we can now write for the time-dependent case

$$d\eta/dt=-\gamma(2a\eta+4b\eta^3). \tag{14}$$

Equation (14) is an ordinary first-order nonlinear equation in time and can be easily solved with the initial condition

$$\eta=\bar{\eta} \quad \text{at} \quad t=0. \tag{15}$$

The solution is

$$\eta^2=\frac{\eta_0{}^2\exp(-4a\gamma t)}{\exp(-4a\gamma t)-1+(\eta_0/\bar{\eta})^2}. \tag{16}$$

Observe that above $T_c$, $a>0$, $\eta^2$ diminishes to zero, the correct equilibrium value; below $T_c$, $a<0$, and the exponentials cancel out for large $t$, giving $\eta^2=\eta_0{}^2$, the correct equilibrium value. These are independent of the initial condition (15) as they should be. The long time behavior is governed by an exponential;

$$\begin{aligned}\eta&=[\eta_0{}^2\bar{\eta}^2/(\eta_0{}^2-\bar{\eta}^2)]^{1/2}\exp(-2a\gamma t), && T>T_c;\\ \eta&=\eta_0+[\tfrac{1}{2}\eta_0(\bar{\eta}^2-\eta_0{}^2)\exp(4a\gamma t)/\bar{\eta}^2], && T<T_c.\end{aligned} \tag{17}$$

Note that as formally defined by (13), $\eta_0{}^2$ above the critical temperature is a negative quantity. We can introduce a relaxation time $T_1{}^+$ above the critical temperature by

$$\exp(-2a\gamma t)\equiv\exp(-t/T_1{}^+). \tag{18}$$

Then

$$T_1{}^+=1/2a\gamma=1/2a_0\gamma(T-T_c), \tag{19}$$

or

$$T_1{}^+(T-T_c)=\text{const}. \tag{20}$$

A similar equation holds for the relaxation time $T_1{}^-$ below $T_c$ except for a factor of 2. An analogous relaxation time was actually derived by Landau and Khalatnikov.[5] Equation (20) is reminiscent of the Korringa relation for paramagnetic relaxation.[9] This relaxation time gets long as $T\rightarrow T_c$. However, the rate of change for short time interval is not really a pure simple exponential.

Exactly at $T=T_c$, $a=0$, and then the nonlinear part determines the rate. We have

$$d\eta/dt=-4b\gamma\eta^3. \tag{21}$$

The solution with the initial condition (15) is

$$\eta^2=\bar{\eta}^2/(8b\gamma t\bar{\eta}^2+1). \tag{22}$$

$\eta$ decays to zero as it should at the critical temperature, and the decay rate goes essentially as $t^{-1/2}$.

Since $a$ and $b$ are determined from thermodynamic measurements, the relaxation time $T_1$ determines the kinetic coefficient $\gamma$.

It turns out that using Eq. (4) itself for the temperature $T$, it is still possible to reduce Eq. (14) to quadrature. Details are given in the Appendix.

## IV. A COMPLICATED EXAMPLE

We now pass over to a much more complicated case and examine the situation that the free energy may also depend on the gradient of the order parameter. This leads to a nonlinear elliptic equation in the equilibrium case and to a nonlinear partial differential equation of the parabolic type for the time-dependent case. We shall discuss the latter part only in a linearized version.

Consider the total free energy

$$\Phi[\eta]=\int F[\eta]d^3x,$$

where the free-energy density is

$$F[\eta]=F_N+A\eta(\mathbf{x})^2+B\eta(\mathbf{x})^4+\tfrac{1}{2}C\,|\,\nabla\eta\,|^2. \tag{23}$$

