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Time-Dependent Ginzburg-Landau Theory of Nonequilibrium Relaxation

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The system is considered which is brought into a state far from thermal equilibrium by a sudden change of independent variables. Its approach towards the equilibrium state is studied introducing nonequilibrium relaxation functions. Near the equilibrium state the lowest-order relaxation functions reduce to the time-dependent pair correlation functions. The relaxation process is especially interesting near a first-order phase transition, where metastable states can occur. Characterization of these states in terms of the nonequilibrium relaxation functions is discussed, and a "constructive" definition of the metastable states in terms of a "flatness" property of the relaxation curve is proposed. In order to give explicit results, the time-dependent Ginzburg-Landau theory is treated in detail, and exact solutions for the relaxation functions are given. If an equilibrium state is described by a real-valued order parameter, the inverse lifetime of a metastable state is determined from the imaginary part of its order parameter. Transition from the "metastable" to the stable state is characterized by fluctuations which increase with time for wave vectors up to some critical value, and later decrease again because of the nonlinearity of the Ginzburg-Landau equations. The validity of these results is discussed with respect to systems with long-range interactions, and also a few remarks are given concerning systems with short-range interactions and the nucleation picture.

I. INTRODUCTION

The equilibrium aspects of interacting many-body systems which exhibit phase transitions are now rather well understood[1-3] within the framework of equilibrium statistical mechanics. Thus it seems legitimate to proceed to the investigation of phenomena far from thermal equilibrium in terms of a statistical theory, where linearized irreversible thermodynamics[4,5] cannot be applied. Some of the most striking phenomena of this kind associated with phase transitions are hysteresis and metastability. These phenomena are indeed very frequently observed in all kinds of experimental investigations of first-order phase transitions.

It is the aim of the present paper to make a contribution to the theoretical description of such nonequilibrium processes; we are especially interested in making the connection of the treatment to the theory of second-order phase transitions as transparent as possible. Stimulated by the experimental procedure, an isolated system is considered, which is assumed to be in some thermal equilibrium state, and it is supposed that at time $t=0$ a sudden change of some external variables is performed. Then it is asked in what way the system relaxes (eventually) towards a new equilibrium state.

The first step in this task consists in providing a formal statistical description, which is both appropriate to nonequilibrium processes and as simple as possible. In Sec. II it is suggested that this can be done conveniently defining a nonequilibrium relaxation function [Eq. (13)]; this function is easily related to the familiar description in terms of the equilibrium correlation functions for all states apart from the phase boundary. In Sec. III it is then discussed in which way the existence of a metastable state should show up in such a nonequilibrium relaxation function. A "constructive" definition of metastable states is proposed, i.e., a prescription to derive their properties from the nonequilibrium relaxation function. This method is briefly compared to some previous general treatments.[6-10] It is a well-known fact that approximate methods of evaluating a partition function in equilibrium statistical mechanics also yield easily metastable states, e.g., all types of mean-field[1] or van der Waals approximations. From rigorous treatments[11] it is clear that a correct treatment of the thermodynamic limit does *not* yield these states even in cases where the van der Waals description is correct for the true equilibrium states. Thus the both fascinating and difficult question, in which way one can extend equilibrium statistical mechanics to include both equilibrium and metastable states, is circumvented by our procedure. A disadvantage of the dynamic descriptions may be that it does not yield a precise distinction between unstable and metastable states; but note, the same difficulty may occur also in the experiment. We then treat a simple example, the time-dependent Ginzburg-Landau theory,[12-18] which is outlined in Sec. IV. The nonequilibrium relaxation function for the Fourier component $k=0$ is calculated and its analytical properties discussed in detail. Exact formulas are given for the associated relaxation times. It is shown that "metastable states" exist according to our definition for fields slightly exceeding the usual limit of metastability h^*. It is argued, however, that the metastable region will stop at some $h < h^*$ in a more realistic case (Sec. V).

In our case (and in the work of Griffiths *et al.* on finite mean-field systems[18]) the order-parameter field associated with true equilibrium states is strictly real valued, in contrast to the complex field in the case of superconductors.[12–17] However it is observed that the inverse lifetime of nonequilibrium states (i.e., for fields exceeding the limit of metastability) increases like the imaginary part of the associated order parameter, while it is strictly zero for fields not exceeding this limit. Section V is devoted to a critical discussion of the validity of the present treatment and tentatively generalizing some exact results of Penrose and Lebowitz[10] a validity criterion is proposed in analogy to the "Ginzburg-Brout criterion"[1–3,19] for systems with a large but finite range of interaction. Possibilities for experimental applications of the present results are also discussed. Finally, Sec. VI contains some conclusions, and we give some brief remarks concerning the most interesting case of systems with short-range interactions. In this case it is clear that the present approach cannot be carried out in a similarly exact fashion, since rigorous treatments of dynamic relaxation near the equilibrium state are not available either. Approximate treatments like nucleation theories[20,21] or numerical calculations like molecular dynamics or Monte Carlo computer experiments[22] immediately yield the nonequilibrium relaxation functions.[23] It is stressed that the Ginzburg-Landau results for spatial fluctuations (i.e., nonequilibrium functions for Fourier components $\vec{k} \neq 0$) are in qualitative agreement with the nucleation picture.

II. DYNAMIC DESCRIPTION OF NONEQUILIBRIUM PHENOMENA

A system of $N \gg 1$ particles is considered, where each particle (labeled i) is described by a set of dynamical coordinates $\{a_i^\nu(t)\}$, and it is assumed that only the νth degree of freedom, $a_i^\nu(t) \equiv \mu_i(t)$, will be essential to characterize the state of the systems with respect to the phase transition considered. The evolution in time is given by the quantum-mechanical (or classical) equations of motion

$$i\hbar \frac{d}{dt} a_i^\nu(t) = [a_i^\nu(t), \mathcal{H}_a]. \tag{1}$$

Macroscopically, the state of the system will be described by thermodynamic coordinates, one of the (independent) intensive variables being the temperature T and the others being denoted by $\{I\}$ (e.g., the magnetic field H). Then the expectation value of some operator A_a in this state is

$$\langle A\rangle_{T,\{I\}} \equiv \mathrm{Tr}\rho^a_{T,\{I\}} A_a = \frac{\mathrm{Tr}\, e^{-\mathcal{H}_a/k_B T} A_a}{\mathrm{Tr}\, e^{-\mathcal{H}_a/k_B T}} . \tag{2}$$

The total Hamiltonian $\mathcal{H}_a$ containing all coordinates $\{a_i^\nu(t)\}$ may have a part depending on the coordinates $\{\mu_i(t)\}$ only; this part of the Hamiltonian is denoted simply by $\mathcal{H}$. As an example, one may think of $\mu_i(t)$ being the magnetic moment of the particle, and the reduced Hamiltonian $\mathcal{H}$ may be the Ising Hamiltonian

$$\mathcal{H} = -\sum_{i \neq j} J_{ij}\, \mu_i \mu_j - \sum_j H \mu_j , \quad \mu_i = \pm 1. \tag{3}$$

Provided that coupling between the $\mu_i(t)$ and the other degrees of freedom is sufficiently weak, the expectation value of an operator A_μ can be expressed with the reduced density matrix $\rho^\mu_{T,H}$;

$$\langle A_\mu \rangle_{T,H} \equiv \mathrm{Tr}\rho^\mu_{T,H} A_\mu = \frac{\mathrm{Tr} e^{-\mathcal{H}/k_B T} A_\mu}{\mathrm{Tr} e^{-\mathcal{H}/k_B T}} . \tag{4}$$

Without restricting further analysis to the Ising example it is assumed that there is only one independent variable (in addition to T), namely, field H which couples to the order parameter $\psi(T,H)$,

$$\psi(T,H) \equiv \langle \mu \rangle_{T,H} = \frac{1}{N} \sum_{i=1} \langle \mu_i \rangle_{T,H} . \tag{5}$$

For simplicity, periodic boundary conditions are considered throughout, and because of translational invariance we have $\langle \mu_i \rangle_{T,H} = \langle \mu \rangle_{T,H}$.

Introducing a Liouvillean $\mathfrak{L}$ by

$$\mu_i(t) = e^{-i\mathfrak{L}t} \mu_i(0) \tag{6}$$

leads to the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy[24] for the correlation function;

$$\begin{aligned} \frac{d}{dt} \langle \mu_i(t) \rangle_{T,H} &= -i \langle \mathfrak{L}\mu_i(t) \rangle_{T,H} , \\ \frac{d}{dt} \langle \mu_i(t)\, \mu_j(t) \rangle_{T,H} &= -i \langle [\mathfrak{L}\mu_i(t)] \mu_j(t) \rangle_{T,H} \\ &\quad - i \langle \mu_i(t) [\mathfrak{L}\mu_j(t)] \rangle_{T,H} . \end{aligned} \tag{7}$$

In general it will be inappropriate to replace $\mathcal{H}_a$ by $\mathcal{H}$ in Eq. (1) in order to derive Eqs. (6) and (7), although the weak-coupling assumption has been made [replacing Eq. (2) by (4)]. This fact is easily recognized in the Ising example Eq. (3) where μ_i commutes with $\mathcal{H}$; all the dynamics in Eqs. (6) and (7) come from coupling to the other degrees of freedom.

