# Spinodal expansions in the study of the decay of deeply quenched metastable states

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We study the decay of close to the spinodal metastable states through isobaric processes. One usually studies these processes by considering a Landau expansion of the free energy around the critical point, which may lie far away from the region of phase space where the dynamics are relevant, both in temperature and pressure. By relying on the critical nature of the spinodal points, apparent from the divergence of the compressibility and the presence of scaling in their vicinity, we propose an alternate view. By using, as a toy model, an analytical equation of state which describes a system that can exist in a liquid or vapor phase, we construct a generalized Gibbs-Landau free energy expansion around any spinodal point, which includes the critical point as a special case. This expansion is then used to study the dynamics of nucleation of the stable phase out of the metastable region.

## I. INTRODUCTION

First-order phase transitions are ubiquitous in nature. They appear in connection with a large number of physical phenomena, from superconductivity and superfluidity to magnetic ordering and surface structures, to name but a few. A simple and elegant theory, arising directly from first principles, allows for an equilibrium description of these transitions [1]. The behavior of actual physical systems undergoing first-order phase transitions may feature, however, complex dynamical phenomena, outside the scope of an equilibrium framework. These phenomena are associated with metastable states and their decay, as well as with the growth of phase domains, and are still the objects of active research.

In nuclear physics, experimental data involving the emission of intermediate mass fragments (IMF), such as in multifragmentation processes following heavy-ion collisions, have led to conjectures about the presence of a liquid-gas phase transition [2]. The distribution of these IMF would be one of the signals left by this transition, or, more properly, by its remnants for a finite size system [3–5]. This signature has been identified, for example, in the yield of IMF produced in $p+$Xe and $p+$Kr reactions [6], which show a power law distribution, such as predicted by the Fisher model [7] and is typical of critical systems [8]. The study of the caloric curve, or the dependence of temperature on the excitation energy per particle in heavy-ion collisions, which allows the determination of the specific heat and shows in some cases a plateau characteristic of first-order transitions, has also served as support for the claim of the presence of this transition [9]. Theoretical calculations of asymmetric nuclear matter have predicted a phase separation between a neutron-rich gas and neutron-deficient liquid matter [10]. These results were enriched by the addition of Coulomb interaction and surface terms [11], resulting in a moderation of isospin fractionization. All these claims may be well pictured by a description of nuclear systems in terms of a fluid that undergoes first-order and continuous transitions.

In an equilibrium description of a thermodynamic system, long-lived metastable states may appear as local extrema of some free energy. For such systems, the equilibrium isotherms below the critical temperature show metastable branches, corresponding to those extrema, whose end points are called spinodal points. The validity of an analytic continuation of the free energy beyond the stable points, and within the phase coexistence region of the phase diagram for these physical systems, in the region where those local extrema may appear, is still a matter of debate. If such a continuation can be justified, the above characterization of metastability will hold. Although these are clearly nonequilibrium states, it has been suggested that their long lives may allow for locally ergodic behavior. For this reason, the construction of a quasiequilibrium Landau-Ginzburg functional consistent with a postulated equation of state can be justified [1].

These considerations are particularly appealing when one faces a mean-field equation of state. It is well known that mean-field models can provide at best a qualitative understanding of equilibrium processes, for all but a few physical systems. Nevertheless, they are still a powerful element of the tool box of a theoretician, in particular, when dealing with problems for which no microscopic theory stands up as either plausible or solvable. The description of the nonequilibrium dynamics of metastable states is one such problem, and mean-field theories are, so far, the only ones that can address these dynamics with some internal consistency. It is to be noted that the mean-field model of van der Waals for the fluid-gas phase transition was the first to suggest the above mentioned description of metastability. In this and similar models, metastable branches appear as sections of isotherms which are mechanically stable, but beyond the coexistence points derived by the Maxwell construction. These branches end at spinodal points, which are the milestones at the beginning of the mechanically unstable regions.