The coefficients $A$ and $B$ have the dimensions of energy per unit volume and $C$ has the dimension of energy over length. The coefficient $C$ which will be found to be connected with the diffusion coefficient is positive in the neighborhood of $T_c$. The free energy is now a functional of $\eta(\mathbf{x})$ and the Euler-Lagrange variational equation gives

$$\frac{\partial F}{\partial\eta}-\frac{\partial}{\partial x}\frac{\partial F}{\partial(\partial\eta/\partial x)}-\frac{\partial}{\partial y}\frac{\partial F}{\partial(\partial\eta/\partial y)}-\frac{\partial}{\partial z}\frac{\partial F}{\partial(\partial\eta/\partial z)}=0,$$

or

$$2A\eta+4B\eta^3-C\nabla^2\eta=0. \tag{24}$$

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[8] For a critique of the Landau theory, see M. E. Fisher, J. Math. Phys. 5, 944 (1964).

[9] J. Korringa, Physica 16, 601 (1959).

Before we use (24) in (1), however, we must multiply $A$, $B$, and $C$ by a quantity of the dimension of volume. This may be taken to be the volume of the system; but then the relaxation time will be inversely proportional to the volume. In actual practice the order parameter, even if it is uniform in the equilibrium stage as in Sec. III, remains so only over a certain effective size determined by such things as domain size, impurity concentration, etc. Quite generally we may call this region $\xi^3$ and define

$$a = A\xi^3, \qquad b = B\xi^3, \qquad c = C\xi^3. \tag{25}$$

$\xi$ is a characteristic length. The existence of such a characteristic coherence length is implicit in the very fact that $F[\eta]$ depends on the gradient of $\eta(\mathbf{x})$. That the relaxation time either decreases with volume or is independent of it was argued by Griffiths, Weng, and Langer.[3] Consequently, we consider the equation

$$2a\eta + 4b\eta^3 - c\nabla^2\eta = 0. \tag{26}$$

We consider solutions depending on radial distance only and no angle-dependent solutions. We have therefore

$$\frac{d^2\eta}{dr^2} + \frac{2}{r}\frac{d\eta}{dr} - \frac{2a\eta}{c} - \frac{4b\eta^3}{c} = 0. \tag{27}$$

We have to specify the acceptable class of solutions. Obviously we must have $\eta$ bounded everywhere, sufficiently smooth, and by definition positive everywhere. A constant $\eta$ is perfectly acceptable, since it leads to the total free energy in (23) proportional to the volume of the system.

Now we are ready to discuss the solutions of Eq. (27). Put

$$r = \alpha\rho, \qquad \eta = \beta u, \tag{28}$$

where

$$\alpha^2 = c/2\,|\,a\,|, \qquad \beta^2 = |\,a\,|/2b. \tag{29}$$

Above the critical temperature, $a$ is positive, and we get

$$d^2u/d\rho^2 + (2/\rho)\,du/d\rho - u - u^3 = 0. \tag{30}$$

Below the critical temperature, $a$ is negative, and we obtain

$$d^2u/d\rho^2 + (2/\rho)\,du/d\rho + u - u^3 = 0. \tag{31}$$

We shall employ the standard phase plane plots to discuss the solutions of Eqs. (30) and (31).

(i) Above the critical temperature, Eq. (30).

Let us define

$$v = du/d\rho, \tag{32}$$

and the phase energy

$$E_1 = \tfrac{1}{2}v^2 - \tfrac{1}{2}u^2 - \tfrac{1}{4}u^4. \tag{33}$$

Then from (30)

$$dE_1/d\rho = v[d^2u/d\rho^2 - u - u^3] = -(2/\rho)v^2 \leq 0. \tag{34}$$

$dE_1/d\rho$ is zero only when $v$ remains zero as $\rho$ changes; otherwise $E_1$ decreases as the reference point moves in the $uv$ plane (Fig. 1).