An approach to avoid the complicated derivation of Eqs. (6) and (7) from Eq. (1) is to postulate the "Liouvillean" $L \equiv i\mathfrak{L}$ in a more or less *ad hoc* fashion, as done for example in the stochastic Ising model.[25,26] In Sec. V it will be pointed out that this model is closely related to our Ginzburg-Landau treatment of Sec. IV, thus we quote this model in more detail. Postulating a master equation for the

N particle probability distribution

$$P(\mu_1, \ldots, \mu_i, \ldots, \mu_N, t),$$

$$\frac{d}{dt} P(\mu_1, \ldots, \mu_i, \ldots, \mu_N, t) = -\sum_i W(\mu_i \rightarrow -\mu_i) P(\mu_1, \ldots, \mu_i, \ldots, \mu_N, t) + \sum_i W(-\mu_i \rightarrow \mu_i) P(\mu_1, \ldots, -\mu_i, \ldots, \mu_N, t), \tag{8}$$

one[26] again derives Eq. (7) for the correlation functions

$$\langle \mu_i(t) \rangle \equiv \sum_{\{\mu_l\}} \mu_i P(\mu_1, \ldots, \mu_N, t), \qquad \langle \mu_i(t) \mu_j(t) \rangle \equiv \sum_{\{\mu_l\}} \mu_i \mu_j P(\mu_1, \ldots, \mu_N, t). \tag{9}$$

In order that Eq. (9) be consistent with Eq. (4) it is sufficient to require the detailed balance for the single spin-flip transition probability per unit time W and the canonic equilibrium distribution $P^{eq} = \rho^{\mu}_{T,H}$,

$$W(\mu_i \rightarrow -\mu_i) P^{eq}(\mu_1, \ldots, \mu_i, \ldots, \mu_N) = W(-\mu_i \rightarrow \mu_i) P^{eq}(\mu_1, \ldots, -\mu_i, \ldots, \mu_N), \tag{10}$$

$$i = 1, \ldots, N.$$

Because of this property the stochastic Ising model is ergodic by construction. Without restricting further analysis to the example the ergodicity property of the systems considered will be assumed throughout.

For the general case, van Hove[27] has been able to show that a description in terms of a Markoffian master equation together with a detailed balance condition can be derived from Eq. (1) in the weak-coupling and large-time ($t \rightarrow \infty$) limit under fairly general assumptions about the nature of that coupling. A derivation for the Ising case postulated in Eq. (8) is due to Heims and Goldstein *et al.*[28]

The higher one proceeds in the above hierarchy of correlation functions, the more detailed will be the information about the system. Adhering to the "philosophy" that the essential information one wants to know is already contained in these lowest-order functions, which contain "structure" both in space and time, only a small number of correlation functions has to be considered in thermal equilibrium: the one-particle function $\langle \mu_i(t) \rangle_{T,H}$, i.e., the order parameter [(Eq. (5)], having neither structure in space nor in time. The equal time correlation $S(\vec{k})$ has "structure" in space only,

$$S(\vec{k}) = \sum_r e^{i\vec{k}\cdot\vec{r}} \langle \delta\mu_i \delta\mu_j \rangle_{T,H}, \quad \delta\mu_i \equiv \mu_i - \langle \mu_i \rangle_{T,H}, \tag{11}$$

where $\vec{r} \equiv \vec{r}_i - \vec{r}_j$. With the knowledge of $\psi(T,H)$ [Eq. (5)] and $S(\vec{k})$, a description of static phenomena is obtained which is sufficient for most purposes. Usually these quantities are derived from methods of the equilibrium statistical mechanics without any reference to dynamic considerations.

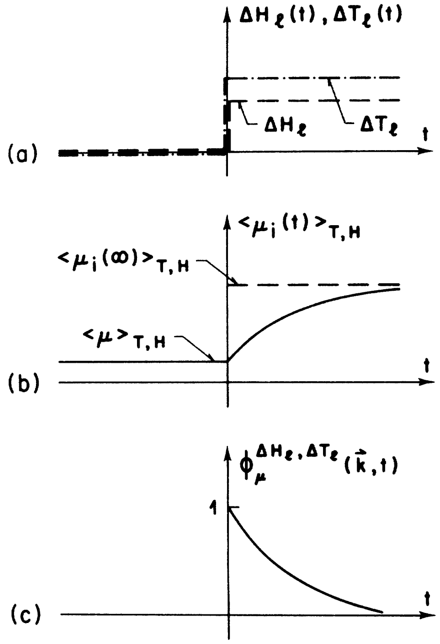


FIG. 1. Dynamic description of the nonequilibrium relaxation process of the order parameter $\langle \mu i(t) \rangle_{T,H}$ (b), after a sudden change of external variables $\Delta H_l(t)$, $\Delta T_l(t)$ at time $t=0$ (a), in terms of the relaxation function $\phi_{\mu}^{\Delta H_l, \Delta T_l}(\vec{k}, t)$ (c).

In order to have "structure" also with respect to time it is appropriate to consider a time-displaced pair correlation function $\langle \mu_i(t_0)\, \mu_j(t_0 + t) \rangle_{T,H}$[29]; its normalized Fourier transform will be denoted an "equilibrium relaxation function" $\phi^{eq}_{\delta\mu\delta\mu}(\vec{k}, t)$,

$$\phi^{eq}_{\delta\mu\delta\mu}(\vec{k}, t) = [S(\vec{k})]^{-1} \sum_r e^{i\vec{k}\cdot\vec{r}} \langle \delta\mu_i(t_0) \delta\mu_j(t_0 + t) \rangle_{T,H}. \tag{12}$$

With the knowledge contained in Eqs. (5), (11), and (12) one is fairly able to interpret available experiments, for example, linewidth measurements in resonance techniques, or scattering experiments with energy analysis of the scattered radiation,[29] etc.

Now consider a nonequilibrium process. It is supposed that the system is in thermal equilibrium at times $t < 0$ in some state T, H. At time $t = 0$ a sudden change of variables Δt_l, ΔH_l is performed [Fig. 1(a)] which may depend on the coordinates of the particles. Now we must have some relaxation process also of the order parameter from $\langle \mu_i \rangle_{T,H}$ to $\langle \mu_i(\infty) \rangle_{T,H}$ [Fig. 1(b)]. Evidently the one-particle function will have "structure" both with respect to space and time during the course of the relaxation process; in a sense it is thus a function analogous to the equilibrium relaxation function Eq. (12).

To make this analogy more transparent we define a "nonequilibrium relaxation function" [Fig. 1(c)] by

$$\phi_\mu^{\Delta H_l,\Delta T_l}(\vec{k},t)\equiv\frac{\sum_{r_i}e^{i\vec{k}\cdot\vec{r}_i}[\langle\mu_i(t)\rangle_{T,H}-\langle\mu_i(\infty)\rangle_{T,H}]}{\sum_{r_i}e^{i\vec{k}\cdot\vec{r}_i}[\langle\mu_i(0)\rangle_{T,H}-\langle\mu_i(\infty)\rangle_{T,H}]}\,. \tag{13}$$

Special functions of this type have been considered previously in connection with kinetic Ising models by Suzuki[30] and by Bedeaux *et al.*[31] It is interesting to note the connection with the equilibrium case for the limit of small changes $\Delta H_l \to 0$, $\Delta T_l \to 0$.

Since the Liouvillean governing the motion of $\mu_i(t)$ depends on ΔT_l and ΔH_l,[32] it is convenient to transform also the expectation values from the state $\{T,H\}$ to the state $\{T+\Delta T_l,\ H+\Delta H_l\}$. Introducing the abbreviations

$$\sum_l \mathcal{H}_l=\mathcal{H}-\sum_l \mu_l\Delta H_l\,,\quad T_l=T+\Delta T_l\,,\quad H_l=H+\Delta H_l\,, \tag{14}$$

we have from the ergodicity property

$$\langle\mu_i(\infty)\rangle_{T,H}=\langle\mu_i\rangle_{T_l,H_l}\,. \tag{15}$$

For the present purpose it is sufficient to consider a case where $\mathcal{H}$ and μ_l commute; then it is found for $\Delta H_l \to 0$, $\Delta T_l \to 0$

$$e^{-\mathcal{H}/k_BT}=e^{-\Sigma_l\mathcal{H}_l/k_BT_l}\times\left(1-\sum_l\frac{\mathcal{H}_l}{k_BT}\frac{\Delta T_l}{T}-\sum_l\frac{\mu_l\Delta H_l}{k_BT}\right). \tag{16}$$

From Eqs. (4), (15), and (16) it is seen that

$$\begin{aligned}\langle\mu_i(t)\rangle_{T,H}=\langle\mu_i\rangle_{T_l,H_l}-\frac{1}{k_BT}&\times\sum_l[\langle\mu_i(t)\,\mu_l(0)\rangle_{T_l,H_l}\\&-\langle\mu_i\rangle_{T_l,H_l}\langle\mu_l\rangle_{T_l,H_l}]\Delta H_l\\&-\frac{1}{k_BT}\sum_l[\langle\mu_i(t)\mathcal{H}_l(0)\rangle\\&-\langle\mu_i\rangle_{T_l,H_l}\langle\mathcal{H}_l\rangle_{T_l,H_l}]\frac{\Delta T_l}{T}\,.\end{aligned} \tag{17}$$

On the right-hand side of Eq. (17) we could omit time arguments of the single-particle functions.

Most interesting is the case $\Delta T_l\equiv 0$, and $\Delta H_l \neq 0$. Then it is found from Eqs. (13) and (17) that

$$\lim_{\Delta H_l\to 0}\phi_\mu^{\Delta H_l,0}(\vec{k},t)=\phi_{\delta\mu\delta\mu}^{\mathrm{eq}}(\vec{k},t)\,. \tag{18}$$

Taking into account higher-order terms in the expansion Eq. (16) would allow to represent the nonequilibrium relaxation function Eq. (13) in terms of higher-order equilibrium correlation functions also for finite $\Delta H_l \neq 0$. But if such a change is performed near a first-order phase transition, this expansion breaks down necessarily. Now it is precisely this situation in which we are interested (with $\Delta H_l\equiv\Delta H$) to discuss the properties of an (eventually occurring) metastable state. The definition Eq. (13) has always a precise meaning, however, and in Secs. IV and V it will be pointed out that $\phi_\mu^{\Delta H_l,\Delta T_l}(\vec{k},t)$ can be calculated rather directly, without using explicit representations in terms of equilibrium properties.

In the thermal equilibrium the description by $\psi(T,H)$ and $S(\vec{k})$ is appropriate for static phenomena and by $\phi_{\delta\mu\delta\mu}^{\mathrm{eq}}(\vec{k},t)$ for dynamic phenomena. The static phenomena may be studied quite independently from the dynamic ones. These findings do not apply to the nonequilibrium case, however; here the correlation function of lowest order—the single-particle function—is time-dependent, of course. Thus the crudest possible description—in terms of Eq. (13)—has already dynamic character. From this "first-principles" point of view all attempts to construct properties of metastable states from the evaluation of a partition function turn out to be somewhat dubious. It is seen that a well-defined characterization of the phenomena of metastability, hysteresis, etc., should be given in terms of the dynamic description of nonequilibrium processes.

