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Nucleation Processes Close to the Spinodal

C. E. Cordeiro · J. B. Silva · S. Moss de Oliveira · A. Delfino · J. S. Sá Martins

Abstract Using an analytical equation of state (EOS) which describes a system that can exist in a liquid or vapor phase, a generalized Landau free-energy expansion around any spinodal point is constructed. For this simple model, the critical exponents associated with the spinodal line are obtained, and the model reduces to the usual expansion around the critical point as a particular case. The approach may become an interesting starting point to study phase separation mechanisms, such as nucleation and spinodal decomposition, far from the critical point. The decay of deeply quenched metastable states close to the spinodal through a nucleation process is analyzed and their mean lifetime is obtained. The results are compared with those obtained through the use of the usual Landau free-energy expansion around the critical point.

Keywords Landau–Gibbs free energy · Nucleation · Spinodal expansion

1 Introduction

Mean-field models of thermodynamic systems can often be used to describe, at least qualitatively, features related to phase transitions. For these models, the isotherms describing the mechanical equation of state (EOS) $p = p(\rho, T)$ for temperatures below critical show regions of thermodynamical instabilities, whose boundaries are called spinodal points and which can be viewed as critical points [1,2]. Models with local interactions have been shown to develop mean-field characteristics, including the appearance of spinodals, which then have

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C. E. Cordeiro (✉)· J. B. Silva · S. Moss de Oliveira · A. Delfino · J. S. Sá Martins
Instituto de Fisica, Universidade Federal Fluminense Avenida Litoranea s/n, Niteroi, Rio de Janeiro 24210-340, Brazil
e-mail: clau@if.uff.br

critical point-like behavior, in the limit of infinite range [3]. This fact suggests the conjecture that an expansion of the Landau–Ginsburg free energy about spinodal points [4,5] may be an useful tool to develop insight for transition processes following a deep quench into the thermodynamically unstable region of phase space.

In previous work, a particular point of the spinodal line was studied in reference to its critical nature [6]. The so-called flash point lies at the smallest density and highest temperature for which a self-bound system can still exist in hydrostatic equilibrium. It is defined as the solution to the equations $p = \partial p/\partial \rho = 0$ and so belongs, by definition, to a spinodal line. A simple EOS, derived from a Skyrme-type interaction [7], was chosen as a prototype model for that study. Such an interaction is short-ranged and typically used in nuclear physics. Without any loss of generality in our study, it is well suited for our purpose of analyzing scaling properties. In terms of the usual reduced variables, with respect to their critical values, the EOS reads

$$p' = \rho'^3 - 3\rho'^2 + 3\rho' T' \tag{1}$$

and the incompressibility is given by

$$\frac{K(T)}{K(0)} = \frac{1}{2}\left[1 + \sqrt{1 - \frac{4}{3}T'} - \frac{4}{3}T'\right] \tag{2}$$

where $p' = p/p_\mathrm{c}$, $\rho' = \rho/\rho_\mathrm{c}$, and $T' = T/T_\mathrm{c}$.

In Ref. [6], it was shown that the same equation, now written in terms of the “flash” variables, reads

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

and

$$\frac{K(T)}{K(0)} = \frac{1}{2}\left[1 + \sqrt{1 - T^*} - T^*\right] \tag{4}$$

where

$$p^* = p/(k_\mathrm{B}\rho_\mathrm{f} T_\mathrm{f}), \quad \rho^* = \rho/\rho_\mathrm{f}, \quad T^* = T/T_\mathrm{f}. \tag{5}$$

This suggests that the flash temperature can provide an alternate natural scale of temperature other than the critical temperature.

2 Model

In the present article we generalize the previous discussion to apply to any point on a spinodal line. Written in terms of a set of generalized reduced dimensionless variables scaled with spinodal coordinates, defined as values p_s, ρ_s, and T_s that satisfy $\partial p/\partial\rho = 0$, which include the flash point as a particular case, the EOS has the form,

$$p^* = (1 - 2\mathrm{A_s})\rho^{*3} + (3\mathrm{A_s} - 2)\rho^{*2} + \rho^* T^*, \tag{6}$$

where

$$p^* = p/(\mathrm{k_B}\rho_\mathrm{s}T_\mathrm{s}), \quad \rho^* = \rho/\rho_s, \quad T^* = T/T_s \tag{7}$$

and

$$A_\mathrm{s} = \frac{p_s}{k_B \rho_s T_s} \tag{8}$$

Equations 1 and 3 are limiting cases of Eq. 6 when $A_\mathrm{s} \to 1/3$ and $A_\mathrm{s} \to 0$ describing the critical and flash points, respectively, since $p^* = p' \frac{p_\mathrm{c}}{\rho_s T_s}$. As already pointed out by several authors [1–5], the spinodal line can be considered as a "criticality" line. Indeed, several derivatives of the free energy, such as 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 a mean-field approach, the critical (spinodal) exponents α, β, γ, and δ are 0 (1/2), 1/2 (1/2), 1(1/2), and 3(2), respectively. Notice that both sets of exponents satisfy the Rushbrooke and Widom scaling relationships,

