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A generalised Landau theory for chemical instabilities

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Abstract. A generalised Landau theory for non-equilibrium phase transitions in chemical reactions is developed. This theory is based on the construction of a generalised free energy which describes just the fluctuations in excess of equilibrium. This is accomplished most readily via the Poisson representation. This theory yields results for the spatial correlation function in agreement with those of the stochastic master equation. The range of validity of the Landau theory and the Gaussian approximation to the master equation are found to be equivalent and both are shown to yield satisfactory results for non-equilibrium chemical phase transitions.

For a one-component chemical system, fluctuations in excess of equilibrium require only the introduction of a single additional parameter a 'generalised temperature'. However in general, a generalised Landau theory for non-equilibrium phase transitions is not so simple, an n -component system requires $\frac{1}{2}n(n+1)$ additional parameters to describe it.

1. Introduction

The Landau theory of phase transitions has been of great utility in providing a simple theoretical treatment of equilibrium systems, and thus it is of great interest to determine whether it can be generalised to non-equilibrium systems as well. Simple examples of non-equilibrium phase transitions are provided by chemically reacting systems for which Pimpale and Landsberg (1977, to be referred to as PL) have conjectured a straightforward generalisation of the Landau theory. The predictions of the method are in agreement with those of stochastic master equation methods for global fluctuations. However, their method retains the inadequacies of the usual Landau theory in describing local fluctuations. In magnetic systems or liquids the interest has been in the long-range correlations near an instability point and here the Landau theory has been useful. In chemical systems however the local fluctuations are important. For example in chemical equilibrium there are no long-range correlations and the system is completely characterised by the local fluctuations.

A generalised Landau theory including local fluctuations may be constructed by a choice of the generalised free energy which describes only the fluctuations in excess of equilibrium. This may be accomplished using the Poisson representation (Chaturvedi *et al* 1976, Gardiner and Chaturvedi 1977). The generalised Landau theory is then shown to be in exact agreement with the results of the stochastic master equation in the Gaussian approximation. We also investigate the range of validity of the Landau theory for chemical reactions and show that it is the same as that of the Gaussian approximation.

The problems in extending the generalised Landau theory to systems with more than one variable are investigated.

2. Comparison of the results of Pimpale and Landsberg with the predictions of equilibrium statistical mechanics and stochastic master equations

We considered a simple chemical system with one component, X , which diffuses and reacts chemically. The macroscopic equation describing these processes is taken to be

$$\frac{\partial x}{\partial t} = D \nabla^2 x + \Phi(x) \quad (2.1)$$

where x is the number of molecules of chemical species X , D is the diffusion coefficient, and $\Phi(x)$ describes the chemical reaction. For this system PL introduced a generalised free energy of the form

$$H = f \left[\int d\mathbf{r} \left(H_0 - \int^x \Phi(x) dx + \frac{1}{2} D (\nabla x)^2 \right) \right]. \quad (2.2)$$

Using the standard methods of Landau theory they derive for the spatial correlation function

$$p(\mathbf{r}, \mathbf{r}') = \langle x(\mathbf{r}), x(\mathbf{r}') \rangle = \langle x(\mathbf{r})x(\mathbf{r}') \rangle - \langle x(\mathbf{r}) \rangle \langle x(\mathbf{r}') \rangle \quad (2.3)$$

an expression of the form

$$p(\mathbf{r}, \mathbf{r}') = \frac{kT}{4\pi f D} \frac{\exp(-|\mathbf{r} - \mathbf{r}'|/l_c)}{|\mathbf{r} - \mathbf{r}'|} \quad (2.4)$$

with

$$l_c = \left(\frac{D}{\lambda} \right)^{1/2} \quad \text{and} \quad \lambda = - \frac{d}{d\langle x(\mathbf{r}) \rangle} [\Phi(\langle x \rangle) - \Phi_0]$$

is assumed to be independent of \mathbf{r} . T is the thermodynamic temperature and the quantity f is left unspecified by PL.

Spatial correlation functions in chemical reactions have been derived by stochastic master equation methods (Gardiner *et al* 1975, 1976, Lemarchand and Nicolis 1976, van Kampen 1976b) and equivalent methods (e.g. fluctuation dissipation theory, Keizer 1977).

These methods yield a correlation function of the form

$$p(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \langle x(\mathbf{r}) \rangle + F(\langle x(\mathbf{r}) \rangle) \frac{\exp(-|\mathbf{r} - \mathbf{r}'|/l_c)}{|\mathbf{r} - \mathbf{r}'|} \quad (2.5)$$

where $F(\langle x(\mathbf{r}) \rangle)$ is a function dependent on the reaction Φ . The first term in equation (2.5) describes local fluctuations whereas the second term describes global fluctuations. The first term is absent in equation (2.4) derived by PL using a generalised Landau theory since Landau theory usually uses an approximate form of the free energy which cannot include local fluctuations. We show in the appendix how the Landau theory can be formulated to include local fluctuations in chemical reactions in thermodynamic equilibrium.

Local fluctuations play an important role in the understanding of chemical reactions. There are no long-range correlations in equilibrium in chemical reactions in

contrast to the situation in magnetic or liquid systems usually treated by the Landau theory. In chemical equilibrium $F(\langle x(\mathbf{r}) \rangle)$ is zero and the system is completely characterised by the local Poissonian fluctuations. This prediction is in precise agreement with results obtained using the standard methods of equilibrium statistical mechanics (in the grand canonical ensemble) (Gardiner and Chaturvedi 1977, van Kampen 1976a). These equilibrium fluctuations are not given by the PL generalisation of the Landau theory.

