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Canonical and grand canonical theory of spinodal instabilities

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Abstract In the context of the mean field approximation to the Landau-Ginzburg-Wilson functional integral describing the equilibrium properties of a system with a conserved order parameter, we analyze the conditions for critical instabilities in the canonical ensemble. By introducing a constraint into the functional integral to guarantee the global conservation of the order parameter in a closed system, we conclude that the usual mean-field grand canonical phase diagram is modified in the supersaturared region. In fact, we find that the spinodal line separating the unstable and metastable regions becomes a line of critical points on which the order parameter profile changes continuously with temperature. The critical exponentes which characterize this line are the same as those of the usual critical point. This conclusion contrasts with the one-sided singular behavior of the metastable branches' end point of the grand canonical case. These results are derived by ignoring nucleation, which in this regions is expected to render the direct observability of this line nearly impossible. It is argued, however, that the critical point effects can be important in the metastable or even the stable region before the onset of strong nucleation takes place. This conclusion agrees qualitatively with some experiments on light scattering in binary mixtures and single-component systems near the liquid-gas transition. The effect of this critical line on the problem of spinodal decomposition is briefly discussed.

1. Introduction

The classical theory describing the phase diagram of a binary mixture in the vicinity of a critical point is characterized by the coexistence curve separating homogeneous and inhomogeneous states of the system (fig. 1). This curve corresponds to a line of first-order phase transitions with a critical point laying at its top. If $\mu_{a,b}$ are respectively the chemical potentials of each component a, b in the mixture and $C_{a,b}$ are the corresponding concentrations, the critical point is determined by the conditions

$$\left(\frac{\partial\mu}{\partial C_a}\right)_{\mathrm{T}} = \left(\frac{\partial^2\mu}{\partial C_a^2}\right)_{\mathrm{T}} = 0, \tag{1}$$

where $\mu = \mu_a - \mu_b$ and T is the temperature. Below the coexistence curve the true equilibrium states correspond to an inhomogeneous mixture of phases. However, it is also possible to have in this region metastable homogeneous phases corresponding to supersaturation. These states are locally stable under small-amplitude concentration fluctuations but unstable to decay to a lower free energy inhomogeneous phase by nucleation, that is by localized large amplitude fluctuations. Depending on the activation energy necessary to overcome the minimal free energy barrier to produce a spontaneous nucleating fluctuation, the lifetime of a metastable state can be long on a laboratory time scale, so that experiments can be performed and interpreted as if the system were in a true equilibrium state. As the degree of supersaturation is increased, by properly varying the temperature or the concentrations, the metastability is reduced. According to the classical theory the system becomes unstable under infinitesimal concentration fluctuations at the spinodal line. This line is determined by the condition

$$\left(\frac{\partial\mu}{\partial C_a}\right)_{T} = 0. \tag{2}$$

The decay of a metastable or unstable state after a temperature quench is an interesting problem, which has attracted the attention of numerous researchers[1]. So far theory and experiment seem to agree only qualitatively. Among the most outstanding properties of these processes is the scaling behaviour observed in the late stages of a spinodal decomposition, as expressed by the time-dependent correlation function, even for noncritical values of the concentrations[2,3]. Although this property is not fully understood, it seems that the conservation of the order parameter plays a key role in this respect[4].

In this paper we shall focus our attention on how the effect of having a conserved order parameter, together with the fact that experiments in binary mixtures

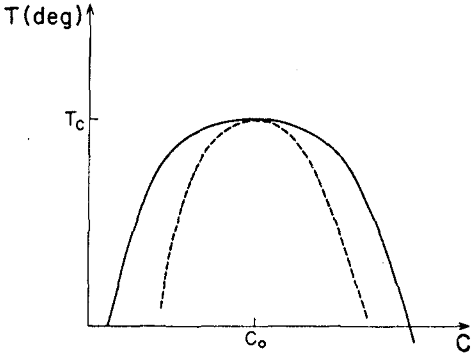

Fig. 1 - Phase diagram for a binary mixture close to the critical consolute point in the concentration-temperature plane. The continuous line corresponds to the coexistence curve at which the system undergoes a first order phase transition. The critical point corresponds to T = T_0 and C = C_0 (where C_0 is the molar fractional concentration of one component of the mixture). The dashed curve represents the spinodal line at which the system is thermodynamically unstable. In the region enclosed between the two curves, metastable supersaturated homogeneous states can exist, but they decay by nucleation into the inhomogeneous phase.

are almost invariably performed in closed containers, so that the overall concentration is a fixed nonfluctuating quantity, can affect the instability behavior of such systems particularly near the spinodal line. As far as the equilibrium properties are concerned the proper ensemble for the thermodynamical description is clearly the canonical'rather that the usually employed grand canonical framework. We will not be concerned with the dynamics of a decay process, but rather we will study the (pseudo) equilibriurn behavior of the matastable supersaturated mixture.

Anticipating some of our results, we will find that, within the context of the classical theory, the usual spinodal irreversible instability line, which occurs in the grand canonical ensemble, is converted into a line of critical points for which the average local concentration changes continuously and reversibly. It must be stressed from the outset that all the results which follow are derived in the mean field approximation to the Landau-Ginzburg-Wilson functional integral for the partition function. It is well known that a mean field theory of metastability is questionable for several reasons. In first place it has been argued by Langer that the mean field spinodal line which results from the Landau-Ginzburg theory is somewhat arbitrary, since it is a function of the coeficients of the free energy functional which themselves depend on the somewhat arbitrary coarse graining[5]. An exact functional integration for the free energy can give no metastable states. On the other hand, several authors have argued, with a varying degree of rigour, that metastable states can be obtained by analytic extension of the free energy function of the stable homogeneous region into the metastable region[6]. A more practical limitation of the classical theory comes from the fact that there seems to be no sharp distinction as one crosses into the unstable region from the metastable one. In fact, as supersaturation is increased the rate of nucleation is greatly enhanced, up to the point that it is experimentally impossible to observe the spinodal line on any reasonable experimental time scale[7]. Classical theory predicts that the nucleating barrier approaches zero as the spinodal line is approached, so that no difference exists between nucleation and spinodal decay[8]. In spite of these limitations there exists experimental results that indicate that a spinodal line can be indirectly established, by measurements of light scattering intensity on binary mixtures with varying concentrations *away* from the instability region[9,10]. The curve fitting to the empirical results can be adequately adjusted by defining a spinodal temperature which is a function of the concentration and which, in addition, possesses the behavior expected on theoretical grounds (see ref. 10 for details).