These are the guidelines with which we approach, in this paper, the dynamical problem of the decay of metastable states, within the framework of a particular mean-field model for nuclear matter. These guidelines have already been used before for a similar problem in, e.g., Ref. [12]. There, an analytic continuation was constructed for the Gibbs free energy with an expansion around the critical point. The difficulties with such an expansion arise from two perspectives.
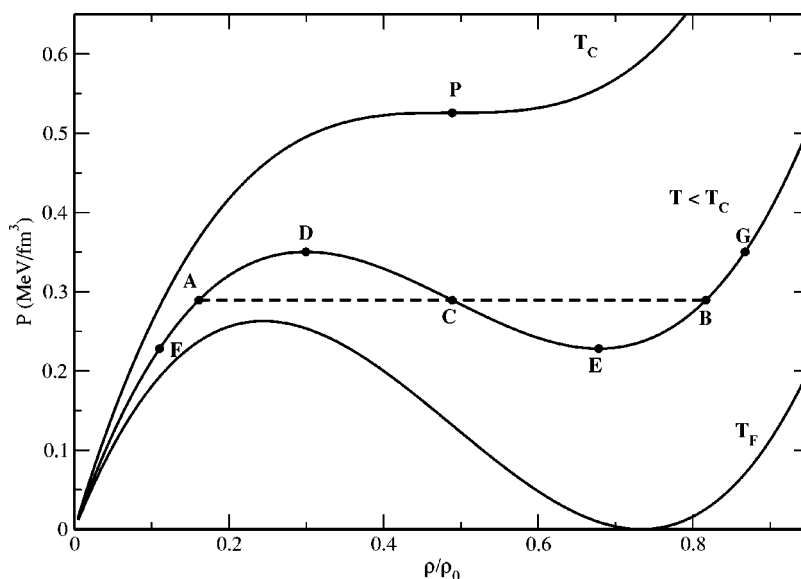
FIG. 1. Isotherms in the $p$ vs $\rho/\rho_0$ plane for $T=T_F$, the flash temperature, $T<T_c$ and $T=T_c$, the critical isotherm. On the latter, the critical point is identified. For the isotherm at $T<T_c$, points $A,B,$ and $C$ lie on the Maxwell construction and identify the range of densities where, at that temperature, liquid and gas phases may coexist. Points $D$ and $E$ are the two spinodal points at temperature $T$, bounding the unstable region. Point $F(G)$ is at the equilibrium density and at the same pressure as the spinodal point $E(D)$. If the system is quenched in a metastable state lying between $A$ and $D$ ($E$ and $B$) its isobaric decay will lead to a stable density on the branch $B$-$G$ ($F$-$A$) after having overcome the free energy barrier corresponding to a point in the branch $D$-$C$ ($C$-$E$). The density is expressed as a dimensionless quantity in units of the density at saturation for $T=0$, and the pressure is in units of MeV fm$^{-3}$.

If we want to study the decay of a nuclear system after a deep quench inside the metastable region, such as is conjectured to happen after a high-energy collision of heavy ions, the point of departure of the process is, in general, not close to the critical point; and usually proceeds through nearly isobaric processes, which are not well described by the expansion.

We present an alternate perspective, namely, an expansion of the free energy around a spinodal point. For deep quenches, the spinodal will lie closer in parameter space to the initial point of the nucleation process in the phase diagram, and the nonequilibrium process that follows is most likely controlled by the critical characteristics of the spinodal. On the other hand, a spinodal expansion can be made around the spinodal point at the same pressure, allowing for an analysis of the isobaric process.

## II. THE MODEL

Let us start with a simple equation of state (EOS) derived from a Skyrme-type interaction [12]. Such an interaction is short ranged and typically used in nuclear physics. Without any loss of generality in our study, it is very well suited for our purpose of an analytical analysis of scaling properties,

$$p = -a_0\rho^2 + 2a_3\rho^3 + \rho k_B T. \tag{1}$$

This equation has an explicit cubic dependence on the density $\rho$, in much the same way as in the van der Waals fluid. This form for the EOS is typical of a system that can exist in a liquid or vapor phase, and suggests the existence, at low density, of a line of first-order liquid-vapor phase tran-

sition in a $p$ versus $T$ phase diagram, ending up at a critical point, where the transition is continuous. The temperature $T_c$ associated with this critical point is an upper bound for the range of temperatures in which the two phases coexist. Many other models for nuclear matter have been studied [13], all of them exhibiting EOS with analogous van der Waals fluidlike behavior.