Of course only small parts of this formal introduction are new, but we have given this discussion in order to make our notation precise, and to justify the restriction to study nonequilibrium phenomena associated with first-order phase transitions using a correlation function of lower order than appropriate for the equilibrium case, which might be contrary to naive expectations. In Sec. III a definition of metastable states is proposed, based on the properties of the nonequilibrium relaxation function $\phi_\mu^{\Delta H,0}(\vec{k},t)$ [Eq. (13)].

III. DYNAMIC DEFINITION OF "METASTABILITY"

Here we consider the relaxation function for $\vec{k}=0$ which will be abbreviated by $\phi(t)$,

$$\phi(t)\equiv\phi_\mu^{\Delta H,0}(0,t)\,. \tag{19}$$

A characterization of a metastable state will be based on a "flatness" property of this relaxation curve [cf. Fig. 2]. It is assumed that the area beyond this relaxation curve is finite, i.e., we may define a relaxation time τ_R by

$$\tau_R=\int_0^\infty\phi(t)dt. \tag{20}$$

We introduce the averages

$$\overline{\mu}_{t_1,t_2}=\frac{1}{t_2-t_1}\int_{t_1}^{t_2}\langle\mu(t)\rangle_{T,H}\,dt \tag{21}$$

and formulate the following *criterion*: During the course of a nonequilibrium relaxation process a "metastable" state occurs (with order parameter $\overline{\mu}_{\mathrm{MS}}\pm\delta\mu$) if two times $t_I\ll\tau_R$, t_F can be found, so

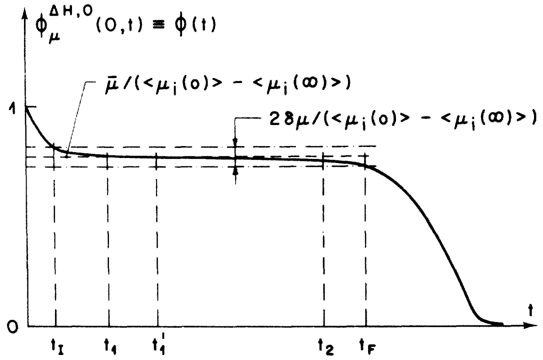


FIG. 2. "Flatness" property of the relaxation curve $\phi_{\mu}^{\Delta H,0}(0, t)$. For the explanations of the various times t_I, t_1, t_1', t_2, and t_F, see the text.

that for all times t_1, t_1', t_2 which satisfy Eq. (22), the inequalities Eqs. (23) and (24) hold;

$$t_I \le t_1 \le t_1' < t_2 \le t_F, \tag{22}$$

$$\bar{\mu}_{t_1,t_2} - \bar{\mu}_{t_1',t_2} < \delta\mu \ll \bar{\mu}_{t_1,t_2}, \tag{23}$$

$$\delta\mu/\delta\mu_R \ll (t_F - t_I)/\tau_R, \tag{24}$$

where the notation is introduced,

$$\delta\mu_R \equiv \min(\bar{\mu}_{t_1,t_2} - \langle\mu\rangle_{T,H+\Delta H}). \tag{25}$$

Then the order parameter $\bar{\mu}_{\mathrm{MS}}$ of the metastable state can be defined by

$$\bar{\mu}_{\mathrm{MS}} = \bar{\mu}_{t_I t_F}, \tag{26}$$

and its lifetime τ_{MS}

$$\tau_{\mathrm{MS}} = t_F - t_I, \tag{27}$$

or alternatively in terms of the $\langle\mu(t)\rangle_{T,H}$ function,

$$\tau_{\mathrm{MS}}' = \frac{\langle\mu(0)\rangle_{T,H} - \langle\mu(\infty)\rangle_{T,H}}{\bar{\mu}_{\mathrm{MS}} - \langle\mu(\infty)\rangle_{T,H}}\,\tau_R. \tag{28}$$

The basic ingredients of this definition are the following: (i) A metastable state has a finite lifetime per definition. This time can be very large, however; it must be large in comparison with the characteristic relaxation times of the system at equilibrium, which are roughly of order t_I. (ii) Any property characteristic for the metastable state has a finite inaccuracy, for example, the order parameter is $\bar{\mu}_{\mathrm{MS}} \pm \delta\mu$. The lifetime τ_{MS} may depend on the choice of $\delta\mu$ to some extent. In the limit $\delta\mu \to 0$ eventually no metastable states exist. In a practical case $\delta\mu$ may be nonzero but extremely small. (iii) There is no sharp limit between metastable and instable states, both of them change with time. The precise location of the "coercive field" separating the metastable states from the instable ones may show some dependence on the choice of $\delta\mu$. Again in a practical case this inaccuracy of the coercive field may be extremely small as will be discussed later on. It is also likely from a discussion of the mechanisms by which metastable and unstable states decay (e.g., some brief remarks are given at the end of Sec. IV), that no sharply defined "coercive field" or "spinodal" exists in real systems.

Note that we are speaking of a large finite N and have not given any assumption of the dependence of τ_{MS} and $\bar{\mu}_{\mathrm{MS}}$ on N.

It is interesting to compare the definition by Eqs. (22)-(28) to previous work. A concise formulation is due to Gibbs[33] where it is assumed that also metastable and instable states are described by a thermodynamic potential $G(T,H)$. Equilibrium is characterized by

$$(\delta G)_{\mathrm{eq}} = 0, \tag{29}$$

while stability of a state against perturbations is ensured by

$$(\Delta G)_{\mathrm{eq}} > 0. \tag{30}$$

If for a state Eq. (30) is violated for certain finite perturbations, but still holds for infinitesimal ones,

$$(\delta^2 G)_{\mathrm{eq,MS}} > 0, \tag{31}$$

this state is called metastable. This criterion has been recently discussed from more general points of view,[6] and it is stressed that the existence of a thermodynamic potential outside thermal equilibrium is an open question.[34] In fact, it is not clear how to construct such potentials explicitly, since equilibrium statistical mechanics yields information about true equilibrium states only, as shown from the rigorous treatment of the van der Waals gas.[11] Langer[7-9] postulates the existence of the thermodynamic potential as an analytic continuation of the equilibrium potential; its imaginary part is identified with the lifetime of this metastable state. The latter conjecture is substantiated by dynamic considerations of the nucleation process.[8] Later it will become evident that our different method leads to a similar result. Then the kinetic theory of stability[6] is to be mentioned; this method separates the instable states from stable and metastable states by considering their normal modes. If modes occur whose frequencies have a positive real part, i.e., increase with time, the state of the system is called instable. Again, it will later become evident that our method leads to a similar result. Perhaps the most interesting definition is contained in the recent important work of Penrose and Lebowitz.[10] These authors call a state metastable if

(i) only one thermodynamic phase is present,

(ii) a system that starts in this state is likely to take a long time to get out. (32)

(iii) once the system has got out, it is unlikely to return.

It is intuitively clear that our "flatness" criterion of the relaxation curve [Eqs. (22)–(28)] is also consistent with Eq. (32). But like the other definitions mentioned, Eq. (32) does not provide an immediate tool for constructing the properties of the metastable states, as done by Eqs. (26) and (28). In fact, additional considerations had to be given in Ref. 10 to draw more precise conclusions from Eq. (32).[35] It is not claimed, however, that the criterion Eq. (20)–(28) provides a unique definition of metastability. While the inequalities Eq. (22)–(24) describing the flatness of Fig. 2 mathematically are certainly necessary conditions for the occurrence of a metastable state, they may not be sufficient. In fact, one may like to call some of these states "long-living unstable states" because of other grounds. We do not treat this question further, however, since it is less important from the experimental point of view, and we believe this distinction is doubtful in models with short-range forces.[23] Thus we use Eqs. (20)–(28) as a working hypothesis in Sec. IV.

IV. TIME-DEPENDENT GINZBURG-LANDAU THEORY

In Sec. IV A the time-dependent Ginzburg-Landau (TDGL) equations are formulated for the case of small spatial variations of the order parameter. In Sec. IV B, we rederive the equilibrium properties needed for comparison. In Sec. IV C, the kinetic equation for $\psi_0(t)$ is solved to derive the nonequilibrium relaxation function $\phi(t)$ [Eq. (19)], whose behavior is discussed in detail. The properties of the metastable states found by using Eqs. (22)–(28) are also given. In Sec. IV D, the question of whether spatial fluctuations die out also in the course of the nonequilibrium relaxation process is investigated. A brief comparison with the spatial fluctuations considered by the nucleation theory[20,21] is also made.

A. Time-Dependent Ginzburg-Landau (TDGL) Equation

A real-valued order-parameter field $\psi(\vec{r}, t)$ is assumed obeying the equation

$$-\tau_s \frac{\partial\psi(\vec{r},t)}{\partial t} = -a\left(1-\frac{T}{T_c}\right)\psi(\vec{r},t) + B\psi^3(\vec{r},t) - C\nabla^2\psi(\vec{r},t) - H(\vec{r},t). \qquad (33)$$

Here a, B, C, and τ_s are phenomenological (positive) parameters; T_c is the critical temperature of the second-order transition. This is essentially the same equation as in the case of superconductors,[12–17] but there ψ is complex, and the conjugate field $H(\vec{r}, t)$ has no simple meaning so is usually omitted. We want to study the relaxation effects produced by a sudden change of the homogeneous part of this field; therefore our treatment will be different from the extensive investigations of the TDGL theory of superconductors (for calculations of the resistivity see, for example, Refs. 14–17). The Langevin noise term added in the treatment of Tucker and Halperin[17] will not be included in the present treatment.

