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Dynamical interpretation of a classical complex free energy

W Zwerger†

Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, IL 61801, USA

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Abstract. Using a functional Fokker-Planck equation for a scalar ϕ^4 model, it is shown that the initial decay rate out of a metastable state after an instantaneous quench to an unstable situation is proportional to the corresponding imaginary part of the free energy, as calculated by Langer.

1. Introduction

Since Langer's fundamental work on the behaviour of the free energy at first-order phase transitions (Langer 1967) and on thermally activated decay in systems with many degrees of freedom (Langer 1969), there has been considerable interest in the question of whether there exists a sufficiently general connection between the analytic continuation of the *equilibrium* free energy and the *dynamics* of metastability (Newman and Schulman 1980). This interest has been increasing, in particular after instanton type calculations (Coleman 1977) had been applied to discuss the quantum behaviour of macroscopic order parameter fields (Caldeira and Leggett 1981). In quantum mechanics the relation between the decay rate of a pure state and the imaginary part Im E_0 of its energy E_0 is well established, and using the Feynman-Kac formula one may calculate Im E_0 by an analytic continuation of the corresponding equilibrium density matrix in the zero temperature limit. This method is essentially based on the fact that the ground-state energy of a d-dimensional quantum system can always be represented as the free energy of an associated classical problem in $d+1$ dimensions. Thus the quantum decay rate $(2/\hbar)$ Im E_0 becomes equivalent to the imaginary part of the corresponding free energy‡.

Starting from a classical partition function alone, however, does not specify a corresponding time evolution, and one has to introduce a consistent dynamical model in addition. Thus the situation in this case is much less clear, which is even more true, if quantum and classical fluctuations are both present (Affleck 1981). In accordance with Langer's original treatment, we will restrict ourselves to rhe purely classical case, with a Fokker-Planck description of the dynamics. The problem is then to determine the transition rate for a thermally activated process which proceeds via a saddle point—usually called the critical droplet—in a multidimensional space. In a steady

† On leave of absence from Institut für Theoretische Physik, Universität Hamburg, West Germany.

‡ This has recently been demonstrated in the case of a dissipative two-level system and its corresponding 1D Ising model with $1/r^2$ interaction by Fisher and Dorsey (1985).

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state situation, in which the metastable state is replenished continuously, the corresponding constant probability current can be written as the product of the initial growth rate of the unstable mode at the saddle point, times an equilibrium factor, which coincides with an appropriately defined imaginary part of the free energy of the corresponding metastable configuration (Langer 1969). In a usual nucleation experiment however, one generally considers a situation in which an initially stable equilibrium relaxes to a new one after a sudden change in the effective potential, which changes the original configuration into a metastable one. It will be shown in the present work, that for the specific example of a ϕ^4 model, the *initial* decay rate after an instantaneous quench to a metastable situation is again directly proportional to the corresponding Im F as defined by Langer. Similar to the steady state result, the prefactor depends on the kinetic coefficient in the underlying Fokker–Planck equation and on properties of the unstable mode. In the limit of a small ordering field however, it is much larger than the critical droplet's growth rate, which determines the steady state prefactor.

2. Initial decay rate and relation to Im F

For the sake of simplicity let us first consider a one-dimensional potential which at $t=0$ is suddenly changed from $V_-(q)$ to $V_+(q)=V_-(q)+\Delta V(q)$ (see figure 1). In the large damping limit, the probability distribution $p(q, t)$ for the coordinate q satisfies a kinetic equation

$$\partial_t p(q, t)=\hat{L}p(q, t) \tag{1}$$

where the operator $\hat{L}$ has the Smoluchowski form

$$\hat{L}p=\Gamma\partial_q(p\partial_q V+\partial_q p) \tag{2}$$

with a kinetic coefficient Γ inversely proportional to the damping (the potential V and also the action S below are measured in units of $k_B T$). The short-time behaviour of the relaxation to the new equilibrium distribution in $V_+(q)$ may be characterised by