For $E_1 = 0$ and small $v$, $u$, we get $v^2 - u^2 = 0$, or a pair of straight lines at 45° to the $u$, $v$ axes. For large $v$, we have $v^2 - \frac{1}{2}u^4 = 0$, i.e., two parabolas. The entire phase plane is divided by these lines into four distinct parts. The two parts containing the $v$ axis have $E_1 > 0$, and $E_1$ increasing outward. The other two parts containing the $u$ axis have $E_1 < 0$ and the phase energy diminishes as we proceed along $v = 0$ away from the origin. Consequently, if we start from any finite value of $u$ and $v = 0$, the representative point is constrained to move outward and $u$ becomes unbounded. Starting at any finite value of $v$ produces a singularity at the origin. The only acceptable solution is $\eta = 0$, which is the point $u = 0$, $v = 0$, the crossing point of two "equipotential" curves. This case is rather trivial.

(ii) Below the critical temperature, Eq. (31).

We construct again the phase energy function

$$E_2 = \tfrac{1}{2}v^2 + \tfrac{1}{2}u^2 - \tfrac{1}{4}u^4, \tag{35}$$

and as before

$$dE_2/d\rho \leq 0. \tag{36}$$

Start with $E_2 = 0$; for $v = 0$

$$\tfrac{1}{2}u^2(1 - \tfrac{1}{2}u^2) = 0, \tag{37}$$

and there are three solutions $u = 0$, $\pm\sqrt{2}$; $u = 0$ is degenerate. For small but positive $E_2$, there are essentially circular equipotential curves around the origin (Fig. 2), which collapse at the origin. Considering $v = 0$ and $E_2 > 0$,

$$E_2 = \tfrac{1}{2}u^2 - \tfrac{1}{4}u^4$$

or

$$u^2 = 1 \pm [1 - 4E_2]^{1/2}.$$

So long as $0 \leq E_2 < \frac{1}{4}$ we have 4 real $u$ solutions, two smaller and two larger than 1 in absolute value. $E_2 = \frac{1}{4}$ is the critical value, when we have only two solutions $u = \pm 1$, a degenerate situation requiring careful study. For $E_2$ negative, there are always two real $u$ solutions, but these equipotentials never cross the $v$ axis, because for $u = 0$, $v$ cannot then be real.

Examining $E_2 = \frac{1}{4}$ we find for $u = 0$, $v = \pm\frac{1}{2}\sqrt{2}$. Hence, this equipotential separates a diamond-shaped region about the origin, inside which the equipotentials are closed curves with energy values diminishing toward the origin. Beyond $u = \pm 1$, the equipotentials have lower and lower energy values as we move out along the $u$ axis. Along the $v$ axis the energy is steadily increasing as we move out.

We have thus found two solutions $u = 0$ and $u = 1$ which are presumably stationary ($u = -1$ is neglected, because a negative order parameter is meaningless). $u = 0$, or $\eta = 0$ gives the normal-state free energy. $u = 1$ or $\eta_0{}^2 = \beta^2 = |\,a\,|/2b$ gives us the same ordered state as we obtained in the example of Sec. III.