In the TDGL theory the lowest-order term of the gradient expansion is included only, thus only slow spatial variations of $\psi(\vec{r}, t)$ can be considered. We cannot hope to obtain a faithful description of nucleation which starts on the atomic scale of lengths. Thus we further assume that either ψ is itself small (e.g., for $T > T_c$, here the term $B\psi^3$ can be neglected) or at least the fluctuations $\psi_k(t)$ are small in comparison with the homogeneous part of $\psi(\vec{r}, t)$ $[\psi(\vec{r}, t) = \sum_k \psi_k(t) e^{i\vec{k}\cdot\vec{r}}]$,

$$\psi_k(t) \ll \psi_0(t). \qquad (34)$$

While in the equilibrium case Eq. (34) is necessary for the justification of Eq. (33) itself,[2,19,36] in the nonequilibrium case Eq. (34) restricts us to consideration of situations where Eq. (34) holds for the initial condition (at $t = 0$). Using Eq. (34) it is easy to linearize Eq. (33) in terms of the $\psi_k(t)$,[37]

$$-\tau_s \frac{d\psi_0(t)}{dt} = -a\left(1-\frac{T}{T_c}\right)\psi_0(t) + B\psi_0^3(t) - H_0(t) \quad \text{for } k = 0, \qquad (35)$$

$$-\tau_s \frac{d\psi_k(t)}{dt} = -\left[a\left(1-\frac{T}{T_c}\right) - Ck^2\right]\psi_k(t) + 3B\psi_k(t)\psi_0^2(t) - H_k(t) \quad \text{for } k \neq 0. \qquad (36)$$

Once the solution $\psi_0(t)$ of Eq. (35) is known, it is easy to solve the linear inhomogeneous first-order differential equation (36) for $\psi_k(t)$. The stationary solutions $d\psi_0/dt = 0$, $d\psi_k/dt = 0$ describe the well-known static equilibrium case.[1,2,36]

B. Summary of the Equilibrium Properties of the TDGL Equations

If the static homogeneous field H_0 is zero, one finds from Eq. (35)

$$\psi_0 = 0, \qquad T \geq T_c$$
$$= \left[\frac{a}{B}\left(1-\frac{T}{T_c}\right)\right]^{1/2}, \quad T < T_c. \qquad (37)$$

Defining the susceptibility χ_k by

$$\psi_k = \chi_k H_k, \quad H_k \to 0, \qquad (38)$$

one gets from Eq. (36) the Ornstein-Zernike formula[38]

$$\chi_k = \frac{1}{C}\frac{1}{k^2+\kappa^2}, \qquad (39)$$

with the inverse correlation length $\xi^{-1} = \kappa$,

$$\kappa^2 = \frac{a}{C}\left(\frac{T}{T_c} - 1\right), \quad T \geq T_c,$$

$$= \frac{2a}{C}\left(1-\frac{T}{T_c}\right), \quad T<T_c . \tag{40}$$

If $H_0 \neq 0$, three real solutions ψ_0^1, ψ_0^2, ψ_0^3 exist for $H_0 > H_0^*$ (the "coercive field" or "limit of metastability"),

$$H_0^* = -2.\, 3^{-3/2} a^{3/2} B^{-1/2} (1-T/T_c)^{3/2} . \tag{41}$$

Scaling the variables

$$m = \frac{\psi(T,H)}{\psi(T,0)}, \quad h = -H_0 a^{-3/2} B^{-1/2}\left(1-\frac{T}{T_c}\right)^{-3/2}$$
$$t' = \frac{t}{\tau_s} a \left(1-\frac{T}{T_c}\right), \tag{42}$$

Eq. (35) reads

$$-\frac{dm}{dt'} = -m(t') + m^3(t') + h . \tag{43}$$

For $h > h^* = 2/3\sqrt{3}$ the one real solution m_3 is

$$m_3 = [-\tfrac{1}{2}h + (\tfrac{1}{4}h^2 - \tfrac{1}{27})^{1/2}]^{1/3} + [-\tfrac{1}{2}h - (\tfrac{1}{4}h^2 - \tfrac{1}{27})^{1/2}]^{1/3}, \tag{44}$$

while the three solutions for $h < h^*$ are expressed in terms of $\varphi = \arccos(-3^{3/2}\frac{1}{2}h)$ as

$$m_1 = 2\times 3^{-1/2} \cos\frac{\varphi}{3}, \quad m_2 = 2\times 3^{-1/2}\cos\frac{\varphi+4\pi}{3},$$
$$m_3 = 2\times 3^{-1/2}\cos\frac{\varphi+2\pi}{3} . \tag{45}$$

Note for h near h^*

$$m_1 = 3^{1/2} + \frac{2^{1/2}}{3}\left(1-\frac{h}{h^*}\right)^{1/2} = m^* + \frac{2^{1/2}}{3}\left(1-\frac{h}{h^*}\right)^{1/2}, \tag{46}$$

which implies a divergent susceptibility at $h = h^*$,

$$\chi_k = \frac{1}{C}\left[k^2 + \frac{a}{C}\left(1-\frac{T}{T_c}\right)(3m_1^2 - 1)\right]^{-1}, \tag{47}$$

and a divergent correlation length

$$\kappa^2 = 3^{-1/2} 2^{3/2} (a/C)(1-T/T_c)(1-h/h^*)^{1/2}. \tag{48}$$

Since the second solution m_2 implies a negative susceptibility it is necessary to consider the stability of these solutions m_1, m_2, and m_3.[6] This can be done[39] using Eq. (43). It is assumed that the system is in a state $m_0 \neq m_1$, m_2, or m_3 at the time $t=0$. It is then asked to which of the three "equilibrium" states the system will relax (cf. Fig. 3; here it is convenient to construct m_1, m_2, and m_3 graphically as indicated).

If $m_0 > m_1$, it follows from Eq. (43) that the final state will be m_1, since $dm/dt' < 0$. But at m_1 the sign of dm/dt' changes, if $m_2 < m_0 < m_1$, $dm/dt' > 0$, and again m_1 is reached, and not m_2, however close to m_2 the state m_0 may be. Similarly, for $m_0 < m_2$ it is always found that the third solution m_3 is reached. Including an arbitrary small Langevin random force [cf. Ref. 17], the unstable solution m_2 would be removed from the equilibrium states, and no extra thermodynamic stability requirements are needed to exclude the states with negative susceptibility.[6] In the limit of vanishingly small random forces the lifetime of the "metastable" states m_1 (for fields in the range $0 < h \leq h^*$) is infinite.

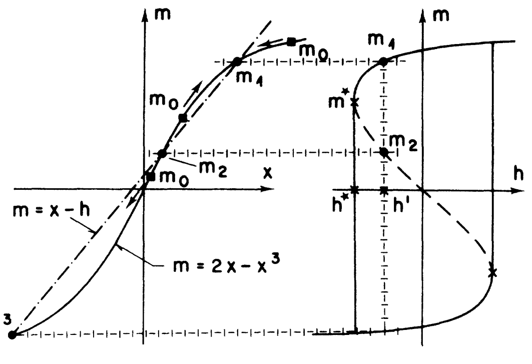


FIG. 3. Kinetic consideration of stability for the three solutions m_1, m_2, and m_3. No value of m_0 leads to a relaxation ending at m_2; the right-hand part of the figure is the corresponding construction of hysteresis.

Next let us briefly treat the dynamic susceptibility of the equilibrium states. One has to put $\psi_0^2(t) \equiv \psi_0^2$ (independent of t) in Eq. (36) and then consider the linear response to a time-dependent field $H_k(t)$. Introducing the Fourier transforms

$$H_k(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t} H_k^\omega \, d\omega, \quad \psi_k(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{i\omega t}\psi_k^\omega \, d\omega, \tag{49}$$

and defining a dynamic susceptibility $\chi(k,\omega)$ by

$$\psi_k^\omega = \chi(k,\omega) H_k^\omega , \tag{50}$$

it is found from Eq. (36) that

$$\chi(k,\omega) = \chi_k (1 + i\,\omega/\omega_k)^{-1}, \quad \omega_k = \tau/\chi_k . \tag{51}$$

Equation (51) is consistent with the dynamic scaling hypothesis,[40,41] of course. Since χ_0 diverges not only for $T \to T_c$ but also for $h \to h^*$, Eq. (51) implies a "soft-mode" behavior not only for $T \to T_c$, but also near the limit of metastability h^*. Similar instabilities have been conjectured for various other kinds of first-order transitions, too, for example, in the case of the liquid-solid transition.[42] It is straightforward to find the equilibrium relaxation function defined in Eq. (12) from Eqs. (51) and (47),

$$\phi^{\mathrm{eq}}_{\delta\mu\delta\mu}(\vec{k}, t) = e^{-\omega_k t}$$
$$= \exp\left\{-t'\left[(3m_1^2 - 1) + \frac{C}{a}k^2\left(1-\frac{T}{T_c}\right)^{-1}\right]\right\}, \tag{52}$$

i.e., a simple exponential behavior. If the system is in the state m_3 instead of m_1 as assumed here, the factor $3m_1^2 - 1$ is replaced by $3m_3^2 - 1$.