Although we have chosen a binary mixture as the prototype system to be studied, it is obvious that our conclusion will equally apply to a lattice gas or a binary alloy, which normally satisfy the conditions of the canonical ensemble. On the other hand the Ising model in which the number of spins up and down are fixed permanently will also fall into this category, although this situation can hardly be encountered in real magnetic systems.

This paper is arranged as follows: In Section 2 we will review the general conditions for criticality in the context of the Landau-Ginzburg-Wilson theory. In Section 3 we extend these conditions to the canonical ensemble and derive the phase diagram plus other relevant thermodynamical quantities. In Section 4 we introduce a general scaling hypothesis and compare it with the results of Section 3. In section 5 we analize the relevance of our theory to experimental results and consider the effect of gravity and walls on our conclusions. Section 6 contains a summary and some final remarks.

2. Criticality and the Landau-Ginzburg-Wilson Theory

The Landau-Ginzburg-Wilson theory assumes that close to a critical point the grand canonical partition function of a system is given by a functional integral of the form

$$Z = \int D\phi \exp\{-H[\phi]/kT\} \tag{3}$$

where

$$H[\phi]/k_BT = \int d^dx \left\{ \frac{(\nabla\phi)^2}{2} + \frac{t}{2}\phi^2 + \frac{\lambda}{4!}\phi^4 - \mu\phi \right\} \tag{4}$$

where as usual we assume

$$\mathrm{t} = \tau_0(T - T_0)/T_0 \ , \quad \text{and} \quad \lambda > 0$$

with T_0 being the critical temperature, X and τ_0 some system dependent constant kg is the Boltzmann constant and ϕ, in the binary mixture case, measures the deviations from the critical concentrations and μ is the change of the chemical potential difference from its critical value. As is well known, the mean field approximation (saddle point) consists of expanding the integrand about the minimum of H[+]. Let ϕ_{mf} denote such minimum. Then clearly it must satisfy

$$\left.\frac{\delta H}{\delta\mu}\right|_{\phi_{mf}} = 0 \Rightarrow \nabla^3\phi_{mf} = t\phi_{mf} + \frac{\lambda}{6}\phi^3_{mf} - \mu \tag{5}$$

The requirement for a minimum is that

$$\int\int d^dxd^dx' \left.\frac{\delta^2 H[\phi]}{\delta\phi(x)\delta\phi(x')}\right|_{\phi_{mf}} \eta(x)\eta(x') > 0 \tag{6}$$

for any arbitrary function $\eta(x)$. This latter condition will be satisfied provided the operator

$$\hat{H} = -\nabla^2 + t + \frac{\lambda\phi^2_{mf}}{2} \tag{7}$$

has a positive spectrum. To investigate this requirement let us assume that the system is enclosed in a cube of volume V and that the eigenfunctions of H satisfy non-wetting boundary conditions at the walls[11]

$$\hat{n} \cdot \vec{\nabla}\psi|_{\text{walls}} = 0, \tag{8}$$

where $\hat{n}$ is the normal vector to the walls.

Let $\{\epsilon_n\}$ be the spectrum of H and $\{\psi_n\}$ the corresponding eigenfunctions. Let us now state the necessary and sufficient conditions for criticality.

i) The first (necessary) condition for criticality is that the lowest lying eigenvalue of H, ϵ_0, vanishes for some values of the external fields (t and μ). It is a straightforward exercise to show that this condition is equivalent to a divergent correlation length ξ. In fact, it can be shown in the mean field approximation that ξ^{-2} is proportional to ϵ_0. Equivalently the generalized susceptibility, defined as

$$\chi(\vec{x},\vec{x}') =< (\phi(\vec{x})- < \phi >)(\phi(\vec{x}')- < \phi >) >, \tag{9}$$

where < ... > denotes statistical average, satisfies the following equation

$$\left(- \nabla^2 + t + \frac{\lambda\phi^2_{mf}(X)}{2}\right)\chi(\vec{x},\vec{x}') = \delta(\vec{x} - \vec{x}'), \tag{10}$$

whose solution can be expressed in terms of the spectrum of H as follows

$$\chi(\vec{x},\vec{x}') = \sum_n \frac{\Psi_n(\vec{x})\Psi_N(\vec{x}')}{\epsilon_n} \tag{11}$$

Thus the vanishing of ϵ_0 guarantees the divergence of the susceptibility.

ii) The second condition for criticality is that

$$\int \phi_{mf}(x)\Psi_0^3(x)dx = 0 \tag{12}$$

To show this let us note that $\epsilon_0 = 0$ implies that the second functional derivative in the "direction" of $\Psi_0(x)$ in function space is zero. Therefore in order to have a minimum of H at $\phi_{mf}(x)$, the third functional derivative at ϕ_{mf} in the direction of $\Psi_0(x)$ must also vanish, since otherwise ϕ_{mf} would be an "inflection" point of the functional H[#]. Needless to say that the fourth functional derivative is λ and consequently positive along all directions in function space. Although stated in a different language, conditions (i) and (ii) were stated by van der Waals in the last century.

iii) There is one further condition for criticality which requires ϕ_{mf} to be the absolute minimum of H[$],so that it corresponds to a true equilibrium state of the system. If ϕ_{mf} satisfies condition (i) and (iii) but not (iii), it will represent a metastable state[5] which would decay eventually into the absolute minimum of H$[\phi]$.

The restrictions imposed by conditions (i) and (ii) in the case of a constant solution of Eq.(5) such that $\phi_{mf}(x) = \phi_0$ are

$$t\phi_0 + \frac{\lambda}{6}\phi_0^3 = \mu, \quad t + \frac{\lambda\phi_0^2}{2} = 0 \ \text{ and } \ \phi_0 \int \Psi_0^3(x)dx = 0. \tag{13}$$

Since in this case $\Psi_0(x)$ is constant, the solution to Eqs. (13) is $t = 0 = \mu$. This is the well-known Landau solution. It is important to emphasize two known facts: first we note that for $\mu \neq 0$ the system cannot become critical. Moreover if $t < 0$ and $\mu \rightarrow 0$ the transition is first order[12].