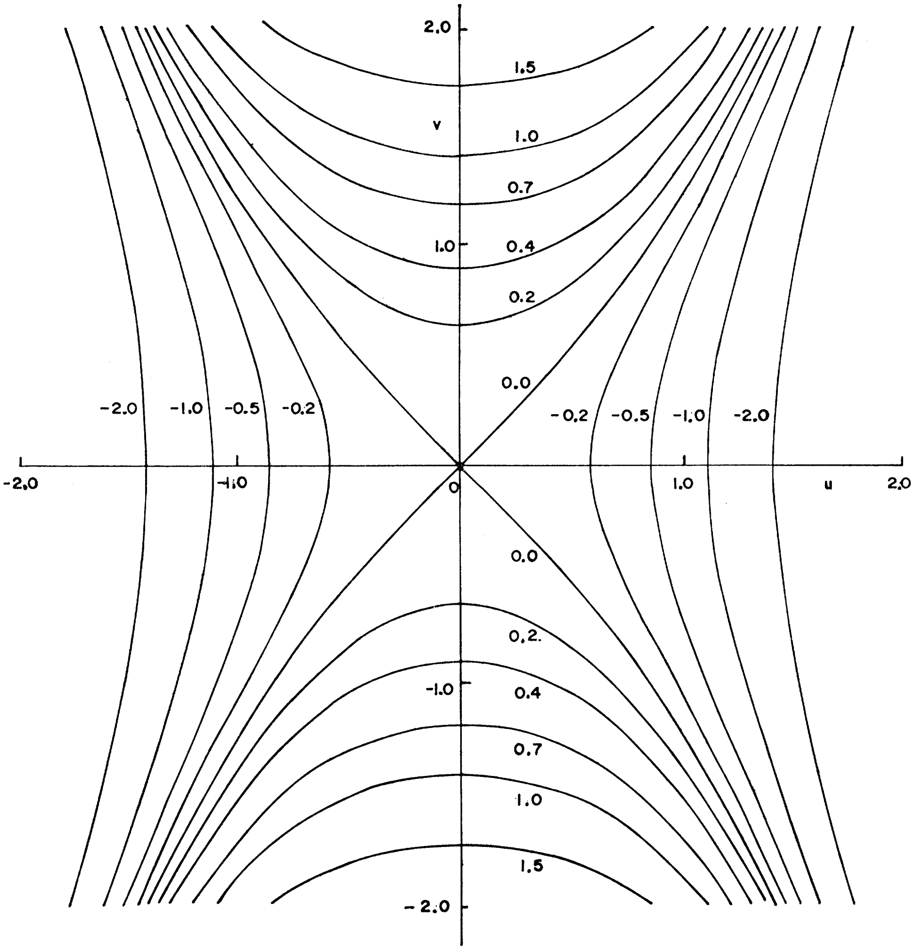

FIG. 1. The phase plane for Eq. (33). $u=0, v=0$ is the only critical point.

There are other well-defined bounded positive solutions, in fact an entire continuum of them, in the fourth quadrant inside the diamond-shaped region. These start with finite $u$, $v=0$ at $\rho=0$ and then go to zero as $\rho$ varies, in accordance with Eq. (36). Such a possibility is indicated by the dashed line in Fig. 2. Since $u\rightarrow 0$ as $\rho$ increases, such solutions do not have, so to speak, any long-range order.

We now show that the solution $\eta_0$ gives a minimum of the free energy. Write

$$\eta=\eta_0+\epsilon\phi(\mathbf{x}). \tag{38}$$

Here $\phi(\mathbf{x})$ is a bounded spatially varying function, and $\epsilon$ is a small parameter. Considering the free energy of Eq. (23),

$$\Phi[\eta]=\int F_N d^3x+\int d^3x[A(\eta_0+\epsilon\phi)^2 +B(\eta_0+\epsilon\phi)^4+\tfrac{1}{2}C\,|\,\nabla(\eta_0+\epsilon\phi)\,|^2],$$

and keeping terms up to order $\epsilon^2$,

$$\begin{aligned}\Phi[\eta]&=\int F_N d^3x+\int d^3x[A\eta_0^2+B\eta_0^4+2\epsilon\eta_0\phi(A+2B\eta_0^2)\\&\qquad+\epsilon^2(A\phi^2+6B\eta_0^2\phi^2+\tfrac{1}{2}C\,|\,\nabla\phi\,|^2)]\\&=\int F_N d^3x-VA^2/4B\\&\qquad+\epsilon^2\int[\tfrac{1}{2}C\,|\,\nabla\phi\,|^2-2A\phi^2]d^3x.\end{aligned} \tag{38'}$$

The coefficient of $\epsilon$ vanishes. The coefficient of $\epsilon^2$ is positive, since $A$ is negative. The value of free energy for $\eta_0$ is lower than that of the normal state. The short-range order solutions have higher free energy. Note that in (38′) no statement about the angular dependence of $\phi(\mathbf{x})$ is necessary. The fact that the thermodynamic solutions are again the same as those of the previous example is not surprising, since we have