C. Investigation of the Nonequilibrium Relaxation: Spatially Homogeneous Case

One has to integrate Eq. (35) for a given initial condition (for algebraic details see the Appendix). The result is typically a transcendental equation for $m = m(t')$, for example, for $h < h^*$ and $m_0 > m_2$ it is found

$$\phi(t') \equiv \frac{m(t') - m_1}{m_0 - m_1}$$

$$= \left[\left(\frac{m(t') - m_2}{m_0 - m_2} \right)^{(m_1 - m_3)/(m_2 - m_3)} \Big/ \right.$$

$$\left. \left(\frac{m(t') - m_3}{m_0 - m_3} \right)^{(m_1 - m_2)/(m_2 - m_3)} \right] e^{-(3m_1^2 - 1)t'} . \quad (53)$$

If the initial state m_0 is very close to the final state m_1, we may replace $m(t')$ on the right-hand side of Eq. (53) by the initial state, and thus see that Eq. (53) immediately reduces to Eq. (52) [for $k = 0$]; this is an illustration of the general result Eq. (18). If the initial state differs appreciably from the final state, however, the decay law is more complicated; but for large times the decay is always exponential with the same relaxation time as in the equilibrium case, independent of the initial condition [compare for example, the "large-time approximations" of the Appendix, Eqs. (A3) and (A4)]. Because of this property, $\phi(t')$ will also exhibit a critical slowing down if $h \to h^*$, since then $m_1 \to m^* = 3^{-1/2}$, and the relaxation time vanishes. The amplitudes in the Eqs. (A4) and (A3) still depend on the initial state m_0 also in the final stage of the relaxation process. As an example in Fig. 4(b) the relaxation functions have been plotted for several values of m_0 at a field $h/h^* = 0.5$ as indicated in Fig. 4(a). More interesting is the case $h > h^*$. As indicated in Fig. 4(a), two solutions m_1, m_2 become complex,

$$m_1, m_2 = y \pm iz ; \quad (54)$$

near h^* the imaginary part increases as a square root, while the real part remains nearly constant,

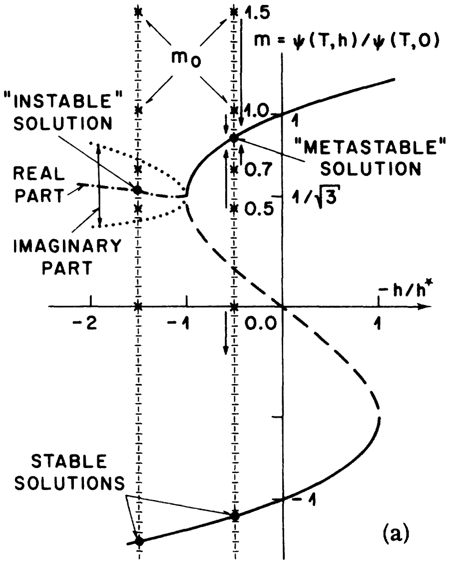
$$z = (\tfrac{3}{4} m_3^2 - 1)^{1/2} \approx (h/h^* - 1)^{1/2}, \quad y = -\tfrac{1}{2} m_3 \approx m^* . \quad (55)$$

Straightforward integration of Eq. (43) yields

$$-t'(m_3^2 - 1) = \ln \left[\frac{m(t') - m_1}{m_0 - m_3} \left(\frac{(m_0 - y)^2 + z^2}{[m(t') - y]^2 + z^2} \right)^{1/2} \right]$$

$$+ \frac{y - m_3}{z} \left(\arctan \frac{m(t') - y}{z} \right.$$

$$\left. - \arctan \frac{m_0 - y}{z} \right) . \quad (56)$$



NONEQUILIBRIUM RELAXATION FUNCTIONS

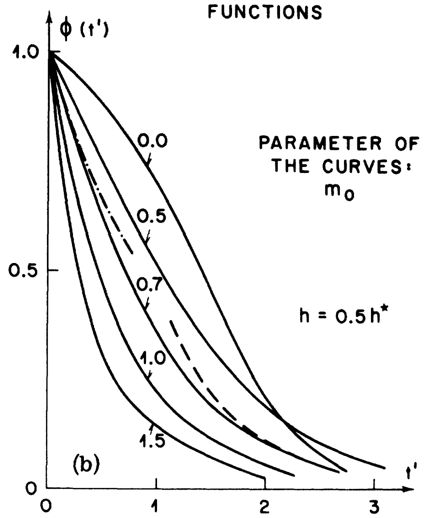


FIG. 4. (a) Relaxation processes considered in the m-h plane. Stable, "metastable," and instable solutions are shown (in the latter case both real and imaginary parts are indicated). The various starting values m_0 are shown. (b) Nonequilibrium relaxation functions for various m_0 (parameter of the curves). The corresponding equilibrium states are seen in (a). At $m_0 = 0.7$ the short-time approximation [Eq. (A5), dashed-dotted curve] and the large-time approximation [Eq. (A3), broken curve] are also shown.

From this result it is readily recognized, that y behaves as a metastable state according to our definition Eqs. (22) to (26), if z is small and $m_0 > y$, since a small variation of $m(t')$ around y in the arctan leads then to a large variation of time. In this regime the relaxation function may be approximated by a linear variation of the order parameter with time

$$\phi(t') \approx \frac{y - m_3 + \frac{1}{2}\pi z}{m_0 - m_3} - \frac{z^2(3m_3^2 - 1)t'}{(y - m_3)(m_0 - m_3)} . \quad (57)$$

The change of the order parameter δm in this state is proportional to z^2, i.e., very small. From Eq. (56) it is also recognized that the lifetime of this "metastable state" is proportional to z^{-1}. [This fact is also borne out by the direct calculation of τ_R, Eq. (A15).] It is seen that asymptotically for $h/h^* - 1 \to 0^+$, $m_0 > y$, the lifetime of the metastable state is according to Eq. (28)

$$\tau'_{\mathrm{MS}} \cong \frac{1}{z} \frac{y - m_3}{3m_3^2 - 1} \pi \propto \left(\frac{h}{h^*} - 1\right)^{-1/2}, \tag{58}$$

which is independent of m_0, as it should be. In Figs. 5 and 6 the relaxation functions are plotted for several $h/h^* > 1$. Both for $h/h^* = 1.01$ and 1.03 one might call the state y a metastable state according to the definition Eqs. (22) to (28). The lifetimes of these states are large in comparison with the characteristic time $(3m_3^2 - 1)^{-1}$ of the corresponding equilibrium state, as expected from Eq. (58).

D. Spatial Fluctuations and Nucleation

We briefly discuss now the spatially inhomogeneous case [Eq. (36)] with the restriction of small inhomogeneities [Eq. (34)]. In equilibrium it follows from Eq. (36) that a spatial fluctuation ψ_k^0 at time $t = 0$ will decay exponentially with time

$$\psi_k(t) = \psi_k^0 \exp\left(-C(k^2 + \kappa)\frac{t}{\tau_s}\right) + \frac{H_k}{C(k^2 + \kappa^2)}\left[1 - \exp\left(-C(k^2 + \kappa^2)\frac{t}{\tau_s}\right)\right]. \tag{59}$$

In the nonequilibrium case one gets from Eq. (36)

$$\psi_k(t) = \psi_k^0 \exp\left(-\frac{t}{\tau_s} C[k^2 + \kappa^2(t)]\right) + \frac{H_k}{C[k^2 + \kappa^2(t)]}\left[1 - \exp\left(-\frac{t}{\tau_s} C[k^2 + \kappa^2(t)]\right)\right.$$
$$\left. - \frac{3B}{\tau_s} \exp\left(-\frac{t}{\tau_s} C[k^2 + \kappa^2(t)]\right)\int_0^t \left(\psi_0^2(t_1) - \frac{1}{t}\int_0^t \psi_0^2(t_2)\,dt_2\right) \exp\left(+\frac{t_1}{\tau_s} C[k^2 + \kappa^2(t_1)]\right) dt_1\right], \tag{60}$$

where we formally introduced a time-dependent inverse correlation length $\kappa(t)$,

$$\kappa^2(t) = -\frac{a}{C}\left(1 - \frac{T}{T_c}\right) + \frac{3B}{C}\frac{1}{t}\int_0^t \psi_0^2(t_1)\,dt_1. \tag{61}$$

If $\psi_0^2(t)$ and hence $\kappa^2(t)$ are very slowly varying, the integral in Eq. (60) can be neglected and then Eq. (61) has precisely the same structure as Eq. (59). This is a fair approximation for a system in a metastable state, and thus Eq. (60) meets the requirement[10] that thermodynamic relations should apply to a system in a metastable state, too.

From Eq. (61) it is immediately recognized that $\kappa^2(t)$ may assume negative values: In such a situation a spatial fluctuation $\psi_\kappa(t)$ tends to grow instead of decay as in an equilibrium state. Since $\psi_0(t)$ is a monotonously varying function of time, a sufficient condition for decaying fluctuations is

$$\psi_0(t) > \psi_0^* = \left[\frac{a}{3B}\left(1 - \frac{T}{T_c}\right)\right]^{1/2} \quad \text{or } m(t) > m^*,$$
$$\psi_0(t) < -\psi_0^*. \tag{62}$$

The homogeneous state is stable as long as $\psi_0^2(t)$ exceeds its critical value. This happens for $m_0 > m_1$ and $h < h^*$ during the whole course of the relaxation—for $h > h^*$ this is only true as long as $m(t) > m^* \approx y$—when the system leaves this metastable state spatial fluctuations get enhanced. This also occurs for $h < h^*$ if m_0 is in the range $-m^* < m_0 < m^*$. A similar enhancement has been found in the linear mean-field theories for the spinodal decomposition of alloys.[43] In these treatments the fluctuations $\psi_k(t)$ increase indefinitely [corresponding to a $\kappa^2(t)$ which consists only of the first contribution to Eq. (61)], while due to the nonlinear term present in our treatment a stabilization of the fluctuation takes place, and afterwards the fluctuation decreases again when $\psi_0(t)$ approaches its new equilibrium value. This behavior can be seen more clearly by studying in detail the k-dependent nonequilibrium relaxation function [Eq. (60), $H_k = 0$]

$$\phi_\mu^{\Delta H,0}(\vec{k}, t) \equiv \phi_{k'}(t') = \exp\{-t'[k'^2 + \kappa'^2(t)]\}, \tag{63}$$

where we introduced $k' = C^{1/2} a^{-1/2}(1 - T/T_c)^{-1/2} k$, and from Eq. (61) it is deduced that

$$\kappa'^2(m) = -1 + \frac{6}{t'(m)}\left(\int_{m_0}^m t'(m)\, m\, dm + \tfrac{1}{2}m^2\right) \text{ for } m > 0, \tag{64}$$

$$\kappa'^2(m) = -1 + \frac{6}{t'(m)}\left(\int_{m_0}^0 t'(m) m\, dm - \int_0^m t'(m) m\, dm + \tfrac{1}{2}m^2\right) \text{ for } m < 0. \tag{65}$$

Using Eqs. (64), (65), and (56) it is not difficult to calculate $\phi_{k'}(t')$ [Eq. (63)]. Since the resulting expressions are rather lengthy, they will not be reproduced here, but rather we show the results of this calculation in Fig. 7 for $h/h^* = 1.05$, $m_0 = 1$, and various k'. $\phi_{k'}(t')$ decreases steadily with time for large k'. For smaller k' it decreases first but