3. The Landau theory and criticality in the canonical ensemble

Let us assume that our system is sealed inside a box with edges L,, L_y L_z. The constraint of having a total fixed numbers of particles of each species requires

$$\frac{1}{V}\int \phi(\vec{x})d^3x = c \tag{14}$$

where c is the fixed global concentration. In this section we will not require $c = 0$, but only c small to guarantee the validity of Eq. (4). Let us assume that the corresponding canonical partition function, Z_c, is given by the Landau-Ginzburg-Wilson functional integral but subject to the constraint[13,14] Eq. (14) so that

$$Z_0 = \int D\phi(\exp\{-H[\phi]/k_BT\})\delta\Big(V^{-1}\int \phi(x)d^3x - c\Big), \tag{15}$$

where $H[\phi]$ is given by Eq. (4) but contains no μ term. In this case the value of μ will be determined by c, as we will see below. We will now extend the Landau mean field approximation to Eq. (15). It is possible to exponentiate the 6 function and absorb it into $H[\phi]$ but at this point this is not necessary. Let us find the minima of H but now subject to the constraint Eq. (14). This is readily performed by introducing a Lagrange multiplier h and extremizing

$$(1/k_BT)H[\phi] - h\int \phi(x)d^3x \tag{16}$$

which yields

$$\nabla^2\phi = t\phi + \frac{\lambda}{6}\phi^3 - h. \tag{17}$$

Clearly the value of h must now be adjusted so that Eq. (14) is satisfied. Let $\phi_{mf}(x)$ be a solution of Eqs. (17) and (14). The sufficient condition for a minimum of the constrained problem is that the spectrum of the operator H, as given by Eq. (7), be positive. However we will show below that this condition is not necessary. To investigate this problem further, as well as the conditions for criticality, let us assume that $t > 0$. Then we immediately conclude that a solution to Eqs. (17) and (14) is $\phi_{mf} \equiv$ c, with h given by

$$h = tc + \frac{\lambda}{6}c^3. \tag{18}$$

Moreover, that this solution is a minimum of Eq. (16) can be easily seen by noting that the spectrum of the corresponding operator $\hat{H}$ is in this case

$$\epsilon_{n_x,n_y,n_z} == k_x^2+k_y^2+k_z^2+t+\frac{\lambda c^2}{2} = \pi^2\left(\left(\frac{n_x}{L_x}\right)^2+\left(\frac{n_y}{L_y}\right)^2+\left(\frac{n_z}{L_z}\right)^2\right)+t+\frac{\lambda c^2}{2}, \tag{19}$$

with n_x, n_y, n_z being non-negative integers and, consequently, it is always positive. Furthermore, it is also clear that $\phi_{mf} \equiv$ c is the absolute minimum and coincides with the solution of the unconstrained problem if the chemical potential is chosen to be h. Let us next consider the case $t < 0$. Let us assume L, $> L_y > L_z$ and define

$$t^* = -\left(\frac{\pi}{L_x}\right)^2 - \frac{\lambda c^2}{2} \tag{20}$$

If $t^* < t < 0$ the solution $\phi_{mf} \equiv$ c is still a minimum of the constrained functional $H[\phi]$ satisfying Eq. (14). To prove this assertion let us note that any arbitrary variation of ϕ about $\phi_{mf} \equiv$ c can be expressed in terms of the complete set of eigenfunctions of the corresponding self-adjoint operator H as follows:

$$\delta\phi(\vec{x}) = \sum_{n_x,n_y,n_z} C_{n_x,n_y,n_z} \Psi_{n_x,n_y,n_z}\left(\frac{\pi n_x x}{L_x}, \frac{\pi n_y y}{L_y}, \frac{\pi n_z z}{L_z}\right), \tag{21}$$

where the eigenfunctions Ψ_{n_x,n_y,n_z} are products of sines and cosines such as to satisfy the boundary conditions Eq. (8). If we impose that $\delta\phi(x)$ must satisfy. Eq.(14) we conclude that $C_{0,0,0} = 0$, indicating that spatially constant are precluded by the constraint. Consequently if we insert the expression for $\delta\phi$ into Eq. (6) we find that $\phi_{mf} \equiv$ c is índeed a minimum of $H[\phi]$ for 0 > t > t^* [15]. At t = t* we have that the next lowest lying eigenvalue vanishes and, therefore, the first condition for criticality is satisfied. Let us next consider the second condition, Eq. (12). It is obvious that the corresponding eigenfunction

$$\Psi_{1,0,0} = \left(\frac{2}{L_x}\right)^{1/2} \sin\frac{\pi x}{L_x} \tag{22}$$

satisfies Eq. (12) since it is an antisymmetric function of x in the range $|x| < L_x/2$. Therefore we may conclude that t^* corresponds to a new critical point[16]. This result constrasts with the unconstrained case in which criticality requires c = 0 as dictated by Eq. (12). The main difference in these two case stems form the fact that the lowest lying eigenfunction of H is symmetric (constant) for the unconstrained case and antisymmetric in the constrained case, so that when inserted into Eq. (12) they yield c = 0 and c arbitrary respectively.

It is instructive to analyse the above results from a somewhat different perspective. Let is suppose that we want a solution of Eq. (17) which only depends on the coordinate x. It is obvious that the resulting equation admits a mechanical analogy. In fact it corresponds to a point particle of unit mass whose coordinate is ϕ, x being the ficticious time. It moves in a potential given by

$$V(\phi) = -\left(\frac{t}{2}\phi^2 + \frac{\lambda}{4!}\phi^4 - h\phi\right) \tag{23}$$

The initial and final point conditions are

$$\left.\frac{d\phi}{dx}\right|_{x=\pm L_x/2} = 0 \tag{24}$$

Furthermore the average "position" must be equal to c, to comply with Eq. **(14)**. For $t > 0$ the potential **V(4)** is concave and therefore the only solution is $\phi_{mf} \equiv c$. For $t < 0$ the choice $\phi_{mf} \equiv c$ is also a solution. In Fig. **2** we have schematically depicted the potential $V(\phi)$ assuming that $t < -\lambda c^2/2$ so that $\phi_{mf} \equiv$ c corresponds to the relative minimum of V and h = $tc + Xc^3/6$. It is interesting to search for possible coordinate-dependent solutions which oscillate about the equilibrium point, such that their mean position satisfies **Eq. (14)**. It is evident from fig. 2 that such a solution will exist and will be a small oscillation about c with its period being $2L_x$. In the harmonic approximation this requires

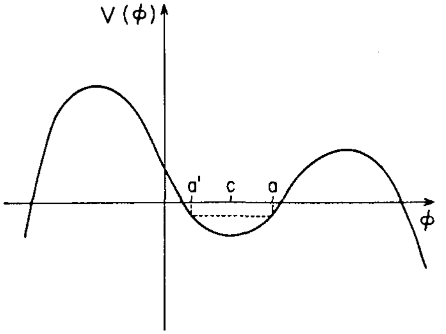

Fig. 2 – Schematic plot of the potential $V(\phi)$ as a function of ϕ for t < $\lambda c^2/2$. The trajectory represents the mean field profile as a function of x. The value of h is determined by Eq. (18). The relative minimum corresponds to a given value of c. The initial and final points $\phi(\pm L/2)$ are c + a and c – a' respectively. In the harmonic approximation, or for small a, the period of oscillation is given by Eq. *(25)*. For larger a the oscillations are anharmonic and they will not be antisymmetric, $\phi(x) = -\phi(-x)$, unless c = 0. Clearly the period of oscillation is a monotonic function of a.

$$\frac{\pi}{L_x}\sqrt{V''(c)} = \left(-\left(t+\frac{\lambda c^2}{2}\right)\right)^{1/2}. \qquad (25)$$

But this is precisely the condition defined t^* in Eq. *(20)*. Moreover, we observe that for $t > t^*$ and h given by Eq. **(18)** no such solution exists, since the period of oscillation for the potential V has a minimum given by the last term in Eq.