Mean-field phase diagrams can be valuable, even below the upper critical dimension of a model, to explore its regions of metastability. As is well known from the study of fluids, a physical system can get trapped in a local minimum of its free energy, from which it escapes only after a finite time. In a mean-field approach, the positions of these local minima are bounded in a phase diagram by the spinodal curves, which lie inside the region of phase coexistence. One usually considers the isothermic, for quenches through processes at constant temperature, and adiabatic spinodals, which can be formally determined by the solutions of $\partial p/\partial\rho=0$, keeping constant the appropriate thermodynamic variable. The processes of fragmentation and superheating are associated with the regions $\partial p/\partial\rho<0$ and $\partial p/\partial\rho>0$, respectively.

Note that the Maxwell construction, with end points $A$ and $B$ of Fig. 1, which singles out the true equilibrium states corresponding to global minima of the free energy, does not include these regions. However, to treat fluctuations in the liquid-gas coexistence region we have to extend the validity of the mean-field equation of state beyond the equilibrium states. This will be done through the Gibbs-Landau free energy expansion. This free energy is usually written as an expansion around the critical point [12], in which, even in the thermodynamic limit, fluctuations of all wavelengths are

important. Away from the critical point, finite systems such as nuclei will also present important fluctuations [12] and a Gibbs-Landau free energy expansion around some other point rather than the critical one may be of interest.

Here we present an expansion of the Gibbs-Landau free energy around the spinodal points $D$ or $E$ of Fig. 1. We will explore to our benefit the critical nature of points over the spinodal line, as already pointed out by several authors [14–17]. We will calculate the critical exponents associated with the spinodal points. The question to be answered here is whether such a study can provide an alternate and natural dimension-dependent scale of temperatures, other than the critical temperature. Again, it is worth mentioning at this point that critical nature of spinodal points has been identified in the study of several mean-field versions of classical models in condensed matter, such as the inconspicuous Ising model [16].

### III. CRITICAL AND FLASH POINTS

A particularly interesting region, still inside the coexistence region, that stands up in the study of nuclear systems is that in which a hydrostatic equilibrium ($p=0$) is still possible and the nuclear matter incompressibility

$$K(T) = \left. \frac{\partial p}{\partial \rho} \right|_{p=0} \tag{2}$$

can be calculated. This region is bounded by $0 < T < T_{fl}$ and $\rho_{fl} < \rho < \rho_o$, where the point $(\rho_{fl}, T_{fl})$ is obtained as the solution to $p = \partial p/\partial \rho = 0$ and is known as the "flash" point. This point has for coordinates the smallest density and the highest temperature at which a self-bound system can exist in hydrostatic equilibrium, and belongs, by definition, to a spinodal.

Here we proceed with the discussion regarding the scaling with critical and flash parameters by studying properties of the simple analytical EOS given by Eq. (1). Although derived for a three-dimensional (3D) system [18], a straightforward reproduction of that reasoning can be used to show that it has the same functional form in every spatial dimension. The relation between its coefficients and those of the interaction potential are dimension-dependent though. These coefficients have dimensions $[a_0] = M^{D+1}$ and $[a_3] = M^{1-2D}$. The density at saturation is obtained as the solution to $p(\rho_0) = 0$, leading to $\rho_0 = a_0/2a_3$. The incompressibility (at saturation) is obtained to be

$$K(T) = \left. \frac{\partial p}{\partial \rho} \right|_{p=0} \tag{3}$$

which yields

$$K(T) = \frac{a_0^2}{4a_3} \left( 1 + \sqrt{1 - \frac{8a_3 k_B T}{a_0^2}} - \frac{8a_3 k_B T}{a_0^2} \right). \tag{4}$$

The limit of $K(T)$ when $T \to 0$ is $K_0 = a_0^2/2a_3$. Rescaled by this parameter, the incompressibility can be written as

$$\frac{K(T)}{K_0} = \frac{1}{2} \left( 1 + \sqrt{1 - \frac{8a_3 k_B T}{a_0^2}} - \frac{8a_3 k_B T}{a_0^2} \right). \tag{5}$$