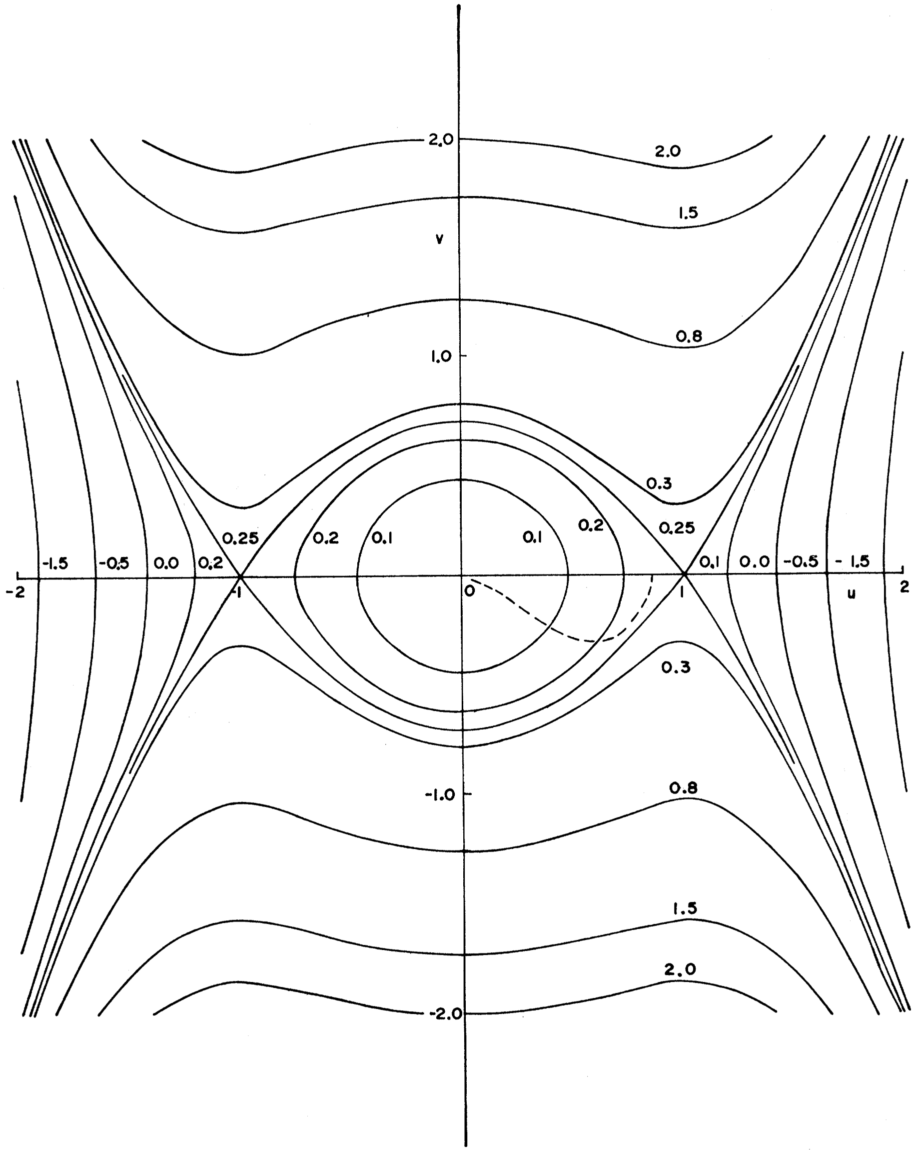

FIG. 2. The phase plane for Eq. (35). $v=0$, $u=0$, $\pm 1$ are three critical points.

provided no stabilizing agency for the spatially varying solutions.