(25) and then increases monotonically with the amplitude. It is interesting also to note that for $t \leq t^{i}$ we expect that there are two possible solutions, which develop continuously from the solution ϕ_{mf} **r** c and are given by

$$\phi_{mf}^{(\pm)}(x) = c \pm a \sin \pi x / L_x, \tag{26}$$

with a going to 0 as $t \to t^*$ from below. It is obvious that $\phi_{mf}^{(\pm)}(x)$ satisfy the constraint Eq. (14) and both yield the same value for $H[\phi]$. It is important to observe that for t $< t^*$, the mean field profiles are antisymmetric about their mean value c. Thus we conclude that parity or reflection symmetry is spontaneously broken[17]. For not so small values of $t - t^{i}$, it is evident that the oscillations will not be harmonic and, furthermore, except for the special case c = 0, they will not be even antisymmetric about x = 0. Thus we conclude that by increasing $t^* - t$ the nodal plane of ϕ_{mf}(x) – c, which originates at x = 0 for $t = t^*$, is then displaced towards $x \gtrless 0$ depending upon the sign of c. (For c = 0 the nodal plane always remains at $x = 0$ for any $t < t^*$). More precisely the resulting solutions will have the following form .

$$\phi_{mf}^{(\pm)}(x) = \tilde{c} + \eta(\pm x), \tag{27}$$

where

$$c = \tilde{c} + \frac{1}{L_x} \int_{-L_x/2}^{+L_x/2} \eta(x) dx \tag{28}$$

and

$$h = t\tilde{c} + \frac{\lambda}{6}\tilde{c}^3. \tag{29}$$

Let us examine the behavior of $\eta(x)$ and c as a function of $\delta t = t - t^* \geq 0$. Let a and a' be the initial and final values of $\eta(x)$. (see fig. **2**). That is, let us assume

$$\eta(L/2) = a, \quad \eta(-L/2) = a', \quad \text{and} \quad \eta'(L/2) = \eta'(-L/2) = 0, \tag{30}$$

where the prime denotes derivative. The integration of **Eq. (17)** yields

$$\begin{aligned} L_x &= \int_{a'}^{a} \frac{d\eta}{[2(V(\tilde{c}+a) - V(\tilde{c}+\eta))]^{1/2}} \\ &= \sqrt{\frac{12}{\lambda}} \int_{a'}^{a} \frac{d\eta}{[(\eta - a)(\eta^3 + (4\tilde{c}+a)\eta^2 + A\eta + aA)]^{1/2}} \end{aligned} \tag{31}$$

where

$$A = a^2 + 4a\tilde{c} + \frac{12}{\lambda}\left(t + \frac{\lambda \tilde{c}^2}{2}\right) \tag{32}$$

In a similar fashion we can rewrite Eq. (28) as follows:

$$c - \tilde{c} = \frac{1}{L_x}\int_{a'}^{a} \frac{\eta\, d\eta}{[2(V(\tilde{c}+a) - V(\tilde{c}+\eta))]^{1/2}}. \tag{33}$$

These two equations determine a and L as a function of δt and c. Their exact solution is too complicated, involving combinations of elliptic functions. It is possible, however, to obtain the solution in the limit $6t \rightarrow 0$, but it turns out to be simpler to deal with the anharmonic terms in Eq. (17) using perturbation theory. The details of this calculation are given in appendix **A.1.** Here we quote the final relationship

$$a^2 = \frac{-(8\delta t/\lambda)}{1 - \lambda c^2/3\left(\frac{\pi}{L}\right)^2} \tag{34}$$

This result is somewhat surprising. It indicates that no real solution of Eqs. (31) and (33) exists unless

$$3\pi^2/\lambda L^2 > c^2. \tag{35}$$

Since we are primarily interested in the limit of large L, we conclude that in spite of the fact that conditions (i) and (ii) are satisfied no real solution of Eqs. (17) and (14) exists beyond the harmonic approximation, except for small values of c. Consequently there is no critical instability at t^* for c not satisfying Eq. (35). In spite of this result we will show below that it is possible to obtain a real solution for finite values of c. To see how this comes about, we must recall that the validity of Eq. (4) is limited to small c and that for larger values other powers of ϕ (ϕ^3, ϕ^6 etc) can no longer be ignored in the expression for $H[\phi]$. We will analyze this point below but for the time being, let us assume c is small so that the solution exists, and proceed to study some of its physical properties. The extension of these conclusions to the case of finite c is straighforward.

It is interesting to calculate the corresponding value of h for $t < t^*$. We showed above that h is given by Eq. (29). For $t - t^* = \delta t < 0$ we recall Eq. (28) and integrate Eq. (17).

$$\frac{1}{L}\int_{-L/2}^{L/2}\left(\frac{d^2\phi_{mf}}{dx^2}\right)dx = tc + \frac{\lambda}{6L}\int_{-L/2}^{L/2}(\tilde{c}+\eta)^3dx - h = 0 \tag{36}$$

Now expanding the cubic factor and retaining terms up to order η^2, we obtain to order a^2

$$h = tc + \frac{\lambda}{6}c^3 + \frac{\lambda c}{4}\pi a^2 \tag{37}$$

with a^2 given by Eq. (34). The physical interpretation of h for $t \geq t^*$ is clear, as it corresponds to the chemical potential difference. For $t < t^*$, where the mean field order parameter becomes space-dependent, the meaning of h is not obvious.