We begin by deriving a law of corresponding states for this EOS by rescaling the thermodynamical variables with their critical values. The critical point in which the liquid-vapor coexistence phase disappears and matter starts to be described as a gas is obtained via

$$\left. \frac{\partial p}{\partial \rho} \right|_{\rho=\rho_c} = \left. \frac{\partial^2 p}{\partial \rho^2} \right|_{\rho=\rho_c} = 0 \tag{6}$$

leading to

$$\rho_c = \frac{a_0}{6a_3}, \quad k_B T_c = \frac{a_0^2}{6a_3}, \quad p_c = \frac{a_0^3}{108 a_3^2} \tag{7}$$

with

$$a_0 = \frac{k_B T_c}{\rho_c}, \quad a_3 = \frac{k_B T_c}{6\rho_c^2}. \tag{8}$$

Substituting the values of $a_0$ and $a_3$ into Eqs. (1) and (5), one obtains

$$p' = \rho'^3 - 3\rho'^2 + 3\rho' T' \tag{9}$$

and

$$\frac{K(T)}{K_0} = \frac{1}{2} \left( 1 + \sqrt{1 - \frac{4}{3}T'} - \frac{4}{3}T' \right), \tag{10}$$

where $p' = p/p_c$, $\rho' = \rho/\rho_c$, and $T' = T/T_c$.

In this particular case, $p_c/k_B T_c \rho_c = 1/3$, close to the $3/8$ value obtained for the van der Waals gas. Equation (9) is an expression of a law of corresponding states valid across different spatial dimensions.

Now, let us show that a similar law can be obtained when the variables are rescaled through their flash point values. At this point,

$$\left. \frac{\partial p}{\partial \rho} \right|_{\rho=\rho_f} = p(\rho_f) = 0. \tag{11}$$

Imposing the above conditions on Eq. (1), we find

$$\rho_f = \frac{a_0}{4a_3}, \quad k_B T_f = \frac{a_0^2}{8a_3}, \quad p_f = 0 \tag{12}$$

with

$$a_0 = \frac{2k_B T_f}{\rho_f}, \quad a_3 = \frac{k_B T_f}{2\rho_f^2}, \tag{13}$$

which when substituted back into Eqs. (1) and (5) leads to

$$p^* = \rho^{*3} - 2\rho^{*2} + \rho^* T^* \tag{14}$$

and

$$\frac{K(T)}{K_0} = \frac{1}{2} (1 + \sqrt{1 - T^*} - T^*), \tag{15}$$

where

$$p^* = p/k_B\rho_f T_f, \quad \rho^* = \rho/\rho_f, \quad T^* = T/T_f. \quad (16)$$

Here, $p^*$ does not scale with the flash parameter $p_f$, which is identically zero by construction, but with $k_B\rho_f T_f$ instead.

We can see in this case that $T_c/T_f = \frac{4}{3}$. Equations (10) and (15) are the incompressibility curves written in terms of rescaled variables relating to different critical points. Our findings indicate that the flash temperature can provide an alternate natural dimension-dependent scale of temperature, other than the critical temperature.

## IV. SPINODAL LINE

Now we generalize the described properties of the flash point to any point on the spinodal line. For this generalization, the constraints of Eq. (11) have to be modified,

$$\left.\frac{\partial p}{\partial \rho}\right|_{\rho=\rho_s} = 0, \quad p(\rho_s) = P_s, \quad (17)$$

where $P_s$ and $\rho_s$ refer to points $D$ and $E$ of Fig. 1 for a given $T=T_s \lesssim T_c$ isotherm. The application of the above conditions to Eq. (1) leads to the determination of the coefficients,

$$a_0 = \frac{2k_B\rho_s T_s - 3P_s}{\rho_s^2}, \quad a_3 = -\frac{P_s}{\rho_s^3} + \frac{k_B T_s}{2\rho_s^2}, \quad (18)$$

which, when substituted into Eqs. (1) and (5), lead to

$$p^* = (1-2A_s)\rho^{*3} + (3A_s-2)\rho^{*2} + \rho^* T^*, \quad (19)$$

where

$$p^* = p/k_B\rho_s T_s, \quad \rho^* = \rho/\rho_s, \quad T^* = T/T_s \quad (20)$$

and

$$A_s = \frac{P_s}{k_B\rho_s T_s}. \quad (21)$$

Equations (9) and (14) are limiting cases of Eq. (19) when $A_s \to 1/3$ and $A_s \to 0$, describing the critical and flash points, respectively. The second derivative of Eq. (19), $\partial^2 p^*/\partial\rho^{*2} = 2(1-3A_s)$ shows the route from a spinodal to the critical point.