We now write the equation for the time-dependent problem from Eq. (1):

$$\partial\eta/\partial t=\bar{c}\nabla^2\eta-2\bar{a}\eta-4\bar{b}\eta^3, \tag{39}$$

where $\bar{a}=a\gamma$, $\bar{b}=b\gamma$, and $\bar{c}=c\gamma$. The recognition of $\bar{c}$ as a diffusion-like term is immediate. Equation (39) is a nonlinear partial differential equation of the parabolic type. Recently, much progress has been made concerning the solutions of such equations.[10] However, we shall simply confine ourselves to considering perturbations about the stable solutions we have obtained and study how these decay.

Above the critical temperature $\eta=0$ is the stationary state. Hence, linearization means directly dropping the nonlinear term;

$$\partial\psi(\mathbf{x},t)/\partial t=\bar{c}\nabla^2\psi(\mathbf{x},t)-2\bar{a}\psi(\mathbf{x},t). \tag{40}$$

Put

$$\psi(\mathbf{x},t)=\phi(\mathbf{x},t)\exp(-2\bar{a}t); \tag{41}$$

then

$$\partial\phi(\mathbf{x},t)/\partial t=\bar{c}\nabla^2\phi(\mathbf{x},t). \tag{42}$$

Given $\phi(\mathbf{x},0)$, the solution of (40) is

$$\psi(\mathbf{x},t)=\frac{\exp(-2\bar{a}t)}{(2\pi)^3}\int d\mathbf{k}[\exp(-k^2\bar{c}t)\times\int\exp[i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')]\phi(\mathbf{x}',0)d\mathbf{x}'. \tag{43}$$

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[10] F. Browder, Ann. Math. 80, 485 (1965).

If we choose for $\phi(\mathbf{x}', 0)$ a simple impulse function

$$\phi(\mathbf{x}', 0) = A\delta(\mathbf{x}'), \tag{44}$$

we get

$$\psi(\mathbf{x}, t) = \frac{A \exp(-2\bar{a}t)}{(4\pi\bar{c}t)^{3/2}} \exp(-r^2/4\bar{c}t). \tag{45}$$

The perturbations decay essentially by the exponential factor, $\exp(-2\bar{a}t)$. However, below the critical temperature, $\eta = 0$ is unstable.

Similarly, we consider linearization about the solution $\eta_0$ below $T_c$. Write

$$\eta = \eta_0 + \bar{\psi}(\mathbf{x}, t). \tag{46}$$

By taking into account (13), the linearized equation from Eq. (1) is

$$\partial\bar{\psi}(\mathbf{x}, t)/\partial t = \bar{c}\nabla^2\bar{\psi}(\mathbf{x}, t) + 4\bar{a}\bar{\psi}(\mathbf{x}, t). \tag{47}$$

The solution for an initial impulse is immediately written;

$$\bar{\psi}(\mathbf{x}, t) = \frac{A \exp(4\bar{a}t)}{(4\pi\bar{c}t)^{3/2}} \exp(-r^2/4\bar{c}t). \tag{48}$$

Remembering that $a$ is negative, we again find an exponential decay to the equilibrium value $\eta_0$, except for a factor of 2 difference from Eq. (45). The decay is not purely exponential, but if one defines a relaxation time $T_1^*$ corresponding to the exponential term, we have the behavior

$$T_1^* \sim 1/|T - T_c|.$$

Exactly at the critical temperature, the term with $a$ vanishes. Recalling that $\eta = 0$ at equilibrium at $T_c$, we get as the linearized version the ordinary diffusion equation

$$\partial\psi/\partial t = \bar{c}\nabla^2\psi,$$

and

$$\psi(\mathbf{x}, t) = [A/(4\pi\bar{c}t)^{3/2}] \exp(-r^2/4\bar{c}t). \tag{49}$$

Incidentally, such diffusion terms cannot be obtained in any obvious way in Tempereley's mechanical analogy.