Let us nex calculate the generalized susceptibility

$$\chi_c(x,x') =< (\phi(x)- < \phi(x) >_c)(\phi(x') - (\phi(x') >_c) >_c, \tag{38}$$

where $< ... >_c$ denotes canonical ensemble statistical average. This quantity is measured by light scattering experiments. Let us denote by $\chi(x,x')$ the unconstrained (grand canonical) susceptibility. It is well known that in the mean field approximation χ satisfies Eq. (10) and that the solution can be written as in Eq. (11). In the case of the constrained system the corresponding canonical susceptibility can be expressed in terms of the grand canonical one as follows[14] :

$$\chi_c(x,x') = \chi(x,x') - \frac{\int \chi(x,x_1)dx_1 \int \chi(x',x_2)dx_2}{\int\int \chi(x_1,x_2)dx_1dx_2} \tag{39}$$

and $\chi_c(x,x')$ satisfies the following equation

$$\hat{H}\chi_c((x,x') = \delta(x-x') - \frac{1}{2}\int[\chi(x',x_1)+\chi(x,x_1)]dx_1. \tag{40}$$

Of course, it is understood that the function $\phi_{mf}(x)$ is the same in both cases. These results are derived in ref. (14). Thus if we assume $t >$ t* then $\phi_{mf} = c$ and

$$\chi_c(x,x') = \sum_{\{k\}}\left(\frac{\Psi_k(x)\Psi_k(x')}{\vec{k}^2+t+\frac{\lambda c^2}{2}}\right) - \frac{1}{t+\frac{\lambda c^2}{2}}, \tag{41}$$

where $\vec{\mathrm{k}} = (\pi n_x/L_x,\ \pi n_y/L_y,\ \pi n_z/L_z)$ with $n_x, n_y, n_z = 0, 1, 2...$ We note that χ_0 is ***not*** singular at $\vec{\mathrm{k}} = 0$ as $t \to 0$, irrespective of the value of c, indicating that t = 0 is not a critical point. Moreover we note that for

$$\vec{k} = \left(\frac{\pi}{L_x}, 0, 0\right)$$

and

$$t \to t^* = -\left(\frac{\lambda c^2}{2} + \left(\frac{\pi}{L_x}\right)^2\right), \tag{42}$$

the susceptibility diverges as $(t-t^*)^{-1}$. Thus we infer that the exponent 7 is unity as for the unconstrained case. In addition if we identify

$$\epsilon_1 = \left(\frac{\pi}{L_x}\right)^2 + t + \frac{\lambda c^2}{2} \propto \xi^{-2},$$

with ξ being the correlation length, we also obtain that ξ diverges when t $\to t^*$ like $(t-t^*)^{-\nu}$ with $\nu = 1/2$.

Let us finally calculate the specific heat at constant concentration. To this end we will first evaluate the Gibbs free energy above and below t^*. For $t > t^*$ we obtain

$$G/V = \frac{1}{2}tc^2 + \frac{1}{4!}\lambda c^4, \tag{43}$$

and therefore the corresponding contribution to the specific heat is zero. For $t < t^*$ we find

$$G/V = \frac{1}{2}a^2\left[\left(\frac{\pi}{L_x}\right)^2 + t + \frac{\lambda}{z}c^2\right], \tag{44}$$

where a is given by Eq. (34). Consequently the specific heat for $t < t^*$ is given by

$$\bar{c} = -\frac{T_c^*}{V}\left(\frac{\partial^2 G}{\partial T^2}\right)_c = \frac{\tau_0^2}{T_c}\left(1 - \frac{\lambda c^2}{3(\pi/L)^2}\right)^{-1}. \tag{45}$$

As for the unconstrained case, the specific heat has a finite discontinuity and the exponent a = 0.

In conclusion, we have found that the critical exponents for the constrained (canonical) system coincide with those of the critical unconstrained (grand canonical) system. The remarkable new feature is the fact that the nature of the transition is changed when we use the canonical ensemble. In this case we have seen that a critical line is always present for some range of the values of the concentrations in the mixture[18]. This result strongly contrasts with the usual grand canonical case in which the transition (at the spinodal line) is discontinuous except for a single point at which it becomes second order.

We have mentioned before that the solution $\phi_{mf}(x)$ we analyzed above corresponds to a relative minimum of the free energy functional. In fact it is well known that at the coexistence temperature

$$t_1(c) = -\frac{\lambda c^2}{6} > t^* \tag{46}$$

the system undergoes a first order phase transition. At this temperature the system becomes inhomogeneous and it is not difficult to derive an approximate expression for the corresponding concentration profile in the case $t_1 L_x^2 >> 1$. For a container of edges L, $> L_y >$ L,, and if the concentration c, is not close to one or zero, the minimal free energy profile corresponds to two distinct homogeneous phases separated by a flat interface[19] perpendicular to L, whose thickness is $t^{-1/2}$. An approximate expression for ϕ_1(x) is the following[20]

$$\phi_1(x) = (-6t/\lambda)^{1/2} \tanh(x - x_0)\sqrt{t} + ..., \tag{47}$$

where the value of x_0 is fixed by the constraint Eq.(14) and deleted terms are of higher order in $(L_x\sqrt{t})^{-1}$. In this case the parameter $h = 0$. It is obvious that the mirror image of $\phi_1(x)$ about the midplane x $= L_x/2$ will also be a solution.

In conclusion, we have found that in the mean field approximation the canonical ensemble yields the same coexistence curve as the grand canonical, but the spinodal line is changed into a line of (pseudo) critical points characterized by the same singular critical behavior as the critical point at T_c.

Let us recall that these conclusions are valid provided the Eq. (35) is valid. In order to extend these results to finite c let us first note that although it was implicit in the derivations of section 2, the average concentration of one component in the mixture must be chosen precisely at its critical value, C_0, for the unconstrained system to become critical[21]. The Landau theory will describe the system properly, provided that local deviations of the concentration from C_0 remain small. As a consequence of our results we may then inquire on how could the Landau-Ginzburg-Wilson theory be modified, to account for the fact that in the constrained system there is not a unique value of C yielding a critical instability.