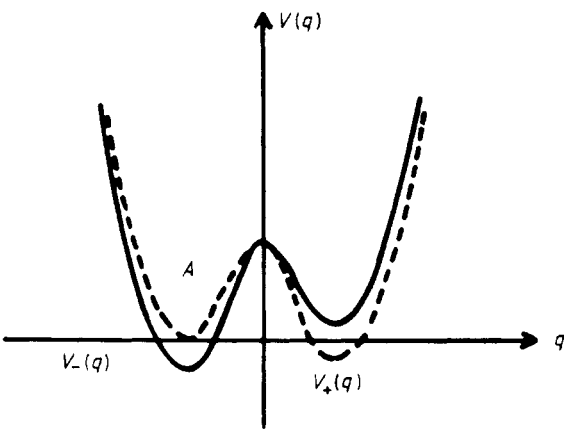

Figure 1. The sudden change in the potential from V_- to V_+ such that the well A becomes metastable.

the initial decay rate

$$\tau^{-1}(0) := -\partial_t p_A(t)/p_A(t)|_{t=0} \tag{3}$$

where $p_A(t) = \int_A p(q, t)\, dq$ is the population in the metastable well A to the left of the maximum in $V_+(q)$. Now it is easy to show, that $\tau^{-1}(0)/\Gamma$ can be expressed only by ΔV and purely equilibrium quantities. The change in the potential induces a change $\hat{L}_- \to \hat{L}_+ = \hat{L}_- + \Delta\hat{L}$ in the evolution operator and since $\hat{L}_- p_0 = 0$ for the initial distribution $p_0 \sim \exp(-V_-)$ we have $\partial_t p_A(0) = \int_A \Delta\hat{L} p_0\, dq$. Since $\Delta\hat{L}$ is a complete derivative, $\partial_t p_A(0)$ is determined alone by the properties of the initial equilibrium distribution at the boundary of the metastable well. Taking this to be at $q = 0$, we obtain

$$\tau^{-1}(0) = -\Gamma \Delta V'(q=0) p_0(q=0) \tag{4}$$

if the initial configuration is fully concentrated in A such that $p_A(0) = 1$. $\tau^{-1}(0)$ is thus proportional to the initial density at the boundary times the corresponding force due to ΔV.

This intuitive result has now a straightforward generalisation to a ϕ^4 model below T_c with a Ginzburg-Landau action

$$S = \int d^3x [\tfrac{1}{2}(\nabla\phi)^2 - \tfrac{1}{2}m^2\phi^2 + \tfrac{1}{4}g\phi^4 - h\phi] \tag{5}$$

and a dynamics given by the functional Fokker-Planck equation

$$\partial_t p[\phi(x), t] = \Gamma \int d^3x \frac{\delta}{\delta\phi}\left(p\frac{\delta S}{\delta\phi} + \frac{\delta p}{\delta\phi}\right) \tag{6}$$

(Hohenberg and Halperin (1977). In their notation we are considering model A. In order to obtain model B for a conserved order parameter ϕ, the kinetic coefficient Γ has to be replaced by $M\nabla^2$.) In order to apply the concept of an initial decay rate as in (3), for a situation where the sign of the magnetic field is suddenly reversed from $-h$ to $h > 0$ at $t = 0$, it is necessary to generalise the notion of the metastable region A to the infinite-dimensional space of possible order parameter realisations $\phi(x)$. In analogy to the one-dimensional case, where the transition point to the new stable region is determined by $\partial_q V_+ = 0$, the division between stable and metastable configurations ϕ now corresponds to a non-trivial solution of $\delta S_+ = 0$ or

