Administration under Contract No. NGR 14-005-037.

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THEORY OF NUCLEATION RATES*

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(Received 15 July 1968)

A general procedure is outlined for the first-principles calculation of the rate of decay of a metastable phase.

One of the more important outstanding problems in statistical mechanics involves the rate of decay of a metastable phase. It would be very useful to know how to make a first-principles calculation of, for example, the rate of condensation of supersaturated vapor, the realignment of a magnetic domain in an applied field, or the decay of a persistent current in a superfluid. All of these processes occur when the system undergoes a statistical fluctuation large enough to nucleate the phase transition. The characteristic fluctuations for the three transitions mentioned above are, respectively, a liquid droplet, a cluster of reversed spins, and a vortex ring.

The problem is an old one. Probably the most important piece of work in the field is the calculation by Becker and Döring in 1935 of the condensation rate for a supersaturated vapor.[1,2] In the absence of a first-principles derivation, however, this semiphenomenological calculation has been subject to frequent criticism, some modern authors claiming correction factors of order 10^{15} or more.[3] Interest in the nucleation theory has been further stimulated recently by its apparently successful application in understanding the onset of resistivity in superfluids[4] and superconductors.[5] Here again, existing theories are phenomenological in certain important aspects, and contain completely unknown factors.

In the following note, we outline a scheme for the calculation of nucleation rates for a class of simple but nontrivial models of phase transitions. The basic ideas seem to be quite general. Work is now in progress on the practical application of this scheme to the calculation of the rate of current-reducing fluctuations in a superfluid.

We consider a system described by a set of classical variables $\eta_i, i = 1, 2, \cdots N$, where N is the number of degrees of freedom. For example, η_i could be the magnetization at the ith site of a magnetic lattice, or the order parameter at the ith position in a superfluid. For the sake of simplicity, we assume that the η's are real numbers varying from $-\infty$ to $+\infty$. It will greatly simplify the following analysis if we further assume that, like an Ising or spherical model, the system under consideration has no internal dynamics of its own. That is, in the absence of interactions with a heat bath, the configuration $\{\eta\}$ remains fixed. It turns out to be fairly easy to generalize this calculation to cases where the motion of $\{\eta\}$ is governed by, say, Newton's laws or the Ginzburg-Landau equation. But such motion is not of direct interest here because it is always energy conserving, whereas first-order phase transitions are nucleated by fluctuations which do not conserve energy.

Next, we assume that, when in interaction with a constant-temperature bath, the system will make a transition from $\{\eta'\}$ to $\{\eta\}$ with a probability P per unit time of the form

$$P(\{\eta\},\{\eta'\})dt = \Gamma\left(\frac{dt}{\Delta}\right)(\pi\Delta)^{-\frac{1}{2}N}\exp\left(-\frac{1}{2kT}E\{\eta\}\right)\exp\left(\frac{1}{2kT}E\{\eta'\}\right)\exp\left[-\frac{1}{\Delta}\sum_i(\eta_i-\eta_i')^2\right], \quad (1)$$

where $E\{\eta\}$ is the energy of the system in configuration $\{\eta\}$.[6] This expression for P is actually quite general. The symmetrized Boltzmann factors simply describe the probability of various energy exchanges with the heat bath. The final Gaussian factor makes it very improbable that two successive configurations will differ drastically from one another. Δ is a small parameter inserted in such a way that, in the limit $\Delta \to 0$, the Gaussian factor becomes a δ function. The overall factor Γ contains the details of the actual interactions which drive the fluctuations, e.g., spin-phonon coupling or the like.