For $C \neq C_0$ such extension can be obtained by postulating that the functional H in Eq. (4) should be replaced by

$$H = \int \left\{ \frac{1}{2}(\nabla\phi)^2 + \frac{\tilde{t}}{2}\phi^2 + \frac{\bar{g}}{3!}\phi^3 \frac{\lambda}{4!}\phi^4 \right\} dx \tag{48}$$

where

$$\tilde{t} = \tau(C)\left(\frac{T - T_0(C)}{T_0(C)}\right) \quad , \quad \bar{g} = \bar{g}(C,T) \quad \text{and} \quad A = \lambda(T,C) > 0 \; . \tag{49}$$

In this expression $T_0(C)$ is the new "critical temperature" corresponding to this value of C, and the parameters g and λ have a mild temperature dependence which we ignore. In addition, the order parameter ϕ measures local deviations from the concentrations C and satisfies $(1/V)\int \phi dx = 0$. Let us note that $g(C_0, T) = 0$, so as to guarantee thermodynamical stability for the unconstrained critical point[22]. For the constrained system $g \neq 0$ does not imply instability because of Eq. (14). The mean field analysis of Eq. (49) for C # C_0 is quite similar to that of section 3. There are, however, some important point worth noting. In the first place it is easily shown that Eq. (34) is replaced by

$$a^2 = -\frac{8\delta t}{\lambda}\left(1 + \frac{5}{3\lambda}\left(\frac{gL}{\pi}\right)^2\right)^{-1} . \tag{50}$$

In addition it is also clear that because of the $g\phi^3$ term, the profile interface will be displaced as one decreases the temperature below $T^*(C)$. Furthermore, we can also establish the shift in critical temperature in the vicinity of C_1. In effect, if we consider $C = C_1 + c$ then the shifted critical temperature $T^*(C)$ is related to $T^*(C_1)$ as follows

$$\frac{T^*(C) - T^*(C_1)}{T^*(C_1)} \cong -\frac{1}{\tau_0}\left(\bar{g}(C_1)c + \frac{\lambda(C_1)}{2}c^2\right) . \tag{51}$$

Consequently the spinodal (this line of critical points in the (T, C) plane) will not be symmetric about $C = C_0$.

4. Scaling and criticality

It has been firmly established that in the vicinity of the critical point the singular part of the free energy satisfies a general scaling form. With the purpose of comparing canonical and grand canonical ensembles let us focus our attention on the Helmholtz free energy. It is important to note that even though the Gibbs free energy is the "natural" thermodynamical potential to deal with in the grand canonical ensemble, it is always possible to construct the corresponding Helmholtz potential, provided the relationship between the order parameter and its conjugate field is invertible. Moreover, it is easily shown that if the Gibbs function is homogenenous then the corresponding Helmholtz potential will have a similar property. For the unconstrained system the Helmholtz free energy has the following general form

$$F = t^{2-\alpha} \mathrm{f}\,(ct^{-\beta}, Lt^{\nu}), \tag{52}$$

where α, β and v are the usual exponents and f is a universal function. We have also assumed that the system is enclosed in a box of edge L so that, according to finite size scaling hypothesis[23], the scaling variable Lt^{Y} must me also present. In this case t involves $T_c(L)$ which strictly speaking is not a critical temperature unless L → ∞ (more appropriately a pseudocritical temperature for this case). For finite but large L, it is possible to identify such $T_c(L)$ [24]. We shall also assume that for the constrained system the Helmholtz free energy has a similar homogeneity form. However, the function f will be different in this case, to account for the fact that there is a critical line in the t, c plane rather than a single isolated point as in the former case (stricktly speaking this refers to the continuation of the free energy into the metastable regime[5]). The critica1 manifold should then correspond to a line of singularities of the function f. If a scaling form for f is assumed, we then conclude that the critica1 temperature t* is a homogeneous function of c and L of the form

$$t^* = -\frac{1}{L^{1/\nu}} g(cL^{\beta/\nu}), \tag{53}$$

with $g(x) \approx x^{1/\beta}$ for x → ∞. (The minus sign is inserted for convenience and there should be two scale system-dependent factors for t* and $cL^{\beta/\nu}$ which we have arbitrarily set equal to one). It is easy to corroborate in the mean field approximation that these conditions are satisfied. In fact **Eq.** (20) can be rewritten as

$$t^* = -\frac{t^2}{L^2}\left(1 - \frac{\lambda c^2 L^2}{2\pi^2}\right), \tag{54}$$

so that the resulting function g is given by

$$g(x) = 1 + x^2 , \tag{55}$$

and clearly it complies with the asymptotic behavior stated above[25]. This simple result can be compared with some experimental data in which the singular temperature for sealed binary mixtures in a range of concentrations has been determined. Although these points (line) could be regarded as belonging to the spinodal curve, according to our theory they should correspond to a line of pseudo critical points. In fig. (3) we reproduce the data for isobutyric acid in water taken by Chu et al[10]; the fitted curve corresponds to $\beta \cong 0.3$ rather that the mean field value 0.5.

We must bear in mind that the expression for $g(x)$ given by Eq. (57) should only be valid for small values of c. This restriction was implicit in the expression for the free energy given by $Eq.$ (4). For c not so small, the form of $g(x)$ as indicated by Eq. (51) will not necessarily be symmetric about $c = 0$.

5. Theory and experiment

In the first place we must consider the problem of nucleation. As is well knows, its rapid increase with the degree of supersaturation implies that the critical spinodal line will not be observable. In spite of this, we may argue that the effect of this critical point is to influence the thermodynamical behavior of the system in regions of metastability, where nucieation is negligible, or even absolute stability, by going above the coexistence line. Let us establish the conditions for which this extrapolation may be expected to hold. It is reasonable to assume that if, for a given $c = C - C_0 \neq 0$ and temperature T, the associated correlation length is much larger that the average interatomic separation a_0 (say 3 Å), then the critical point at $T^*(C)$ will have a strong effect on the thermodynamical functions. Accordingly for these values of c and T we must have

$$|t + \lambda c^2/2|^{-1/2} >> a_0 \ . \tag{56}$$

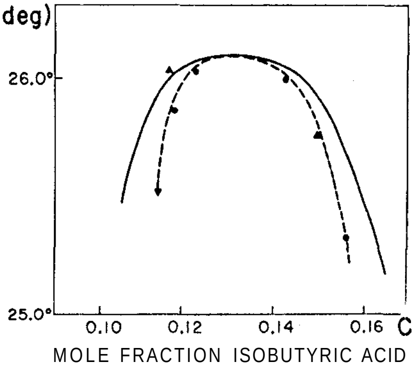

Fig. 3 - We reproduce the experimental coexistence and cntical spinodal curves obtained by Chu et al. for Isobutyric acid in water. The solid line ia the coexistence curve as determined by phase separation observations. The dashed curve is indirectly determined by extrapolation of the light intensity and linewidth measurements in the homogeneous eguilibrium regions. (see ref. 10).