For a given isotherm $T$, $\rho_s$ is obtained analytically from $\partial p'/\partial\rho'|_{\rho=\rho_s} = \rho'(\rho'-2) + T' = 0$,

$$\rho_s = \rho_c(1 \pm \sqrt{1 - T/T_c}). \quad (22)$$

This spinodal density leads to the spinodal pressure,

$$P_s = P_c(1 \pm t(2\sqrt{t}+3)), \quad (23)$$

where $t = 1 - T/T_c$.

Let us now define the following reduced parameters:

$$\bar{\eta} = \frac{\rho - \rho_s}{\rho_s}, \quad \bar{t} = \frac{T - T_s}{T_s}. \quad (24)$$

The usual critical reduced parameters are recovered when $T_s \to T_c$ and $\rho_s \to \rho_c$, leading to

$$\eta = \frac{\rho - \rho_c}{\rho_c}, \quad t = \frac{T_c - T}{T_c}. \quad (25)$$

These reduced parameters are related,

$$\bar{\eta} = \frac{\rho_c}{\rho_s}(\eta+1) - 1, \quad \bar{t} = \frac{T_c}{T_s}(1-t) - 1. \quad (26)$$

Let us point out that $\eta$ plays the role of an order parameter for the continuous transition at the critical point, in close analogy to the van der Waals fluid. By analogy, we will call $\bar{\eta}$ the corresponding spinodal order parameter since its properties are similar to the proper and critical one. The critical order parameters for the points indicated in Fig. 1 are

$$\eta_A = -\sqrt{(3t)}, \quad \eta_C = 0, \quad \eta_D = -\sqrt{(t)}, \quad \eta_F = -2\sqrt{(t)} \quad (27)$$

and

$$\eta_B = -\eta_A, \quad \eta_E = -\eta_D, \quad \eta_G = -\eta_F. \quad (28)$$

In terms of the spinodal order parameters, Eq. (19) may be rewritten as

$$p^* = (A_s + \bar{t}) + \bar{t}\bar{\eta} + (1-3A_s)\bar{\eta}^2 + (1-2A_s)\bar{\eta}^3. \quad (29)$$

Again, this expression also contains the special critical case in which $A_s \to 1/3$ leading us to

$$p' = 1/3 + t + t\eta + (1/3)\eta^3, \quad (30)$$

which is equal to that presented in Ref. [12] if we just relate their reduced variables to ours.

## V. CRITICAL EXPONENTS

The way in which systems approach the critical point in a mean field theory is very well known. As one approaches the critical point, the behaviors of thermodynamic functions are mainly determined by their critical exponents. Since the spinodal line also presents a critical nature, we will see how some thermodynamic functions behave near a point on the spinodal line. Let us start with our generalized scaled equation of state, given by Eq. (29).

From Eq. (29), the deviation of the pressure from its spinodal value $\Delta P = P - P_s$ is given by $\Delta P = k_B\rho_s T_s(\bar{t}) + \bar{t}\bar{\eta} + (1-3A_s)\bar{\eta}^2 + (1-2A_s)\bar{\eta}^3$.

The limit $\bar{t} \to 0$ leads to $\Delta P = k_B\rho_s T_s[(1-3A_s)\bar{\eta}^2 + (1-2A_s)\bar{\eta}^3]$. This gives us two possibilities. In the case $T_s = T_c$, $A_s \to 1/3$ and only the last term of $\Delta P$ survives, indicating $\delta=3$ as the critical exponent. If, however, $T_s \neq T_c$, $\Delta P$ is governed by $(1-3A_s)\bar{\eta}^2 \Rightarrow \delta=2$ is the corresponding spinodal exponent.

The critical exponent $\beta$, also called the degree of the coexistence curve, is usually extracted from the behavior of $(\rho_{liq}-\rho_{gas})/\rho_c = C_{coex}t^\beta$, where $C_{coex}$ is a constant, around the critical point. $\eta_{coex} = \rho_{liq}-\rho_{gas} = \rho_B - \rho_A$ is the order parameter in this case. Proceeding by analogy, the spinodal exponent $\beta$ is obtained from $\rho_E - \rho_D = C_{spinod}\bar{t}^\beta$. Equations (27) and (28) show that $\beta=1/2$ for both critical and spinodal cases.