Now define $\rho(\{\eta\},t)$ to be the probability density for states $\{\eta\}$. This function satisfies the master equation

$$\rho(\{\eta\},t+dt) = W\rho(\{\eta\},t) + dt \int d\eta_1' \cdots \int d\eta_N' \, P(\{\eta\},\{\eta'\})\rho(\{\eta'\},t), \tag{2}$$

where

$$W\{\eta\} = 1 - dt \int d\eta_1' \cdots \int d\eta_N' \, P(\{\eta'\},\{\eta\}). \tag{3}$$

Equation (2) is equivalent to a Fokker-Planck equation in the limit of small Δ. To see this, expand $\rho\{\eta'\}$ and $E\{\eta'\}$ about $\{\eta'\}=\{\eta\}$ and then keep only terms to first order in Δ. The resulting equation is

$$\frac{\partial\rho}{\partial t} = \frac{\Gamma}{4}\sum_i \left[\frac{\partial}{\partial\eta_i}\left(\frac{1}{kT}\frac{\partial E}{\partial\eta_i}\rho\right) + \frac{\partial^2\rho}{\partial\eta_i^{\,2}}\right]. \tag{4}$$

It should be emphasized that, once the transition probability is cast in the form (1), Eq. (4) follows automatically.

Equation (4) is a continuity equation in η space:

$$\partial\rho/\partial t = -\textstyle\sum_i \partial J_i/\partial\eta_i, \tag{5}$$

where the N-dimensional probability-current density is

$$J_i = -\frac{\Gamma}{4}\left(\frac{1}{kT}\frac{\partial E}{\partial\eta_i}\rho + \frac{\partial\rho}{\partial\eta_i}\right). \tag{6}$$

The equilibrium solution is

$$\rho_0\{\eta\} = \exp[-(1/kT)E\{\eta\}], \tag{7}$$

corresponding to $J_i = 0$ for all i. The various stable and metastable configurations occur at the positions of the local minima of $E\{\eta\}$ in the N-dimensional η space. It has been emphasized in several previous papers[4,5,7] that, in passing from one local minimum to a neighboring one, the system point $\{\eta\}$ is most likely to pass across the lowest intervening saddle point of the function $E\{\eta\}$. In general, this saddle point, say $\{\bar{\eta}\}$, will describe a configuration which is everywhere the same as the initial metastable state except for the presence of a single localized fluctuation, e.g., a droplet or a vortex ring. Once $\{\eta\}$ reaches $\{\bar{\eta}\}$, it is energetically favorable for the system to move all the way to the state of greater stability. It is in this mathematical sense that $\{\bar{\eta}\}$ nucleates the phase transition.

This equilibrium description obviously tells us nothing about rates. Having come this far, however, it is not difficult to discover the N-dimensional—and therefore fully microscopic—generalization of the theory of Becker and Döring.[1] The basic idea is to construct, instead of ρ_0, a steady-state solution of Eq. (4) in which a finite probability current flows across the saddle point.

To do this, it is convenient to work with a set of N variables, ξ_n, which are principal-axis coordinates for $E\{\eta\}$ having their origin at the stationary point $\{\bar{\eta}\}$. That is,

$$E\{\eta\} = \bar{E} + \tfrac{1}{2}\sum_{n=1}^{N} \lambda_n \xi_n^{\,2} + \cdots, \tag{8}$$

where $\bar{E} = E\{\bar{\eta}\}$, and the λ_n are the eigenvalues of the matrix $\partial^2 E/\partial\eta_i\partial\eta_j$ evaluated at $\{\bar{\eta}\}$. By the definition of $\{\bar{\eta}\}$, we know that one and only one of the λ's, say λ_1, is negative. That is, E diminishes on either side of the surface $\xi_1 = 0$; and, inasmuch as system points tend to relax in the direction of decreasing E, points on either side of $\xi_1 = 0$ can be thought of as belonging to different phases.

Let us assume that the metastable phase whose relaxation we are computing is described by positive values of ξ_1. Then we seek a solution of (4) near the saddle point in which ρ vanishes for negative ξ_1 and a current J_1 flows parallel to the ξ_1 axis. Somewhat more physically, we imagine maintaining a steady-state situation by removing from the statistical ensemble any system which undergoes a phase transition, i.e., any point which crosses $\xi_1 = 0$, and somehow returning this system to the ensemble in a metastable configuration.

