Nucleation Processes Close to the Spinodal

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Abstract

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 Landau free energy expansion around any spinodal point, for which the usual expansion around the critical point is a particular case. The critical exponents associated with the spinodal line are obtained. The approach we present 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 nucleation process is analyzed and their mean life time obtained. The results are compared with those obtained through the use of the usual Landau free energy expansion around the critical point.

In a previous work, a particular point of the spinodal line was studied in reference to its critical nature [1]. 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 Equation of State (EOS), derived from a Skyrme-type interaction [2], 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 $p' \; = \; p/p_c$, $\rho' \; = \; \rho/\rho_c$ and $T' \; = \; T/T_c$.

In Ref. [1] 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

$$p^* \; = \; p/k_B \rho_f T_f \;\; , \;\; \rho^* \; = \; \rho/\rho_f \;\; , \;\; T^* \; = \; T/T_f \; . \tag{5}$$

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

In the present paper 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, the EOS has the form

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

where

$$p^* \; = \; p/k_B \rho_s T_s \;\; , \;\; \rho^* \; = \; \rho/\rho_s \;\; , \;\; T^* \; = \; T/T_s \tag{7}$$

and

$$A_s \; = \frac{p_s}{k_B \rho_s T_s} \; . \tag{8}$$

Eq. 1 and Eq. 3 are limiting cases of Eq. 6 when $A_s \rightarrow 1/3$ and $A_s \rightarrow 0$ describing the critical and the flash points respectively. As already pointed out by several authors [3–6] 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 the case of mean-field approach we are treating, the critical (spinodal) exponents $\alpha, \beta, \gamma,$ and δ 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

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

The form of the chosen 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 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 $T < T_c$. 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 vapour 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 [7]. The usual way of achieving this goal is by rewriting p' in terms of the order parameter $\eta = (\rho - \rho_c)/\rho_c$ and integrating it to yield the free energy

$$G(p', t, \eta) \;=\; G_o + \frac{T_c N}{3}\;\left(-h'\eta + \frac{3}{2}t\eta^2 + \frac{1}{4}\eta^4\;\right), \tag{10}$$

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 but a single phase present. Nevertheless, we may define expansion parameters

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

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

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

where $\bar{h} = \bar{p} - A_s - \bar{t}$ is defined in analogy with the usual external field in ferromagnetic systems presenting 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 $\bar{\eta} \to \eta$ Eq. 13 becomes Eq. 10.

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($-\Delta G/kT$). 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 controled 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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FIGURES

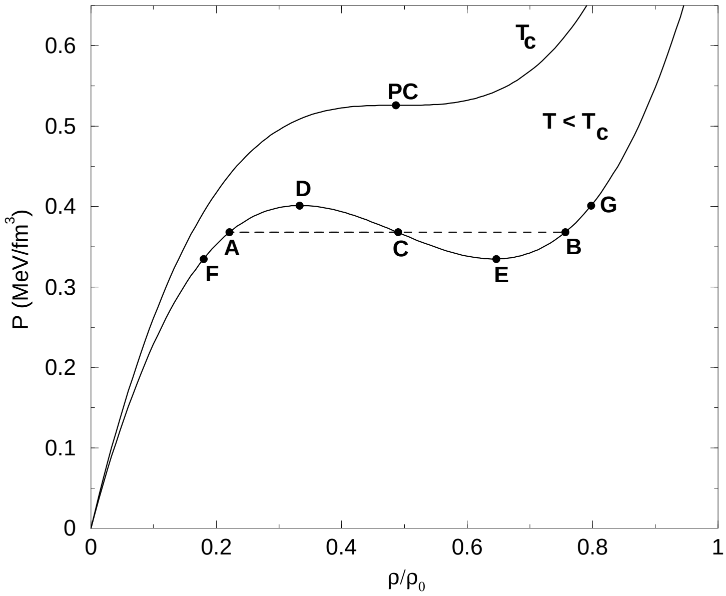

FIG. 1. Isotherms for the critical temperature T_c and some other temperature T are shown, for the Skyrme model. Points A and B at temperature T are defined by the Maxwell construction. C and D are spinodal points.

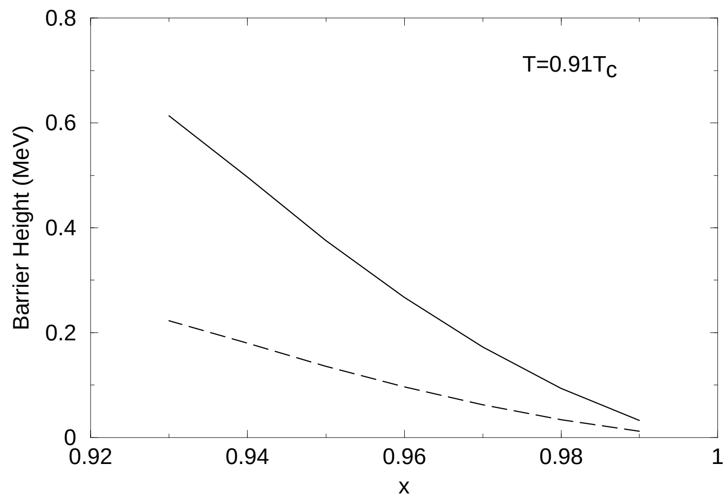

FIG. 2. The barrier height is plotted as a function of $x = p/p_c$ for $T = 0.91T_c$.