The isothermal compressibility is given by $K_T^{-1}$

$=-\rho(\partial p/\partial\rho)$. By using Eq. (29), $K_T^{-1}=\bar{t}+2(1-3A_s)\bar{\eta}+3(1-2A_s)\bar{\eta}^2$. In the case $T_s=T_c$, $A_s\to1/3$ and $K_T^{-1}=t+\eta^2$. By using the result already obtained for $\eta$ around the critical point, and assuming $K_T^{-1}=C_{comp}t^{-\gamma}$, we have $\gamma=1$. If, however, $T_s\ne T_c$, $K_T^{-1}$ is governed by $2(1-3A_s)\bar{\eta}$, leading to $\gamma=1/2$.

The critical exponent for the heat capacity is calculated from $c_p-c_v=\text{const}\times t^{-\alpha}=(NT/\rho^3)(\partial\rho/\partial p)K_T^{-1}$, giving us $\alpha=0$. The spinodal exponent is $1/2$.

To summarize our results up to this point, we addressed the critical nature of the spinodal line, as already pointed out by several authors [14–17]. Indeed, several derivatives of the free energy, such as the compressibility and susceptibility, diverge at any spinodal point. It is important to stress that the critical exponents at a spinodal point are not equal to their values at the critical point itself. For example, for the case of the mean-field model we are treating, the critical (spinodal) exponents $\alpha,\beta,\gamma$, and $\delta$ are $0(1/2),1/2(1/2),1(1/2)$, and $3(2)$, respectively. Let us notice that both sets of exponents satisfy the Rushbrooke and Widom scaling relationships

$$\alpha+2\beta+\gamma=2, \quad \gamma=\beta(\delta-1). \tag{31}$$

## VI. GIBBS-LANDAU FREE ENERGY

The Gibbs-Landau free energy $G(\bar{p},\bar{t},\bar{\eta})$ is constructed by letting $\partial G/\partial\bar{\eta}=0$,

$$G(\bar{p},\bar{t},\bar{\eta})=G_o+N\left(-\bar{h}\bar{\eta}+\frac{1}{2}\bar{t}\bar{\eta}^2+\frac{1}{3}(1-3A_s)\bar{\eta}^3\right.$$
$$\left.+\frac{1}{4}(1-2A_s)\bar{\eta}^4\right), \tag{32}$$

where $\bar{h}=\bar{p}-A_s-\bar{t}$ is defined in analogy with the usual external field in ferromagnetic systems presenting phase transition after quenching and $N$ is the number of particles. The usual Gibbs-Landau free energy in terms of the critical order parameter is obtained by taking $T_s\to T_c$ and $\rho_s\to\rho_c$, leading to

$$G(p',t,\eta)=G_o+\frac{T_cN}{3}\left(-h'\eta+\frac{3}{2}t\eta^2+\frac{1}{4}\eta^4\right), \tag{33}$$

where $h'=p'-1-3t$ and the normalization was chosen to match that of Ref. [12]. As is well known, from the $\phi^4$-field theory, $G(p',t,\eta)$ has the form of the standard double-well potential. The Maxwell construction (points $A$ and $B$ of Fig. 1, with $P_A=P_B$ and $G_A=G_B$) corresponds to $h'=0$, when the wells become equal in depth. As $|h'|$ increases, one well becomes shallower than the other. When we approach the spinodal points $D$ and $E$ of Fig. 1, the shallow wells of which they are minima disappear, and they become inflection points. Now, the extrema of $G(p',t,\eta)$ occur at the points $F$ and $G$ of the same figure. Note that the expansion around a spinodal point brings up a new cubic term, absent from the expansion around the critical point, distorting the double-well depths. In principle, the presence of a cubic term in the Landau free energy is a signal of the presence of a first order transition [1,19]. Another feature of the general Gibbs-
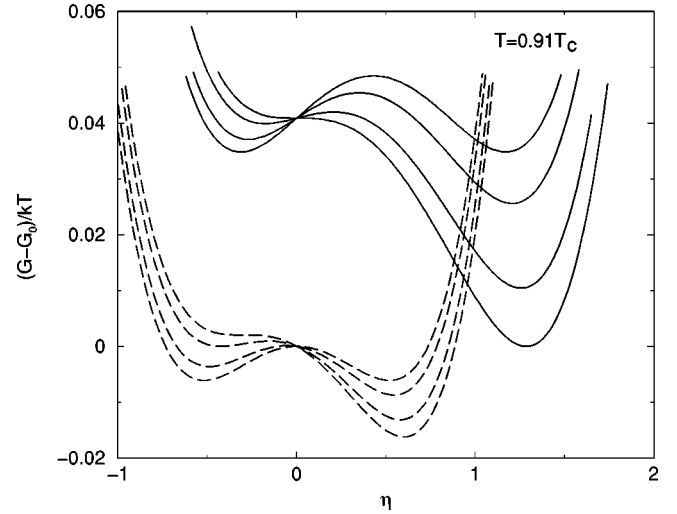