$$\nabla^2\phi = -m^2\phi + g\phi^3 - h. \tag{7}$$

Under the boundary conditions $\phi(|x| \to \infty) = \phi_-$ and $\phi(|x| \to 0) = \phi_+$ equation (7) has a localised and rotation invariant solution $\bar{\phi}$ in the form of a critical droplet, with a finite action $\bar{S}$ compared to the metastable solution $\phi = \phi_- = \text{constant}$ ($\phi_\pm = \pm mg^{-1/2} + h/2m^2$ for small h). This solution is unstable with respect to scale transformations $x \to \lambda x$ and marginally stable with respect to a shift of the origin, i.e. the second-order fluctuation operator $\hat{M}$ defined by

$$S(\bar{\phi} + \delta\phi) = \bar{S} + \tfrac{1}{2}\int \delta\phi(x)\hat{M}\delta\phi(x)\, d^3x + \ldots \tag{8}$$

has precisely one negative eigenvalue $\lambda_0 < 0$ and $d = 3$ zero eigenvalues $\lambda_{1,2,3} = 0$ corresponding to growth and translation of the droplet (Langer 1967, for a rigorous proof see Coleman *et al* 1978). Expanding

$$\delta\phi(x) = \sum_n a_n \phi_n(x) \tag{9}$$

into a complete orthonormal set of eigenfunctions ϕ_n of $\hat{M}$, the metastable region A may be characterised by the condition $a_0 < 0$ and an appropriate measure in function space is $D\phi := \Pi_n da_n$. The reversal of the magnetic field at $t = 0$ induces a change ΔS in the action such that $\delta(\Delta S)/\delta\phi = -2h$. Since $\Delta\hat{L}p_0 = -2\Gamma h \int d^3x \delta p_0/\delta\phi$ is again a complete derivative, the generalised Gauss theorem $\int_A D\phi \delta p_0/\delta\phi = \int_{\partial A} D_s\phi p_0$ can be used to write the initial change of the population in A as a surface integral over the boundary ∂A of the domain of metastability. In order to obtain an explicit form for the measure $D_s\phi$ on ∂A, we use

$$\frac{\delta p_0[\phi(x)]}{\delta\phi(x)} = \sum_n \frac{\partial p_0(\{a_n\})}{\partial a_n}\,\phi_n(x). \tag{10}$$

The a_0 integration in $\int_A D\phi$ can then be performed and gives

$$-\partial_t p_A(0) = 2\Gamma h C_0 \int \prod_{n\geq 1} da_n\, p_0(\{a_0 = 0,\, a_{n\neq 0}\}) \tag{11}$$

where

$$C_0 = \int d^3x\, \phi_0(x) \tag{12}$$

is a constant ($C_0 > 0$ since $a_0 > 0$ corresponds to droplet growth only if $\phi_0 > 0$). Due to the vanishing eigenvalues $\lambda_{1,2,3} = 0$, the expression (11) is not properly defined and $\int da_1 da_2 da_3$ has to be replaced by $(\bar{S})^{3/2}V$, which is the subvolume of ϕ space spanned by allowing the critical droplet to occur at any point in the physical volume (Langer 1967). Thus the nucleation rate becomes an extensive quantity as it should be. Since a_0 is fixed to zero on ∂A, there is no integration over the unstable mode itself, and therefore no analytic continuation is involved in determining $\tau^{-1}(0)$.

In a Gaussian approximation the initial distribution on ∂A is

$$p_0|_{\partial A} = N^{-1} \exp\left(-\bar{S} - \tfrac{1}{2}\sum_{n=4}^{\infty} \lambda_n a_n^2\right) \tag{13}$$

with a normalisation constant N and $\lambda_n > 0$ for $n \geq 4$. Since p_0 is mainly concentrated around $\phi = \phi_-$, $p_A(0)$ may be calculated by using the corresponding quadratic approximation around ϕ_-, which has purely positive eigenvalues $\lambda_n^{(0)}$. The initial decay rate (3) is then well defined and independent of N. Comparing the result with Langer's expression

$$\mathrm{Im}\, F = \frac{1}{2}\frac{(\bar{S})^{3/2}V}{(2\pi/\lambda_1^{(0)})^{3/2}}\left(\prod_n{}' \frac{|\lambda_n|}{\lambda_n^{(0)}}\right)^{-1/2} \exp(-\bar{S}) \tag{14}$$