## V. DISCUSSION

Quite apart from the limitations inherent in the examples discussed, a general theory of this type can explain only qualitative features of various experimental observations. It is apparent from Eq. (45) that the rate of transformation is not a pure exponential. This feature has been known for quite a long time.[11] There is an interplay of diffusion, and nucleation and growth. The diffusion term appears in our treatment to be temperature-independent only because we have restricted outselves to the neighborhood of $T_c$. Here the temperature dependence is naturally manifest in a term which is, so to speak, driving the phase transformation. A dependence of the type of Eq. (19) is qualitatively known to be present.

Many physical properties that change at the transition can be measured for the observation of the rate of the process. For instance, one can observe the Mössbauer splittings in the paramagnetic and the ferromagnetic phase.[12] It would be interesting to analyze the data by allowing for the diffusion term. The simple temperature dependence of Eq. (19) is typical of the Landau theory or the so-called mean-field theories. In thermodynamic equilibrium, deviations from these are known.[8] One can expect deviations from Eq. (19) in time-dependent processes. It would be interesting to know whether these follow the same pattern as in the equilibrium case.

On the theoretical side, the problem remains to derive Eq. (1) or similar equations from first principles. Presumably one starts from the density matrix of the entire system—the material and the heat bath—and looks for an equation of motion of the partial density matrix of the material. The coordinates of the bath can be treated as essentially in an equilibrium condition, provided that the long relaxation-time approximation holds. While the diagonal elements of the density matrix determines the thermodynamic part, the transitions are taken care of by the kinetic coefficient, but one must be able to recognize from a general standpoint the existence of an order parameter.

## APPENDIX

We want to show that the solution of the equations

$$d\eta/dt = -2a\gamma\eta - 4b\gamma\eta^3, \tag{A1}$$

$$dT/dt = -(T - T_f)/\tau, \tag{A2}$$

can be reduced to quadrature, if one neglects the dependence of $\tau$ on $\eta$. Then we have

$$T = T_f + (T_i - T_f)e^{-t/\tau}. \tag{A3}$$

Hence

$$T - T_c = (T_f - T_c) + (T_i - T_f)e^{-t/\tau}, \tag{A4}$$

and

$$\begin{aligned} 2\gamma a_0(T - T_c) &= 2\gamma a_0(T_f - T_c) + 2\gamma a_0(T_i - T_f)e^{-t/\tau} \\ &= \tfrac{1}{2}X + \tfrac{1}{2}Ye^{-t/\tau}, \end{aligned} \tag{A5}$$

where

$$X = 4\gamma a_0(T_f - T_c), \qquad Y = 4\gamma a_0(T_i - T_f). \tag{A6}$$

Hence (A1) becomes

$$d\eta/dt = -\tfrac{1}{2}[X + Ye^{-t/\tau}]\eta - 4b\gamma\eta^3. \tag{A7}$$

Putting

$$z = 1/\eta^2, \tag{A8}$$

we get

$$dz/dt - z(X + Ye^{-t/\tau}) = 8b\gamma, \tag{A9}$$

which is easily solved. If

$$\eta = \bar{\eta} \quad \text{at} \quad t = 0, \tag{A10}$$

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[11] S. Siegel, in *Phase Transformations in Solids* (John Wiley & Sons, Inc., New York, 1951), p. 380.

[12] D. E. Cox, C. Shirane, P. A. Flinn, S. L. Ruby, and W. J. Takei, Phys. Rev. **132**, 1547 (1963).

we have

$$\eta^{-2}\exp[-Xt+\tau Ye^{-t/\tau}]-\bar{\eta}^{-2}e^{\tau Y}$$
$$=8b\gamma\int_0^t \exp[-Xt'+\tau Ye^{-t'/\tau}]dt'. \quad \text{(A11)}$$