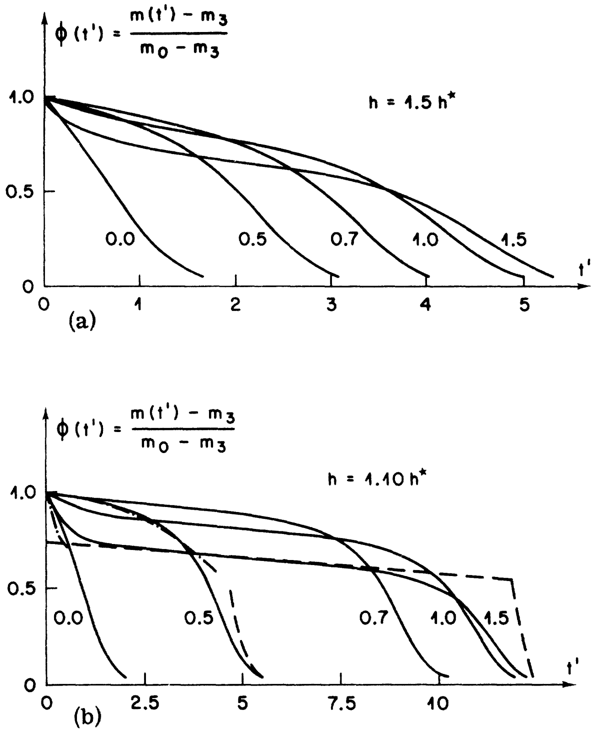


FIG. 5. Nonequilibrium relaxation functions plotted versus time for $h=1.5h^*$ (a), and $h=1.1h^*$ (b). Parameter of the curves: m_0 [cf. Fig. 4(a)]. For $h=1.1h^*$ and $m_0=0.5$ we show the short- [Eq. (A5), dashed-dotted curve] and large-time approximations [Eq. (A13), broken curve], while for $m_0=1.5$ the approximations Eqs. (57), (A13), and (A14) are shown.

starts to increase again. The function $\ln\phi_{k'}(t')$ has its minimum value at $m=(1/\sqrt{3})\,(1-k'^2)^{1/2}$, its maximal slope $1-k'^2$ at $m=0$, and its maximum value at $m=-(1/\sqrt{3})(1-k'^2)^{1/2}$.

Note that in the nonequilibrium case $\lim_{k'\to 0}\phi_{k'}(t') \neq \phi(t')$, contrary to states near the equilibrium. At this stage we should mention the relation of the unstable "spinodal" mechanism to the nucleation mechanism. As will be pointed out in Sec. V, true nucleation is absent in the Ginzburg-Landau model; but in a real system states with $0<h\ll h^*$ will decay by nucleation, while states with $h\gg h^*$ may decay by the growth of unstable modes as described above. Both processes may lead to a rather similar behavior of the $\phi_{k'}(t')$ functions. The maximum value $k'=1$ (for $h>h^*$) corresponds to the minimum size of a "stable" cluster, a "critical cluster" (for $h<h^*$). Clusters larger than the critical cluster tend to grow in the course of the magnetization reversal process, until the new phase is built up and they disappear again. This growth process of clusters corresponds to the shift of the pronounced maxima in the $\phi_{k'}(t')$ function towards smaller k'. Later on, $\phi(t')\to 0$, the magnetization tends to its new equilibrium value, and the fluctuation described by $\phi_{k'}(t')$ decreases again. For $h\lesssim h^*$ the cluster spreads out according to the Cahn and Hilliard theory,[21] its central density diminishes, and its energy of formation goes to zero.[21] One may argue that for fields where this energy is of order k_BT the droplet mechanism is rather indistinguishable from the unstable spinodal mechanism. Note, that the description in terms of the $\phi_{k'}(t')$ functions is unambiguous also in this region. We do not claim, however, that Eqs. (63)–(65) or Fig. 7 provide already an accurate description of the phase transition, since by a TDGL theory only the smallest k could be taken into account.

V. VALIDITY OF THE TIME-DEPENDENT GINZBURG-LANDAU THEORY

Considering the second-order phase transition at $T\to T_c$ it is argued[2,19,36] that the Ginzburg-Landau theory is an accurate description if the range of interaction R gets very large. Writing $J_{ij}=J(\vec{r}_i-\vec{r}_j)=J(\vec{r})$, R is defined by

$$R^2=\frac{\int J(\vec{r})r^2d\vec{r}}{\int J(\vec{r})d\vec{r}}=\frac{1}{J(0)}\int J(\vec{r})r^2d\vec{r}. \tag{66}$$

Since the Ising model considered in Eq. (3) is sup-

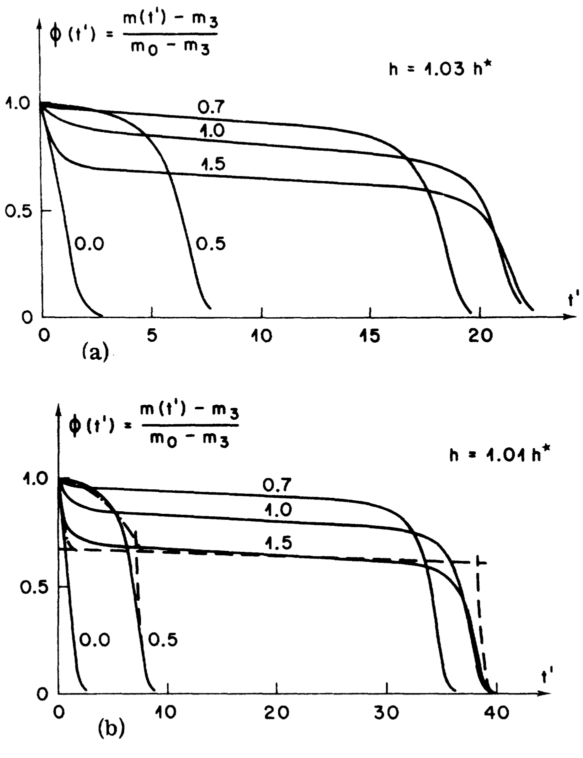


FIG. 6. Nonequilibrium relaxation functions plotted versus time for $h=1.03h^*$ (a), and $h=1.01h^*$ (b). For further explanations, cf. Fig. 5.

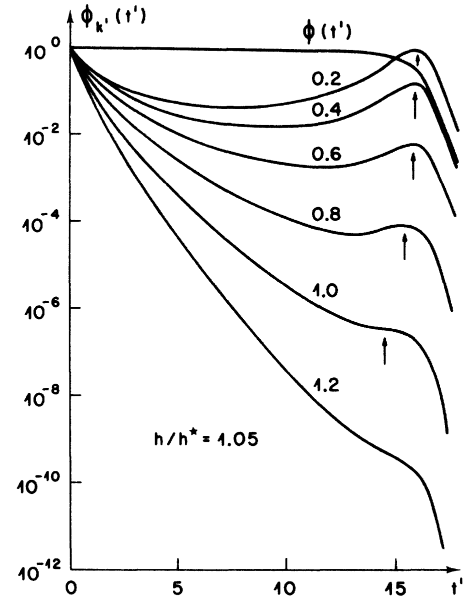


FIG. 7. Wave-vector-dependent nonequilibrium relaxation function plotted versus time. Parameter of the curves: wave vector k'. The arrows indicate the position of the maximum.

posed to be a rather realistic description of anisotropic magnets, liquid-gas systems, and alloys at constant chemical potential, as far as the general properties of the second-order phase transition are concerned,[2] it seems worthwhile deriving the TDGL equations from a long-range kinetic Ising model.[26,44] Following Ref. 26, the transition probability W in Eqs. (8) and (10) is chosen as

$$W(\mu_i \to -\mu_i)=\frac{1}{2\tau_s}\left[1-\mu_j \tanh\frac{1}{k_BT}\left(H_i+\sum_j J_{ij}\mu_j\right)\right], \tag{67}$$

to derive the kinetic equation for $\langle\mu_i(t)\rangle$ [Eq. (9)]

$$\tau_s\frac{d}{dt}\langle\mu_i(t)\rangle=-\langle\mu_i(t)\rangle+\left\langle\tanh\frac{1}{k_BT}\left(\sum_j J_{ij}\mu_j(t)+H_j\right)\right\rangle. \tag{68}$$

If the exchange J_{ij} is long ranged, the fluctuations of $\sum_j J_{ij}\,\mu_j(t)$ may be neglected and $\sum_j J_{ij}\mu_j(t)$ can be replaced by its average value. Near T_c the tanh can be expanded, and one obtains for the homogeneous magnetization [putting $J(0)=k_BT_c$][26,28]

$$-\tau_s\frac{d}{dt}\langle\mu(t)\rangle=-\left(1-\frac{T}{T_c}\right)\langle\mu(t)\rangle+\tfrac{1}{3}\langle\mu(t)\rangle^3-\frac{H_0}{k_BT_c}, \tag{69}$$

which has precisely the form of Eq. (35). Since it has been shown that arbitrary other choices of the single-spin-flip transition probability, which are consistent with the detailed balance condition [Eq. (10)], lead to a renormalization of the time scale τ_s only in this mean-field limit,[45] the result Eq. (69) is independent of the special choice Eq. (67) for W. Expanding

$$J(\vec{k})=\sum_{\vec{r}} e^{i\vec{k}\cdot\vec{r}}J(\vec{r})\approx J(0)\left(1-\frac{k^2R^2}{6}\right), \tag{70}$$

one derives in the same way as Eq. (69) an equation for the inhomogeneous case

$$-\tau_s\frac{d}{dt}\langle\mu_k(t)\rangle=-\left[\left(1-\frac{T}{T_c}\right)-\langle\mu(t)\rangle^2-\frac{R^2}{6}k^2\right]\times\langle\mu_k(t)\rangle-\frac{H_k(t)}{k_BT_c}, \tag{71}$$

which is again equivalent to Eq. (36).