Let us choose for simplicity T to be the coexistence temperature $T_1(C)$. Obviously at this point nucleation is unimportant. From mean field theory we know that $T_1(C)$ is given by Eq. *(46).* Thus we conclude that our assumption will hold

$$(-2t_1)^{-1/2} >> a_0 \quad \text{or} \quad \frac{T_c - T_1(C)}{T_c} << 1 \;, \qquad (57)$$

where we assumed

$$t = \tau(C)(T - T_c)/T_c \;,$$

with $t^{-1/2} = \xi_0 \sim 3$ Å and T_c being the true critical temperature. These conditions are well satisfied by the experiments of B. Chu et al[10]. Below the coexistence line we also expect that if *Eq. (56)* is satisfied, critical behavior will be observed provided we stay above the cloud point.

Another context in which the critical spinodal may have an important and nontrivial role is for spinodal decomposition. According to our results, below $t^*(c)$ the system will become inhomogeneous with a concentration profile which evolves continuously from the homogeneous phase. These states represent metastable inhomogeneous phase, and they can also nucleate to the absolute minimum free energy configuration[26]. We may then conjecture that a quenched homogeneous system below the spinodal line can be trapped by these metastable phases during its time evolution. Although this is only a speculation, it may have a relevant role in the scaling effect observed during the late stages of spinodal decomposition[2,3]. We will analyze this point in a future publication.

It is important to emphasize that these results should contrast with those for a system with nonconserved order parameter, such as a liquid-gas transition at fixed chemical potential. In such a case the spinodal line is a line of discontinuous instabilities whose singular nature has been studied in the grand canonical ensemble by other authors[27]. It must be stressed, however, that for experiments near the liquid-gas transition, but at fixed density, the results derived should also apply[9].

Let us next focus our attention on another condition which will be encountered in most experimental setups. We have seen that sealed binary mixtures provide an ideal system to test the results mentioned above; however, many experiments with these systems are performed in the presence of a vapor phase. This fact can change the results expected above since, in such a case, the liquid mixture will not satisfy the constraint **Eq. (14)** by itself. Another important effect on these systems is produced by the gravitational field. For an unconstrained system gravity can be ignored by choosing mixtures of nearly the same density. In sealed systems the role of gravity will be twofold. In the first place it can unbalance the ordering of the eigenvalues of the operator H in Eq. (6). For example, let us assume that the container is a box of edges L, > L_y > L, and oriented so that its L, edge is perpendicular to the gravitational field[28]. In a gravitationless enviroment and below t^*, the fluid will separate into two regions of different concentrations with a separating interface perpendicular to the x axis. This was of course the conclusion of **Eq.** (26). However, in the presence of gravity, say along the y axis, the force exerted on the denser fluid towards the bottom of the container will force the interface to form parallel to the x axis. How the resulting concentration profile evolves as the temperature is lowered will depend on the relative "strength" of these two competing effects. In addition, gravity can produce another related effect. Let us assume that the system is oriented with L, vertical. If no gravitational force is present, we found in previous sections that below t^* the mean field profile bifurcates into two equally probable configurations. In the presence of gravity, and unless the fluid densities are identical, the configuration with the denser fluid at the bottom will be stable and strictly speaking there will be no transition. (This is similar to having an external magnetic field in the case of an Ising spin system. The stable configuration corresponds to the spins oriented parallel along the field. In this case there is no phase transition). Of course these latter conclusions may be of only academic interest since nucleation will preclude the observation of the critical spinodal line.

6. Summary and Final Conclusions

We have seen that the behavior of systems with a conserved order parameter, such as binary mixtures or binary alloys, depends in their supersaturation metastable region, on the ensemble used to derive their spinodal instabilities. In the specific case of a binary mixture, we have that the spinodal line in the concentration-temperature plane corresponds to a line of discontinuous instabilities in the grand canonical ensemble, whereas it becomes a line of continuous instabilities or critical points in the canonical framework. This latter case corresponds physically to sealed systems in which the overall concentration is not allowed to fluctuate.

We have also shown that the critical exponents characterizing the singular thermodynamical behavior are identical to those of the standard critical point. Our analysis is based on the mean field approximation and we have ignored nucleation effects. Even though in the framework of the classical theory the droplet model predicts that the resulting instability, as the spinodal line is approached, is a continuous one, if the system satisfies the constraint of the canonical ensemble[29], the system will undergo a transition to the more stable inhomogeneous configuration in any reasonable laboratory time scale before the spinodal line is reached[30]. We argue, however, that the existence of this critical (or pseudocritical) spinodal line has important physical effects on the metastable and truly stable homogeneous phases of these systems[31]. The results of Chu et. al[10] seem to confirm this hypothesis and further experiments, particularly in the metastable region, are certainly worthwhile to establish the validity of the above predictions.

Acknowledgements

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Appendix A1

Let us solve Eq. (17) using perturbation theory[32]. Substituting Eq. (27) into Eq. (17) yields

$$\frac{d^2\eta}{dx^2} = \left(t + \frac{\lambda\tilde{c}^2}{2}\right)\eta + \frac{\lambda\tilde{c}}{2}\eta^2 + \frac{\lambda}{6}\eta^3 \tag{A.1}$$

Let us consider a solution of the form:

$$\eta(x) = \eta_1(x) + \eta_2(x) + \eta_3(x) + \ldots \tag{A.2}$$

and for simplicity shift the interval to $0 \leq x \leq$ L. In this case

$$\eta_1(x) = a\cos\ \omega x \tag{A.3}$$

Substituting Eq. (A.2) into Eq. (A.1) we obtain

$$\eta_2 = -\frac{\lambda\tilde{c}a^2}{4\omega_0^2}(1 + (1/3)\cos\ 2\omega x), \tag{A.4a}$$

$$\eta_3 = \frac{\lambda a^3}{192\omega_0^2}\left(1 + \frac{\lambda\tilde{c}^2}{\omega_0^2}\right)\cos\ 3\omega x, \tag{A.4b}$$

and

$$\omega = \frac{\pi}{L} = \omega_0 - \frac{\lambda a^2}{16\omega_0}\left(1 + \frac{5\lambda\tilde{c}^2}{3\omega_0^2}\right) + \ldots\ , \tag{A.4c}$$

where

$$\omega_0 = [-(t + \lambda\tilde{c}^2/2)]^{1/2}\ , \tag{A.5}$$

and ... stands for higher order terms in a. Substituting Eq. (A.2) into Eq. (28) we derive

$$\tilde{c} = c - \frac{\lambda\tilde{c}}{4\omega_0^2}a^2 + \ldots \cong c - \frac{\lambda c a^2}{4\left(t + \frac{\lambda c^2}{2}\right)} + \ldots \qquad (A.6)$$

Finally if we write $t = t^* + 6t$ and recall Eq. (25), we obtain from Eq. (A.4c) the desired relationship between a^2 and δt as $\delta t \to 0$.