As long as J_1 is independent of ξ_1, Eq. (4) will automatically be satisfied with $\partial\rho/\partial t = 0$. To determine J_1, we return to Eq. (6). Since the

transformation from the η's to the ξ's is orthogonal, we have

$$J_1\{\xi\} = -\frac{\Gamma}{4}\left(\frac{1}{kT}\frac{\partial E}{\partial \xi_1}\rho + \frac{\partial \rho}{\partial \xi_1}\right) \tag{9}$$

$$0 = -\frac{\Gamma}{4}\left(\frac{1}{kT}\frac{\partial E}{\partial \xi_n}\rho + \frac{\partial \rho}{\partial \xi_n}\right), \quad n \neq 1. \tag{10}$$

Solving (9) for ρ, we obtain (for $\xi_1 > 0$)

$$\rho\{\xi\} = -\frac{4J_1\{\xi\}}{\Gamma} e^{-E\{\xi\}/kT} \int_0^{\xi_1} d\xi_1' \exp\left[\frac{1}{kT}(\bar{E} - \tfrac{1}{2}|\lambda_1|\xi_1'^2 + \tfrac{1}{2}\sum_{n=2}^{N}\lambda_n \xi_n^2)\right], \tag{11}$$

where we have inserted the expansion (8) for the E appearing in the integrand. In order that (11) also satisfy Eq. (1) for all n other than $n = 1$, we must choose

$$J_1\{\xi\} = -I \exp\left[-\frac{1}{kT}(\bar{E} + \tfrac{1}{2}\sum_{n=2}^{N}\lambda_n \xi_n^2)\right]. \tag{12}$$

Thus,

$$\rho\{\xi\} = \frac{4I}{\Gamma} e^{-E\{\xi\}/kT} \int_0^{\xi_1} d\xi_1' \exp\left(-\frac{|\lambda_1|}{2kT}\xi_1'^2\right). \tag{13}$$

The constant I must be fixed by normalizing ρ. Note that the final factor in (13), the integral over ξ_1', rises from zero at $\xi_1 = 0$ and levels off at a value $(\pi kT/2|\lambda_1|)^{1/2}$ for large enough ξ_1. Assuming that the dominant contribution to the normalization of ρ occurs well beyond this region of variation near $\xi_1 = 0$, we have

$$\int d\eta_1 \cdots \int d\eta_N \rho\{\eta\} \cong (4I/\Gamma)(\pi kT/2|\lambda_1|)^{1/2} Z_0 = 1, \tag{14}$$

where Z_0 is a partition function in which the sum is performed only over metastable configurations. To be specific, let E_0 be the value of $E\{\eta\}$ at the metastable minimum, and let $\lambda_l^{(0)}$ be the eigenvalues of $\partial^2 E/\partial^2 \eta_i \partial \eta_j$ at this point. Then

$$Z_0 = \int^{(0)} d\eta_1 \cdots \int^{(0)} d\eta_N e^{-E\{\eta\}/kT} \cong e^{-E_0/kT} \prod_l (\pi kT/2\lambda_l^{(0)})^{\frac{1}{2}}, \tag{15}$$

where the superscripts (0) denote the restricted range of integration.

Combining these results, we obtain

$$J_1\{\xi\} = -\frac{\Gamma}{4}\left(\frac{2|\lambda_1|}{\pi kT}\right)^{1/2}\frac{1}{Z_0}\exp\left[-\frac{1}{kT}(\bar{E} + \tfrac{1}{2}\sum_{n=2}^{N}\lambda_n \xi_n^2)\right]. \tag{16}$$