For the quenching case, $\tau\rightarrow 0$, and we get

$$\eta^{-2}e^{-Xt}-\bar{\eta}^{-2}=8b\gamma\int_0^t e^{-Xt'}dt'=8b\gamma\frac{1-e^{-Xt}}{X},$$

so that

$$\eta^2=e^{-Xt}/[(8b\gamma/X)(1-e^{-Xt})+\bar{\eta}^{-2}]$$
$$=\frac{\eta_0^2\exp[-4a_0\gamma(T_f-T_c)t]}{\exp[-4a_0\gamma(T_f-T_c)t]-1+(\eta_0/\bar{\eta})^2}. \quad \text{(A12)}$$

For the annealing case, $\tau\rightarrow\infty$, and

$$\tau Ye^{-t/\tau}\simeq\tau Y(1-t/\tau)=\tau Y-Yt.$$

Thus

$$\eta^{-2}\exp[-(X+Y)t+\tau Y]-\bar{\eta}^{-2}e^{\tau Y}$$
$$=8b\gamma e^{\tau Y}\int_0^t e^{-(X+Y)t'}\,dt'.$$

Hence

$$\eta^2=\frac{\eta_0^2\exp[-4a_0(T_i-T_c)\gamma t]}{\exp[-4a_0\gamma(T_i-T_c)t]-1+(\eta_0/\bar{\eta})^2}. \quad \text{(A13)}$$

These are the two special cases of Eq. (16) that are of interest in isothermal relaxation.

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# Critical Correlations in the Ising Model

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The Ising-model correlation function $C(R_{12})=\langle\mu_1\mu_2\rangle$ is studied in terms of a novel $N$-fold integral representation. This formula stems from a procedure proposed by Montroll and Berlin. The integral is estimated by maximizing the integrand, an approximation related to the spherical-model assumptions. The correlation function is not of the Ornstein-Zernike type, just above the critical point, but rather $C(R)\propto R^{-1-\eta}$ for $R\ll 1/\kappa$, and $C(R)\propto\kappa^\eta R^{-1}\exp(-\kappa R)$ for $R\gg 1/\kappa$. The correlation length $1/\kappa$ becomes infinite at the critical point. The calculated value $\eta=0.646$ is too large, reflecting the omission of important terms in the evaluation of the integral. The unusual mechanism inducing the nonclassical behavior is carefully examined.

## I. INTRODUCTION

THERE now exists a large body of evidence concerning anomalous behavior of correlation functions near critical points. For the nearest-neighbor Ising model, in particular, information has been obtained analytically in two dimensions, and numerically in three dimensions. There occur marked qualitative deviations from the correlations predicted by the classical theory of Ornstein and Zernike. In spite of this wealth of data, however, there has been very little progress toward a general analytic theory of the critical point. In fact, it has so far turned out to be remarkably difficult to recover anything but the Ornstein–Zernike correlation function from either soluble models or systematic approximations. In response to this difficulty, we have attempted to find a new formulation of the theory of critical correlations which might provide a means for calculating the known nonclassical behavior. Our attempt has not been completely successful, but we hope that several of our results may provide useful clues in the search for a correct theory.

We consider an Ising model consisting of $N$ spins with values $\mu_i=\pm 1$, $i=1,\cdots,N$, located at sites $\mathbf{r}_i$ on an $s$-dimensional cubic lattice. The energy $E$ is a simple ferromagnetic coupling of the form

$$E=-\tfrac{1}{2}J\sum_{i,j=1}^{N}v_{ij}\mu_i\mu_j. \quad (1.1)$$

Here the dimensionless $v_{ij}$ is a function only of the distance between the lattice points $|\mathbf{r}_i-\mathbf{r}_j|$, and is of strictly finite range. The partition function is

$$Z=\sum_{\{\mu_i=\pm 1\}}\exp\{K\sum_{ij}v_{ij}\mu_i\mu_j\}, \quad (1.2)$$

$$K=J/2k_BT, \quad (1.3)$$

and the pair-correlation function may be written

$$C_{mn}=Z^{-1}\sum_{\{\mu_i=\pm 1\}}\mu_m\mu_n\exp\{K\sum_{ij}v_{ij}\mu_i\mu_j\}. \quad (1.4)$$