$$\alpha + 2\beta + \gamma = 2, \quad \gamma = \beta(\delta - 1). \tag{9}$$

The form of the chosen EOS is typical for a system that can exist in a liquid or vapor phase, and suggests the existence, at low density, of a line of a first-order liquid–vapor phase transition 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 may coexist. In Fig. 1, we sketch two isotherms in a $p \times \rho$ diagram, the upper one for the critical temperature T_c, and the lower for a temperature $T < T_\mathrm{c}$. Points to the left of A and to the right of B are equilibrium points at temperature T. Points A and B correspond to the Maxwell construction, and indicate the densities of the liquid and vapor phases at coexistence. The regions bounded by points A and D, and E and B, are metastable regions, where $\partial p/\partial\rho > 0$. In the region between points D and E, where $\partial p/\partial\rho < 0$, the system is unstable. To treat fluctuations in the metastable region, we have to access states out of equilibrium. This can be done with a Gibbs–Landau free energy expansion [8]. The usual way of achieving this goal is by rewriting p' in terms of the order parameter $\eta = (\rho - \rho_\mathrm{c})/\rho_\mathrm{c}$ and integrating it to yield the free energy,

$$\mathrm{G}(p', t, \eta) = \mathrm{G_o} + \frac{T_\mathrm{c}N}{3}(-h'\eta + \frac{3}{2}t\eta^2 + \frac{1}{4}\eta^4), \tag{10}$$

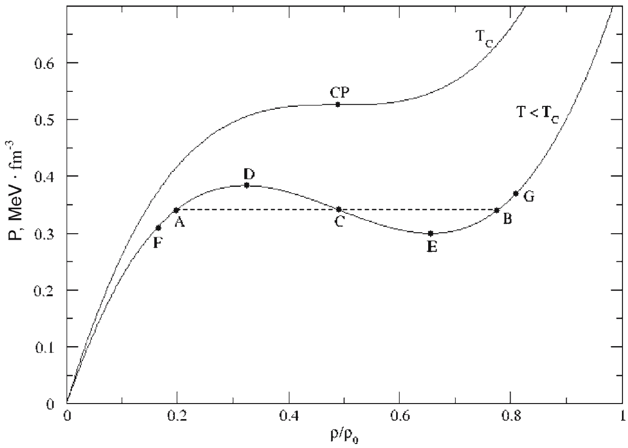

Fig. 1 Isotherms for the critical temperature T_c and some other temperature T are shown for the Skyrme model. Pressure is measured in units of MeV · fm^{-3} (1 fm = 10^{-15} m) while the density is in units of the nuclear saturation density ρ_0 (=0.15 fm^{-3}). Points A and B at temperature T are defined by the Maxwell construction. C and D are spinodal points

where $t = (T_c - T)/T_c$ is the reduced temperature, N is the number of particles, and $h' = p' - 1 - 3t$. We want to generalize this free energy as an expansion around any spinodal point, such as D or E in Fig. 1. Let us remark now that the definition of an order parameter is meaningless in this case, since in a metastable state there is only a single phase present. Nevertheless, we may define expansion parameters,

$$\bar{\eta} = \frac{\rho - \rho_s}{\rho_s}, \quad \bar{t} = \frac{T - T_s}{T_s}. \tag{11}$$

In terms of these variables, Eq. 6 becomes

$$\bar{p} = (A_s + \bar{t}) + \bar{t}\,\bar{\eta} + (1 - 3A_s)\bar{\eta}^2 + (1 - 2A_s)\bar{\eta}^3 \tag{12}$$

Integrating this equation with respect to $\bar{\eta}$, we obtain the generalized Gibbs–Landau free energy,

$$\mathrm{G}(\bar{p}, \bar{t}, \bar{\eta}) = \mathrm{G_o} + N(-\bar{h}\,\bar{\eta} + \frac{1}{2}\bar{t}\,\bar{\eta}^2 + \frac{1}{3}(1 - 3A_s)\bar{\eta}^3 + \frac{1}{4}(1 - 2A_s)\bar{\eta}^4) \tag{13}$$

where $\bar{h} = \bar{p} - A_s - \bar{t}$ is defined in analogy with the usual external field in ferromagnetic systems presenting a phase transition after quenching. As one can see, this equation contains the particular case where the expansion is done around the critical point, since when $\bar{\eta} \rightarrow \eta$, Eq. 13 becomes Eq. 10.

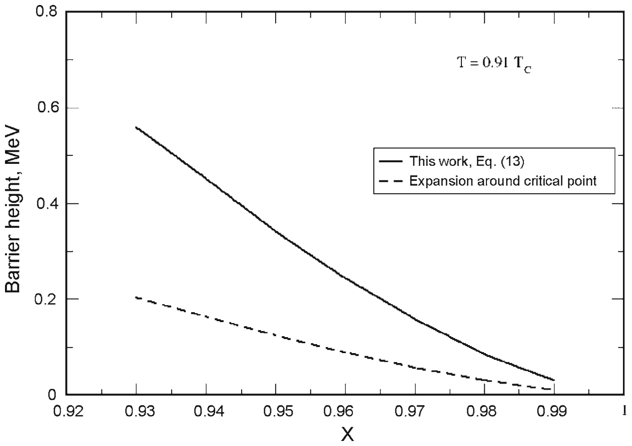

Fig. 2 Barrier height is plotted as a function of $x = p/p_c$, for $T = 0.91T_c$ and $N = 100$

3 Application to Nucleation Processes

As an application of this methodology, we may calculate the mean lifetime of a metastable state by interpreting the free-energy difference ΔG 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 $\exp(-\Delta G/(k_B T))$. We present in Fig. 2 a plot of this barrier 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 lifes 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.

We present an alternate perspective, namely, an expansion of the free energy around a spinodal point. For deep quenches, the spinodal will lie closer to the initial point of the nucleation process in the phase diagram, and the non-equilibrium 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 isobaric processes.

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