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13. Constraints in functional integrals are familiar in gauge field theories. See for example: L. Fadeev and A. Slavnov, Gauge Fields. Benjamin Publishing Co. Massachusetts, 1980.

14. A general formalism for dealing with constraints in critical phenomena in the context of the functional integral has been developed by J. Rudnick and D. Jasnow. Phys. Rev. B 24, **2760 (1981).**

15. This results only indicates that the solution $\phi_{mf} = c$ is a relative minimum of the constrained functional. We know that at the usual coexistence line temperature $t_1 (0 > t_1 > t^*)$ the system undergoes a first order transition with $h \cong 0$. The inhomogeneous state has the lowest free energy.

16. More properly a metastable critical point.

17. Had we chosen L, $= L_y =$ L, then the first excited eigenvalue of H becomes triply degenerate and reflection symmetry (parity) can be spontaneously broken along any of the coordinate axes.

18. Strictly speaking the thermodynamical limit $L \rightarrow \infty$ implies $C = 0$ for the canonical results to yield a critical point. On the other hand finite L implies no critical point. However we will show later that the extension to $C \neq 0$ is achieved by modification of $H[\phi]$.

19. It must be emphasized that these results are very sensitive to the kind of boundary conditions imposed on the system. For example if we impose periodic boundary conditions these conclusions are incorrect. Furthermore if a concentration tends to zero or one, a simple analysis shows that the minimal surface interface corresponds to a spherical bubble centered at one corner of the container.

20. The exact expression for $\phi_1(x)$ cannot be expressed in terms of elementary functions, except for $h = 0$ and $L \rightarrow \infty$.

21. Note that C_0 refers to the absolute value of the concentrations whereas c measures deviations from C_0 and vanishes at the unconstrained critical point.

22. **A.** Patashinskii and V. Pakrovskii; ***Fluctuations Theory of Phase Transitions*** Page **21.** Pergamon Press, Oxford **1978.**

23. For a general review see M. Barber, ***Phase Transitions and Critical Phenomena***, Vol. **8.** C. Domb and J. Lebowitz Editors, Academic Press, London, **1983.**

24. $T_c(L)$ could be defined as the temperature at which the specific heat attains its maximal value. For a discussion see M. Fisher. Proceedings of the International School of Physics Enrico Fermi. Course LI. M. Green Editor, Academic Press, London, 1971.
25. It is a simple excercise to derive this result from the mean field expression for the free energy by inserting $\phi_{mf}(x)$ as given by Eq. (26).
26. Note also that the concentration profile will approach the absolute minimum configuration continuously.
27. Although it is possible to define exponents characterizing the singular behavior at the end points of the metastable branches. See A. Compagner, Physica 72, 115 (1973).
28. Typicaly this is not the case. Experiments are generally done in long containers oriented vertically so as to visualize the formation and evolution of the meniscus separating the phases as the transition point is crossed.
29. At the spinodal line the critical droplet becomes of infinite extent and of infinitesimal amplitude (see ref. 8). Consequently it can be expanded in terms of the eigenfunctions $\{\Psi_n\}$ as in Eq. 21.
30. K. Binder, *Systems Far from Equilibrium.* Edited by L. Garrido (Springer-Verlag, Germany) 1980.
31. It is important to mention an observation made by Chu et al.[10] of the fact that the singular behavior of the inverse susceptibility, Γ^{-1}, resulting from their empirical fitting of the scattered light data $\Gamma^{-1} \cong (T - T_{sp})\gamma$ and $T_c - T_{sp} = |C - C_0|^{1/\beta}$, where $\gamma \cong 1.3$ and $\beta \cong 0.3$, implies a nonphysical, nonanalytic behavior of Γ^{-1} if extrapolated to $T > T_c$ and to the vicinity of the critical isochore, $C \cong C_0$. In our mean field approach this singularity does not arise since $\gamma = 1$ and $\beta = 1/2$. It is obvious then that this asymptotic expression can only be valid in a neighborhood of the coexistence line, but not along the critical isochors. It is possible, at least in principle, to construct a functional form for Γ^{-1} which copes with this difficulty and has the proper asymptotic behavior near the coexistence curve. To see this, it is convenient to introduce a parametric representation for Γ^{-1}, t^* and c. In term of polar coordinates,

r, θ, we identify $t^*/c^{1/\beta} = \theta_{sp}$, $t_{co}/c^{1/\beta} = \theta_{co}$ and $\theta = 0$ as the spinodal, the coexistence and the critical isochore lines respectively $\theta_{sp} < \theta_{co} < 0$). Then if we choose $\Gamma^{-1} = r\gamma \ g(\theta)$ with $g(\theta)$ such that $g(\theta) \cong (\theta - \theta_{sp})^{\gamma}$ for $\theta \cong \theta_{sp}$, but is analytic for $\theta > \theta_{sp}$ we obtain the desired representation.

32. L. Landau and E. Lifchitz, Mechanics. Addison-Wesley, Reading, Mass. 1960.

Resumo

Analisamos as condições para instabilidades críticas no ensemble canônico, no contexto da aproximação de campo médio para a integral funcional de Landau-Ginzburg-Wilson que descreve as propriedades de equilíbrio de um sistema com parâmetro de ordem conservado. Pela introdução de um vínculo na integral funcional para garantir a conservação global do parâmetro de ordem em um sistema fechado, concluímos que o diagrama de fase gran-canônico usual, obtido na aproximação de campo médio, é modificado na região super-saturada. Obtemos que a linha espinodal separando as regiões instável e metastável se torna uma linha de pontos críticos na qual o perfil do parâmetro de ordem varia continuamente com a temperatura. Os expoentes críticos que caracterizam esta linha são os mesmos que os do ponto crítico usual. Esta conclusão está em contraste com o comportamento singular unilateral dos pontos finais dos ramos metastáveis do caso gran-canônico. Estes resultados são derivados desprezando nucleação, o qual fenômeno se espera tornar a observabilidade direta desta linha praticamente impossível, nesta região. Argumentamos no entanto que os efeitos de ponto crítico podem ser importantes na região metastável, ou mesmo na região estável antes que o aparecimento de nucleação forte se dê. Esta conclusão está em acordo qualitativo com alguns resultados experimentais de espalhamento de luz em misturas binárias e sistemas de um componente, próximo à transição líquido-gás. O efeito desta linha crítica sobre o problema de decomposição espinodal é brevemente discutido.