An experimental example for an Ising system with long-range interactions may be provided by hydrogen in metals, for example, H in Nb. If an interstitial lattice site (j) is occupied by an H atom, one has $\mu_j=-1$, while otherwise $\mu_j=+1$. Because of the elastic distortions produced by the H atom in its environment in the Nb lattice the effective interaction between different H atoms is an elastic dipole-dipole interaction.[46] Indeed in these systems the critical exponents of the Landau theory[1] are found to high precision,[46] and also well-defined metastable states are easily observed,[47] investigating the properties of the Nb-H system after changes of the chemical potential (which plays there the role of the magnetic field[2,36]). If it turns out feasible to measure the $\phi_\mu^{\Delta H,\Delta T}(\vec{k}',t)$ functions, an immediate field of application for the present theory would be provided.

So far we tacitly supposed the validity of Eqs. (67) and (71) near the equilibrium state implies also a validity far from equilibrium. This seems a fair approximation, since the local property τ_s (a single-spin-flip rate) should not depend in any critical manner on T/T_c or h/h^*. Thus one may take it as essentially constant.

Having established the validity of the treatment for the limit $R\to\infty$ it is also interesting to ask for the validity, whether R is large but strictly finite. This question has been considered in detail with respect to the second-order transition (the so-called Ginzburg and Brout criteria[2,19,36]).

In order to develop a similar criterion for the metastability it is useful to repeat the argument for $T\to T_c$. In zero field above T_c, Ginzburg-Landau theory predicts the energy to be exactly zero, while it varies as $\psi_0^2(T,0)$ for $T<T_c$. For finite R this result is qualitatively incorrect of course, the energy above T_c will be nonzero. Due to fluctuations there will be a nonzero magnetization inside the interaction volume R^d of a d-dimensional system also above T_c. From fluctuation theory[1] one thus estimates the (relative) energy $e(T)$

$$e(T)=\frac{E(T)}{E(0)}\approx\left(\frac{R}{r_0}\right)^{-d}\left(1-\frac{T_c}{T}\right)^{-1}c_1, \tag{72}$$

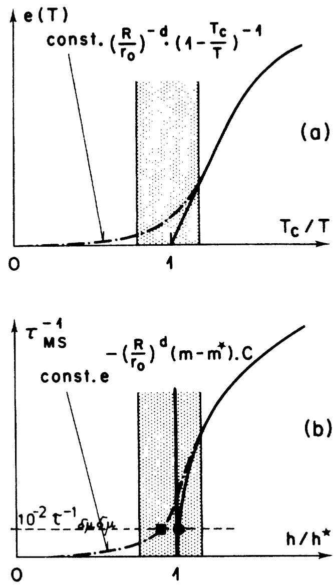


FIG. 8. Validity criterion of mean-field theory (a), and its extension to metastability (b). In (a) the reduced energy $e(T)$ is plotted versus the inverse temperature; in (b) the inverse lifetime of the metastable state τ_{MS}^{-1} is plotted versus the field. The dashed-dotted curves indicate the behavior for systems with large but finite range of interaction R, the cross-hatched areas denote the location of the "critical regions." According to the flatness criterion (Sec. III) states are "metastable" if, say, $\tau_{MS} = 10^2 \tau_{\delta\mu\delta\mu}$ (dashed straight line), where $\tau_{\delta\mu\delta\mu} = \int_0^\infty \phi_\mu^{eq}(0, t)\,dt$. While the limit of metastability in the long-range case (indicated by the solid circles) exceeds h^* slightly, it will be smaller than h^* in a finite-range case (indicated by the solid squares).

where we denote constant factors of magnitude one here and in the following equations by $c_1, c_2, c_3, \ldots$, respectively, and where r_0 is the lattice spacing, and d is the dimensionality of the system. Now it is argued that the Ginzburg-Landau theory is essentially correct as long as this expression is very small, i.e.,

$$|1 - T_c/T| \gg c_1 (R/r_0)^{-d} . \tag{73}$$

This behavior is illustrated in Fig. 8(a); the cross-hatched region where the Ginzburg-Landau theory breaks down can be made arbitrarily small, if R is only made large enough. A more refined discussion[19] than the one reproduced here yields even an improved regime of validity.

Now we study the inverse lifetime $\tau_{MS}^{-1} = 0$ for $h < h^*$ but $\tau_{MS}^{-2} \propto (h/h^* - 1)^{1/2}$ for $h < h^*$. For finite R this result is qualitatively incorrect, of course; the inverse lifetime below h^* is nonzero. As will be discussed below, this lifetime is estimated to be

$$\tau_{MS}^{-1} \approx \exp[-(R/r_0)^d (m - m^*) c_2] . \tag{74}$$

Again it can be argued that the TDGL theory is essentially correct as long as this expression is very small, i.e., using Eq. (46) it follows

$$|1 - h/h^*| \gg c_2^{-2} (R/r_0)^{-2d} . \tag{75}$$

This behavior is illustrated in Fig. 8(b); the cross-hatched region where TDGL theory breaks down can be made arbitrarily small if R is only made large enough. Note that the relaxation processes considered in Sec. IV for $h \gtrsim h^*$ and $R = \infty$ will correspond to relaxation processes at $h \lesssim h^*$ for finite R ! In this case τ_{MS}^{-1} will get large at h^* already, while τ_{MS}^{-1} is still small for fields exceeding h^* slightly for $R = \infty$.

This property is due to the absence of nucleation in the long-range model. We can understand the nonexistence of nucleation treating briefly the derivation of the critical cluster size l^*[20,21,23]; consider the change in energy brought about by the formation of a cluster with l reversed spins. This formation is favorable due to a gain of "bulk energy," the interaction with the magnetic field proportional to $[-(2H/k_BT)l]$, but unfavorable due to a loss of "surface energy," i.e., the spin-spin exchange interactions. If the interactions are short ranged, only spins near the surface of the cluster contribute to this energy change, and one takes this contribution proportional to l^σ with $\sigma < 1$. If l is increased there exists a value $l = l^*$ where the additional loss of "surface energy" is compensated by the gain of Zeeman energy. If the interactions are long ranged, however, all spins of the cluster contribute to the change of interaction energy; thus this change is not of "surface-energy" type, but increases also proportional to l, and the matching of the two contributions does not yield a finite value for l^*.

We have now to justify Eq. (74). This equation is a tentative generalization of a rigorous result obtained by Penrose and Lebowitz[10] in their discussion of the van der Waals gas. Their result applies to a system whose volume Ω is large but finite, too, satisfying the inequality

$$\Omega \gg R^d \gg r_0^d \ln(\Omega/r_0^d) . \tag{76}$$

Letting in this way $\Omega \to \infty$ and $R \to \infty$ together, one obtains metastable states as described by the van der Waals equation and with an inverse lifetime of about $e^{-(R/r_0)^d c_3}$. Note that if one takes $\Omega \to \infty$ first and keeps R finite during this limit process, no metastable states at all are obtained from a precise evaluation of the partition function.[11] (This result is also valid for the Ising model.) If one takes the limit $R \to \infty$ first and then $\Omega \to \infty$, one obtains metastable states with an inverse lifetime of $e^{-(\Omega/r_0^d) c_3}$[18]; this case is physically less interesting, however. The important point of Ref. 10 is, that well-defined and long-living metastable states can occur also for quite microscopic interaction volumes R^d, for example, for $R/r_0 \approx 4-5$ the metastable volume Ω and the lifetime τ_{MS} become macroscopic. Our extrapolation of this result to the stochastic Ising case is only a conjecture, however, since the rigorous proof[10] was based on a classical mechanics study of dynamic fluctuations in the van der Waals gas, while the dynamics of the spin systems considered here are rather different. Furthermore, we have extrapolated the result of Ref. 10 to both $T \to T_c$ and $h \to h^*$, not treated in the exact calculation. A more rigorous justification of Eqs. (75) and (74) seems therefore highly desirable, but is beyond the scope of the present paper.

VI. CONCLUSION

We conclude by summarizing the main results of this investigation, and briefly discuss further applications to models with short-range forces.

(i) The first-principles description of nonequilibrium relaxation phenomena in many-body systems was briefly treated, and an appropriate relaxation function introduced (Sec. II). This function was shown to be a generalization of the well-known time-dependent pair correlation function. It was pointed out that this description remains valid near the first-order phase transitions of the model systems, which we wanted to consider, for example, the kinetic Ising model with long-range forces.

(ii) Since the main subject of this paper was a contribution to the theoretical understanding of metastability associated with first-order phase transitions, we suggested a dynamic definition of metastable states in terms of a "flatness" property of the relaxation curve (Sec. III). This definition is intuitively obvious, and its precise form [Eqs. (22)–(28)] allows a construction of the properties of the metastable states once the nonequilibrium relaxation function introduced in Sec. II is given. A brief comparison with previous treatments suggests that our definition does not contradict the other characterizations of metastability.

(iii) We show that the nonequilibrium relaxation functions can be calculated in the case of the time-dependent Ginzburg-Landau theory (Sec. IV). The TDGL equations are formulated for the case of small spatial inhomogeneities, and the properties of their stationary solutions reviewed. "Metastable" states with infinite lifetimes occur for fields $h < h^*$, while for fields h slightly exceeding h^* relaxation functions are found exhibiting the flatness property postulated in Sec. III. In Sec. V it is pointed out that these functions will in fact be a realistic description for $h \lesssim h^*$ and not $h \gtrsim h^*$ in the case of systems with finite range of interaction. Furthermore it is shown that the inverse lifetimes of the metastable states are proportional to the imaginary part of the order parameter, as long as the imaginary part is small.

(iv) The decay of spatial fluctuations during the course of the relaxation process is also investigated. In the region where the order parameter changes its sign, spatial fluctuations larger than a critical value $(k')^{-1}$ become enhanced, reach a maximum, and decrease again. The smaller k' the later occurs the maximum in the course of the process. Thus, the decomposition process has some (superficial) analogy to the growth of clusters larger than a critical cluster during a nucleation process. True nucleation phenomena are not expected to occur in a model with long-range forces (Sec. V). We believe that this is the reason why the metastable states for $h < h^*$ have infinite lifetime, since conventional nucleation is the only mechanism capable to bring the system from the stable to the metastable phase in the case $h < h^*$.