for the corresponding imaginary part of the free energy (Π' means that the three zero eigenvalues $\lambda_{1,2,3}$ are omitted), one finally obtains the relation

$$\tau^{-1}(0) = 4\Gamma h\, C_0 (|\lambda_0|/2\pi)^{1/2}\, \mathrm{Im}\, F \tag{15}$$

which is our central result. In principle (15) holds independent of whether the order parameter is purely relaxing or conserved. However, in the latter case we have $\Gamma \to M\nabla^2$ and the factor $4\Gamma h\, C_0$ is replaced by

$$2M \int \nabla^2(\phi_0(x)\Delta h(x))\, d^3x \tag{16}$$

which vanishes, unless the change $\Delta h(x)$ in the magnetic field is such as to produce an initial non-zero diffusion field for the critical droplet.

Concerning the meaning of (14) and its real part (which is essentially the free energy of the metastable phase for $h<0$) in an equilibrium context, it should be pointed out, that in a strict sense the free energy of a ϕ^4 model below T_c with $h>0$ but boundary conditions corresponding to $h<0$ is a perfectly well defined and real quantity. It differs from the free energy of the ordered state with $h>0$ only by the surface free energy, which becomes negligible in the thermodynamic limit. In fact the actual $F(h)$ is expected to have a cut along the imaginary h axis (Barnsley *et al* 1979) and (14) should therefore be interpreted only dynamically, either in the manner of Langer's original work, or in the one given above.

3. Behaviour in the limit $h \to 0$ and discussion

In order to explicitly evaluate (15), we first have to determine $\bar{\phi}$ and solve the corresponding eigenvalue problem for $\hat{M}$. In the limit $h \to 0$ this has been done by Langer (1967) and more recently by Günther *et al* (1980), so that we may only briefly sketch the calculation here. $\bar{\phi}$ is found by a variational ansatz in the form of a Bloch wall of width m^{-1}, whose optimal radius $a \sim h^{-1}$ is large compared to m^{-1} if $h \to 0$. This gives (Günther *et al* 1980)

$$\bar{S} = B\frac{m}{g}\left(\frac{m^3}{h\sqrt{g}}\right)^2 \gg 1 \tag{17}$$

with a numerical factor B of order unity. $\hat{M}$ is now a Schrödinger type operator with a central symmetric potential, and the infinite product of eigenvalue ratios in (14) may generally be written as a Fredholm determinant or Jost function (Gottfried 1966)

$$D(z) = \frac{\det(\hat{H}-z)}{\det(\hat{H}_0-z)} = \prod_{l=0}^{\infty} D_l(z)^{2l+1}. \tag{18}$$

Defining a 'Hamiltonian' $H = -\nabla^2 + u(r)$ with an attractive potential

$$u(r) = 3g(\bar{\phi}^2 - \phi_-^2) \tag{19}$$

which vanishes at infinity, we have $\det \hat{M}/\det \hat{M}_0 = D(z=-2m^2)$ in the limit $h \to 0$, where $\hat{M}_0 = -\nabla^2 + 2m^2$. The three zero modes of $\hat{M}$ due to translation invariance correspond to a $l=1$ bound state of u at energy $-2m^2$, which shows up as a zero in the Jost function. In terms of a dimensionless wavevector $\eta > 0$ such that $z = -(\eta/a)^2$ this means

$$D_1(\eta_1 = \sqrt{2}\, ma) = 0 \tag{20}$$

and the infinite product in (14) may be written as

$$\prod_n{}' \frac{|\lambda_0|}{\lambda_n^{(0)}} = |D_0(\eta_1)| \frac{\eta_1}{2} \frac{\partial D_1(\eta)}{\partial \eta}\bigg|_{\eta_1} \exp \sum_{l \geq 2} (2l+1) \ln D_l(\eta_1). \tag{21}$$