FIG. 2. Gibbs-Landau free energy, in dimensionless units and referred to its value at the critical point, for $T=0.91T_c$ and different pressures, as a function of the reduced dimensionless density $\eta$. The full curves are the spinodal expansion, taken around point $D$ of Fig. 1, and the dashed curves show the expansion around the critical point. In either expansion, these curves show the same qualitative behavior. At the pressure that corresponds to the Maxwell construction it has a symmetric double-well shape, and the barrier height— the difference between the local minimum and the neighboring local maximum—is maximum. As the pressure increases toward that of the spinodal point $D$ an asymmetry builds up and the barrier decreases, until it reaches zero at the spinodal point itself: it is the classical limit of metastability and has zero lifetime.

Landau spinodal expansion is that, once we focus on the analysis of a particular isotherm ($T=T_1$), the spinodal expansion itself can be done for any arbitrary value of temperature in the range $T_1\le T_s\le T_c$.
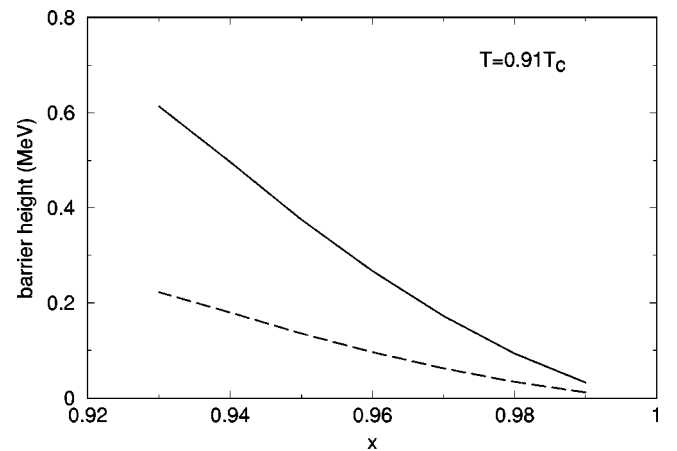


FIG. 3. Height of the barrier to be overcome in the decaying process, in MeV, as a function of the dimensionless pressure $x=p/p_D$. The full curve shows this height calculated via the spinodal expansion and the dashed one relies on the critical point expansion. Although qualitatively similar, the spinodal expansion predicts larger barriers and consequently larger lifetimes for the metastable states.

## VII. APPLICATIONS AND FINAL REMARKS

As an application of this methodology, we may calculate the mean lifetime of a metastable state by interpreting the free energy difference $\Delta G$ between its value at the local minimum and its maximum at the spinodal point as a potential barrier to be overcome. The mean lifetime for nucleation processes occurring at constant pressure will then be proportional to $\exp(-\Delta G/kT)$. We consider isobaric nucleation processes occurring at $p=xp_D$ where $x=1, 0.98, 0.95, 0.93$. These different pressures lie between $p_D$ and $p_A$. The isotherm chosen is $T=0.91T_c$. For comparison, Fig. 2 shows the Gibbs-Landau free energies expanded around the critical point together with those expanded around the spinodal point $D$ of Fig. 1. Notice that for $x=p_A/p_D$ the isobaric process coincides with the Maxwell construction and therefore, $G_A$ and $G_B$ present symmetric extrema around $\bar{\eta}=0$ for the spinodal point expansion and $\eta=0$ for the critical point expansion. As $x$ increases, the distortion of the double-well depth takes place. In the particular case $x=1$, the global minimum of the free-energy corresponds to the point $G$ of Fig. 1. The function $\bar{\eta}(\eta)$ is given in Eq. (26).