Finally, the condensation rate R must be the total flux across the surface $\xi_1 = 0$:

$$R = -\int d\xi_2 \cdots \int d\xi_N J\{\xi\}. \tag{17}$$

Equations (16) and (17) constitute a complete summary of the theory. The evaluation of (17) is perfectly feasible; and the only reason that it has not been written out explicitly here is that the precise integrations required are model dependent. In particular, some of the λ's always will turn out to be zero because of symmetry properties of the system, and the associated integrals must be handled separately. Most important among these symmetries is the invariance of $E\{\eta\}$ to translations of the critical fluctuation; e.g., the critical droplet or vortex ring can occur anywhere within the sample volume. As a result of this symmetry, R always is proportional to the size of the system.[8]

We conclude with some comments regarding the relation of these results to earlier work. First, note that Eqs. (15) and (16) combine to give us an overall factor of $\exp[-(1/kT)(\bar{E} - E_0)]$ in R. The quantity $\bar{E} - E_0$ is the height of the energy barrier which must be surmounted in nucleating the phase transition. Most of the remaining factors in R are fluctuation corrections to this energy difference; i.e., they change ener-

gies into free energies. This observation seems to justify our use of a phenomenological free energy for the barrier height in previous calculations.[4,5]

Finally, the author has argued in another publication[7] that the proper analytic definition of a metastable state requires its free energy to be a complex number. In that paper it was conjectured that the imaginary part of this free energy might be proportional to the condensation rate. This conjecture turns out to be verified under the present assumptions, as can be seen by comparing Eq. (4.64) of Ref. 7 and the above expression for R. The proportionality constant is simply Γ.

*Work supported in part by the National Science Foundation.

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FREQUENCY DEPENDENCE OF MICROWAVE PHONON-PHOTON DOUBLE-QUANTUM TRANSITIONS

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The frequency dependence of phonon-photon double-quantum transitions in MgO:Fe^{+2} was investigated by using 8.7-GHz photons to detect 9.3-, 4.7-, and 3.1-GHz phonons. The transition probability for simultaneous absorption of both a phonon and a photon markedly decreased with decreasing phonon frequency. In the case of 4.7- and 3.1-GHz phonons, a new type of phonon-photon transition was observed.

We have investigated the frequency dependence of phonon-photon double-quantum transitions in Fe^{+2}-doped MgO by using 8.7-GHz photons to detect 9.3-, 4.7-, and 3.1-GHz phonons. The double-quantum detection of 9.45-GHz phonons with 9.21-GHz photons was first observed by Shiren[1] and later discussed in a review article by Tucker.[2] In addition to the type of transition observed by Shiren[1] at a magnetic field where the Zeeman splitting of the $M = \pm 1$ levels satisfies the resonance condition for the absorption of both a phonon and a photon, we have observed a new transition at a lower magnetic field.

Longitudinal microwave phonons were generated with a CdS transducer deposited on the end of a (100)-oriented rod inserted in a coaxial type of reentrant cavity, which could be tuned to resonate in overtone modes at about 3.1, 4.7, and 9.3 GHz. The opposite end of the rod was located in a sapphire-filled TE_{012} rectangular cavity resonant at 8.7 GHz. It was experimentally verified from the polarity of the detected echoes that the double-quantum transition produced an additional absorption of microwave photon power when 0.5-μsec phonon pulses were inside the 8.7-GHz cavity.

Figure 1 (top) shows the experimental magnetic field dependence of the peak power (or pulse height) of the first phonon echo detected by photon-phonon double-quantum transitions in the 8.7-GHz cavity. For 9.3-GHz phonons, this echo is largest at 1.95 kG, where the Zeeman splitting of the $M = \pm 1$ levels shown in the figure (bottom) is equal to the sum of the photon and phonon frequencies. This transition, where both a photon and a phonon are absorbed, is here designated the "high-field transition." The asymmetric line shape is characteristic of a strain-broadened line.[3,4] In the case of 4.7-GHz phonons, high-field transitions for both the fundamental and the second harmonic can be seen. The fundamental is observed at 1.45 kG, which corresponds to the 4.7-GHz phonon frequency, and the second harmonic at 2.0 kG. The height of the second har-