In the thin wall limit $ma \gg 1$, $u(r)$ may be replaced by an equivalent δ potential $u(r) = -\lambda\delta(r-a)$ at the droplet radius, whose strength λ is determined by the condition (20). This approximation is equivalent to the so-called drumhead model (Diehl *et al* 1980), which neglects angular dependent variations in the domain wall thickness, but

retains the relevant low energy modes, which determine the singularity of the prefactor in Im $F(h)$ (Günther *et al* 1980). The exact Jost function for the $d=3$ δ shell potential at purely imaginary momentum is (Gottfried 1966)

$$D_l(\eta) = 1 - \lambda a I_{l+1/2}(\eta) K_{l+1/2}(\eta) \tag{22}$$

and (20) gives $\lambda a = 2\eta_1 + 2/\eta_1 + \ldots$ so that

$$D_l(\eta_1) = \frac{(l-1)(l+2)}{2\eta_1^2} + O(\eta_1^{-4}). \tag{23}$$

Since the continuum model (5) only describes variations of $\phi(x)$ on a scale larger than m^{-1}, the summation in (21) has to be cut off at an l_c of order ma. This finally leads to (Günther *et al* 1980)

$$\operatorname*{Im}_{h\to 0} F(h) = Am^3 \left(\frac{m}{g}\right)^{3/2} \left(\frac{m^3}{h\sqrt{g}}\right)^{7/3} \exp(-\bar{S}(h)) \tag{24}$$

where A is of order unity. The s-wave bound state in the δ potential has the form

$$\phi_0 \sim \begin{cases} r^{-1}(\sinh \eta_0 r/a) \exp(-\eta_0) & \text{for } r < a \\ r^{-1} \exp(-\eta_0 r/a) \sinh \eta_0 & \text{for } r > a \end{cases} \tag{25}$$

where $\eta_0 \approx \lambda a/2$ is the corresponding wavevector, fulfilling $D_0(\eta_0) = 0$. The constant C_0 is then

$$C_0 = 2(4\pi a^3/\eta_0)^{1/2} \tag{26}$$

and since $|\lambda_0| = a^{-2}$ we finally obtain a behaviour for the initial decay rate like

$$\tau^{-1}(0) \sim h^{-4/3} \exp(-\text{constant}/h^2). \tag{27}$$

This is different from Langer's steady state calculation, which leads to a nucleation rate (Langer 1969)

$$\tau_s^{-1} = (\kappa/\pi) \operatorname{Im} F \tag{28}$$

with $\kappa = \Gamma|\lambda_0| \sim h^2$ being the growth rate of the critical droplet. The prefactor in this case is thus proportional to $h^{-1/3}$, which in the limit $h \to 0$ is much smaller than that of the initial decay rate (27). The difference is due to the fact that the prefactor in $\tau^{-1}(0)$ is determined by the initial force $\delta\Delta S/\delta\phi \sim h$ at the boundary instead of the droplet growth rate $\kappa \sim h^2$.

In conclusion, we have shown within a time dependent Ginzburg-Landau model, that the initial decay rate out of a metastable state after a sudden change in the magnetic field is proportional to the corresponding Im F. In accordance with Langer's original idea, the imaginary part of the free energy is defined by calculating the partition function in a Gaussian approximation around the metastable configuration and becomes meaningful only in a non-equilibrium context. It is related to the short time nucleation stage of the dynamics, but does not give information about the kinetics of growth or coarsening. The established connection between the dynamics and quasi-equilibrium properties may be traced back to the fact that $\tau^{-1}(0)/\Gamma$ could be expressed only in terms of the initial equilibrium distribution and the change in the external parameters. Generally however, no *a priori* connection between Im F and the classical dynamics can be expected, since different time evolutions may lead to the same equilibrium state. It is only *a posteriori* by comparing the result of a particular dynamical model with Im F, that such a relation may be shown.

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