In Fig. 3 we show a plot of the barriers as a function of the pressure, compared with what would be obtained via an expansion around the critical point. One can see that this last expansion underestimates the height of the barrier, leading to shorter lives for metastable states. We claim that our method should better correspond to the real situation as the pressure gets farther away from its critical value. It allows the expansion center to lie closer to the region in phase space where the physical processes are actually happening, both in temperature and pressure; the expansion parameters used have smaller values and truncation errors are correspondingly smaller.

To summarize, we presented in this paper an alternate perspective for the analysis of the decay of metastable states, namely, an expansion of the free energy around a spinodal point. For deep quenches, the spinodal will lie closer in parameter space to the initial point of the nucleation process in the phase diagram, and the nonequilibrium process that follows is most likely controlled by the critical characteristics of the spinodal. On the other hand, an expansion of this kind can be made around the spinodal point at the same pressure, allowing for an analysis of isobaric processes. Such a description may also find applications in the study of multifragmentation, where the critical signature of the power law yield of IMF may well be due to the vicinity of a spinodal point, rather than to a continuous transition.

[1] L. Landau and E. Lifshitz, *Statistical Physics*, 3rd ed. (Butterworth-Heinemann, Washington, DC, 2000).

[2] S. Das Gupta, A. Z. Mekjian, and M. B. Tsang, Adv. Nucl. Phys. **26**, 89 (2001).

[3] G. F. Peaslee *et al.*, Phys. Rev. C **49**, R2271 (1994).

[4] C. A. Ogilvie *et al.*, Phys. Rev. Lett. **67**, 1214 (1991).

[5] M. B. Tsang *et al.*, Phys. Rev. Lett. **71**, 1502 (1993).

[6] J. E. Finn *et al.*, Phys. Rev. Lett. **49**, 1321 (1982).

[7] M. E. Fisher, Physics (Long Island City, N.Y.) **3**, 255 (1967).

[8] J. S. Sá Martins and P. M. C. de Oliveira, Nucl. Phys. **A643**, 433 (1998).

[9] J. Pochodzalla *et al.*, Phys. Rev. Lett. **75**, 1040 (1995).

[10] H. Muller and B. D. Serot, Phys. Rev. C **52**, 2072 (1995); Ph. Chomaz and F. Gulminelli, Phys. Lett. B **447**, 221 (1999); S. K. Samaddar and S. Das Gupta, Phys. Rev. C **61**, 034610 (2000).

[11] P. Bhattacharyya, S. Das Gupta, and A. Z. Mekjian, Phys. Rev. C **60**, 054616 (1999); S. J. Lee and A. Z. Mekjian, *ibid.* **63**, 044605 (2001); **68**, 014608 (2003).

[12] Alan L. Goodman, Joseph I. Kapusta, and Aram Z. Mekjian, Phys. Rev. C **30**, 851 (1984).

[13] R. J. Furnstahl and B. D. Serot, Phys. Rev. C **41**, 262 (1990); M. Malheiro, A. Delfino, and C. T. Coelho, *ibid.* **58**, 426 (1998); A. Delfino, Lizardo H.C.M. Nunes, and J. S. Sá Martins, *ibid.* **57**, 857 (1998); J. S. Sá Martins and A. Delfino, *ibid.* **61**, 044615 (2000); Bao-An Li and C. M. Ko, *ibid.* **58**, R1382 (1998), and references therein.

[14] J. S. Langer, Ann. Phys. (N.Y.) **41**, 108 (1967).

[15] K. Binder, Rep. Prog. Phys. **50**, 783 (1987).

[16] C. Unger and W. Klein, Phys. Rev. B **31**, 6127 (1985).

[17] L. Monette, Int. J. Mod. Phys. B **8**, 1417 (1994).

[18] H. Jaqaman, A. Z. Mekjian, and L. Zamick, Phys. Rev. C **27**, 2782 (1983).

[19] J. Cardy, *Scaling and Renormalization in Statistical Physics* (Cambridge University Press, Cambridge, England, 1996).