(v) Discussing the validity of the TDGL treatment (Sec. V) it is shown that these TDGL equations (36) and (35) are easily derived from a long-range kinetic Ising model. Since a description in terms of a master equation (8) is known to be a rather general description of various kinds of dissipative systems in a certain limit,[27] this relation between Eqs. (8), (35), and (36) suggests an applicability of our treatment to various kinds of dissipative systems with long-range forces. A validity criterion for $h \approx h^*$ similar to the Ginzburg criterion for $T \approx T_c$ is also conjectured.

(vi) In the case of models with short-range forces, our treatment of Secs. IV and V is clearly inconclusive. Kinetic equations for the single-particle function $\langle \mu_i(t) \rangle$ can still be formulated [Eqs. (7) and (68)], but cannot be solved explicitly without making an unreliable factorization approximation for the higher-order correlations involved in these equations. Thus it seems questionable whether the program carried out here is applicable in any other case even within some reasonable approximation. Therefore we want to mention two approaches, where the nonequilibrium relaxation function [Eq. (13)] turns out to be a quite natural and immediate result of the calculation: (a) Nucleation theory: Applying the "magnetic language" one has to describe the growth and decay of clusters with l spins; usually it is assumed that their concentration $n_l(t)$ obeys a first-order differential equation

$$\frac{dn_l(t)}{dt} = F(\{n_l(t)\}) . \tag{77}$$

Now the time dependence of the order parameter $\langle \mu(t) \rangle$ and thus the nonequilibrium relaxation function $\phi(t)$ [Eq. (19)] are simply determined by the first moment of the cluster distribution

$$\langle\mu(t)\rangle = 1 - 2\sum_{l=1}^{\infty} l n_l(t). \tag{78}$$

(b) Computer simulations: The Monte Carlo method is known to be an explicit realization of the master equation (8).[22,45] This approach is readily compatible with (a) since "clusters" are immediately seen among the "raw-data" configurations of such a computer experiment, and the connection between the observed cluster distribution[48] and theoretical models[49] has been established.[48]

A detailed investigation of the metastability, nonequilibrium relaxation functions $\phi(t)$ and time-dependent cluster distributions $n_l(t)$ of a two-dimensional nearest-neighbor kinetic Ising model will be the subject of a forthcoming paper.[23]

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APPENDIX: NONEQUILIBRIUM RELAXATION TIMES AND APPROXIMATION FORMULAS

Rewriting Eq. (43)

$$-dt' = \frac{dm}{(m-m_1)(m-m_2)(m-m_3)}, \tag{A1}$$

the solution is easily found explicitly for the inverse function $t'(m)$. Consider the case $h<h^*$ first. Equation (A1) leads to

$$\phi(t') \equiv \frac{m(t')-m_3}{m_0-m_3} = \left[\left(\frac{m(t')-m_1}{m_0-m_1}\right)^{(m_3-m_2)/(m_1-m_2)} \bigg/ \left(\frac{m(t')-m_2}{m_0-m_2}\right)^{(m_3-m_1)/(m_1-m_2)} e^{-(3m_3^2-1)t'}\right] \tag{A2}$$

for $m_0<m_2$, while for $m_0>m_2$ Eq. (53) results. A "large-time approximation" is derived from Eqs. (A2) and (53) by replacing $m(t')$ by m_1 or m_3 on the right-hand side of these equations,

$$\phi(t') \xrightarrow[t'\to\infty]{} \left[\left(\frac{m_1-m_2}{m_0-m_2}\right)^{(m_1-m_3)/(m_2-m_3)} \bigg/ \left(\frac{m_1-m_3}{m_0-m_3}\right)^{(m_1-m_2)/(m_2-m_3)}\right] e^{-(3m_1^2-1)t'} \tag{A3}$$

for $m_0>m_2$, and

$$\phi(t') \xrightarrow[t'\to\infty]{} \left[\left(\frac{m_3-m_1}{m_0-m_1}\right)^{(m_3-m_2)/(m_1-m_2)} \bigg/ \left(\frac{m_3-m_2}{m_0-m_2}\right)^{(m_3-m_1)/(m_1-m_2)}\right] e^{-(3m_3^2-1)t'} \tag{A4}$$

for $m_0<m_2$. A "short-time approximation" results using Eq. (43) to derive

$$m(t') = m_0 + t'(m_0-m_3+m_3^3-m_0^3) + \tfrac{1}{2}t'^2(1-3m_0^2)(m_0-m_3+m_3^2-m_0^3) + \tfrac{1}{6}t'^3\left[(1-3m_0^2)^2(m_0-m_3+m_3^3-m_0^3) - 6(m_0-m_3+m_3^3-m_0^3)^2 m_0\right] + \cdots . \tag{A5}$$

Equation (A5) is valid if $|m(t')-m_0| \ll m_0$, while Eq. (A3) holds for $|m(t')-m_1| \ll m_1$, and Eq. (A4) for $|m(t')-m_3| \ll m_3$. The results for the nonequilibrium relaxation time τ_R[Eq. (20)] are

$$\tau_R = \frac{1}{3m_1^2-1} + \frac{1}{3m_2^2-1}\left(1+\frac{m_1-m_2}{m_1-m_0}\ln\frac{m_0-m_2}{m_1-m_2}\right) + \frac{1}{3m_3^2-1}\left(1+\frac{m_1-m_3}{m_1-m_0}\ln\frac{m_0-m_3}{m_1-m_3}\right) \tag{A6}$$

for $m_0>m_2$, while for $m_0<m_2$ we have

$$\tau_R = \frac{1}{3m_3^2-1} + \frac{1}{3m_2^2-1}\left(1+\frac{m_3-m_2}{m_3-m_0}\ln\frac{m_0-m_2}{m_3-m_2}\right) + \frac{1}{3m_3^2-1}\left(1+\frac{m_3-m_1}{m_3-m_0}\ln\frac{m_0-m_1}{m_3-m_1}\right). \tag{A7}$$

τ_R reduces to the appropriate equilibrium relaxation time [the first term in Eq. (A7) or (A6), respectively], if we proceed to the limit $m_0\to m_1$ or $m_0\to m_3$, respectively.

Consider next the case $h=h^*$, where $m_1=m_2$. Integration of Eq. (A1) yields for $m_0>m_1$

$$\phi(t') \equiv \frac{m(t')-m_1}{m_0-m_1} = \left[1+t'(m_0-m_1)(m_1-m_3)+\frac{m_0-m_1}{m_1-m_3}\ln\left(\frac{m(t')-m_3}{m_0-m_3}\;\frac{m_0-m_1}{m(t')-m_1}\right)\right]^{-1}, \tag{A8}$$

and for $m_0<m_1$

$$\phi(t') \equiv \frac{m(t')-m_3}{m_0-m_3} = \frac{m(t')-m_1}{m_0-m_1}\exp\left(-t'(m_1-m_3)^2+\frac{m(t')-m_0}{m(t')-m_1}\;\frac{m_1-m_3}{m_0-m_1}\right). \tag{A9}$$

The large-time approximations yield for Eq. (A8)

$$\phi(t') \xrightarrow[t'\to\infty]{} [t'(m_0 - m_1)(m_1 - m_3)]^{-1}, \tag{A10}$$

and for Eq. (A9)

$$\phi(t') \xrightarrow[t'\to\infty]{} \frac{m_3 - m_1}{m_0 - m_1} \exp[-t'(m_1 - m_3)^2] \exp\left(\frac{m_0 - m_3}{m_0 - m_1}\right) . \tag{A11}$$

The short-time approximation is still given by Eq. (A5). Note that for $m_0 > m_1$ we have an exceptional case of "slow" relaxation, τ_R [Eq. (20)] does not exist. For $m_0 < m_1$, τ_R is given by

$$\tau_R = [(m_1 - m_3)(m_1 - m_0)]^{-1}. \tag{A12}$$

In the case $h > h^*$ one finds from Eq. (56) the large-time approximation

$$\phi(t') \xrightarrow[t'\to\infty]{} \left(\frac{(m_3 - y)^2 + z^2}{(m_0 - y)^2 + z^2}\right)^{1/2} \exp\left[\frac{y - m_3}{z}\left(\arctan\frac{m_0 - y}{z} - \arctan\frac{m_3 - y}{z}\right)\right] \exp[-t'(3m_3^2 - 1)]. \tag{A13}$$

In the regime of long-living intermediate states y, the short-time approximation of Eq. (A5) is rather poor, of course, and better replaced by some exponential relaxation towards the metastable state

$$\phi(t') = \frac{y - m_3}{m_0 - m_3} + \frac{m_0 - y}{m_0 - m_3} e^{-t'(3m_3^2 - 1)}, \tag{A14}$$

which is also easily derived from Eq. (56) for $t'(3m_3^2 - 1) \lesssim 1$. Integrating Eq. (56) from m_0 to m_3 yields the relaxation time

$$\tau_R = \frac{1}{3m_3^2 - 1} \frac{1}{m_0 - m_3} \left[z\left(\arctan\frac{y - m_3}{z} + \arctan\frac{m_0 - y}{z}\right) + \frac{(y - m_3)^2}{z}\left(\arctan\frac{y - m_3}{z} + \arctan\frac{m_0 - y}{z}\right)\right] . \tag{A15}$$

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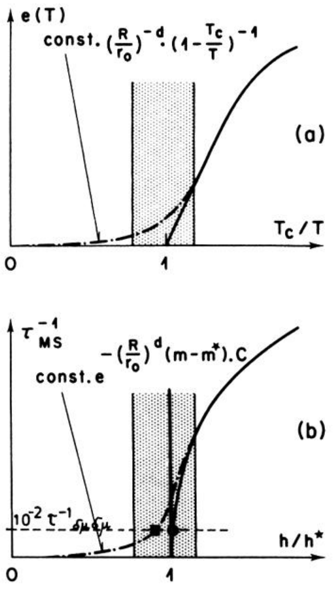

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