In chemical reactions it is only possible to get long-range spatial correlations in non-equilibrium steady states. Here the PL generalisation of the Landau theory gives the correct form for the long-range correlations. However local fluctuations are also of interest in non-equilibrium steady states in chemical reactions. From the master equation we may derive an expression for the variance $\sigma^2(\Delta V)$ of the number of molecules in a small spherical volume ΔV of radius $R \ll l_c$. This yields (Gardiner *et al* 1976)

$$\frac{\sigma^2(\Delta V)}{\langle x \rangle} = 1 + R^2 \rightarrow 1 \quad \text{as } R \rightarrow 0. \quad (2.6)$$

The master equation predicts local Poissonian fluctuations (but global non-Poissonian) even in non-equilibrium steady states agreeing with the local equilibrium postulate of Glansdorff and Prigogine (1971). Again the PL generalised Landau theory cannot give these local fluctuations.

3. Construction of a generalised free energy for chemical reactions

Despite the preceding objections it is possible to construct a generalised free energy which will yield the correct spatial correlation function for both local and global fluctuations via the Landau method. The problem lies in including the fluctuations due to diffusion and chemical reaction in a correct manner. This problem is closely related to that of correctly choosing Langevin forces when introducing fluctuations into reaction diffusion equations, which have been carefully discussed by Gardiner (1976) and Grossman (1976). The Langevin equation for a one-component reaction diffusion system follows from equation (2.1) by the addition of a stochastic Langevin force

$$\frac{dx}{dt} = D\nabla^2 x + \Phi(x) + g(\mathbf{r}, t). \quad (3.1)$$

An appropriate choice for the correlation functions of $g(\mathbf{r}, t)$ is necessary if the predictions of the Langevin equation are to be correct.

A choice of uncorrelated forces

$$\langle g(\mathbf{r}, t)g(\mathbf{r}', t') \rangle = K\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \quad (3.2)$$

where K is a constant, leads to a spatial correlation function of the form of equation (2.4), which, as pointed out in § 2, leads to incorrect results in thermodynamic equilibrium.

It has been shown (Gardiner 1976, Grossman 1976) that a choice of correlation function of the form

$$\langle g(\mathbf{r}, t)g(\mathbf{r}', t') \rangle = (K_c(\mathbf{r}, t) + D^2\nabla\nabla'K_d(\mathbf{r}, t))\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \quad (3.3)$$

leads to a form of the correlation function given by equation (2.5) (K_c and K_d give a measure of the strength of the fluctuating forces due to chemical reaction and diffusion respectively). That is, the form of the Langevin forces must be spatially correlated to give rise to spatially uncorrelated concentration fluctuations in thermodynamic equilibrium.

It is however possible to retain spatially uncorrelated Langevin forces if one works in the Poisson representation of the number distribution (Chaturvedi *et al* 1976, Gardiner and Chaturvedi 1977):

$$P(\mathbf{x}, t) = \int d\boldsymbol{\alpha} \prod_{i=1}^n e^{-\alpha_i} \frac{\alpha_i^{x_i}}{x_i!} f(\boldsymbol{\alpha}, t) \quad (3.4)$$

where we have used the discrete cell description in space where $\mathbf{x} = x_1, \dots, x_i, \dots, x_n$ and x_i is the number of particles in the i th cell and α_i is the associated Poisson variable.

In the continuum notation the Langevin equations may be written in terms of α variables as

$$\frac{d\alpha}{dt} = D\nabla^2 + \Phi(\alpha) + g_\alpha(\mathbf{r}, t). \quad (3.5)$$

It has been shown (Gardiner and Chaturvedi 1977) that the choice of correlation function

$$\langle g_\alpha(\mathbf{r}, t) g_\alpha(\mathbf{r}', t') \rangle = K\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \quad (3.6)$$

leads to the correct form of the spatial correlation function given by equation (2.5) and is completely equivalent to a master equation formulation.

Motivated by these considerations we are lead to construct our generalised free energy in the α representation as

$$H = \int d\mathbf{r} \left(H_0 - \int^\alpha \Phi(\alpha) d\alpha + \frac{1}{2} D(\nabla\alpha)^2 \right). \quad (3.7)$$

We may now follow precisely the method of PL but in α variables to determine the correlation function. The minimum of the generalised free energy gives the macroscopic steady state

$$\Phi(\alpha) + D\nabla^2\alpha = 0. \quad (3.8)$$

Fluctuations are introduced by assuming that the probability of having the system in state $\alpha(\mathbf{r})$ is proportional to $\exp(-H/k\tau)$, where τ gives a measure of the strength of the fluctuations in excess of equilibrium and is analogous to the thermodynamic temperature and k is Boltzmann's constant. The mean of $\alpha(\mathbf{r}) = \langle \alpha(\mathbf{r}) \rangle$ obeys equation (3.8) in the steady state. Taking $\Phi_0(\mathbf{r})$ as the α -independent part of $\Phi(\mathbf{r})$ we may deduce from equation (3.8) that

$$\delta\Phi_0(\mathbf{r}) = \left(-\frac{d}{d\langle \alpha(\mathbf{r}) \rangle} (\Phi(\langle \alpha \rangle) - \Phi_0) - D\nabla^2 \right) \delta\langle \alpha(\mathbf{r}) \rangle. \quad (3.9)$$

The change in $\langle \alpha(\mathbf{r}) \rangle$ induced by a small change in Φ_0 is given by (Kadanoff *et al* 1967)

$$\delta\langle \alpha(\mathbf{r}) \rangle = k\tau \int d\mathbf{r}' \langle \alpha(\mathbf{r}), \alpha(\mathbf{r}') \rangle \delta\Phi_0(\mathbf{r}, \mathbf{r}'). \quad (3.10)$$

From equations (3.9) and (3.10) we arrive at the following equation for the spatial correlation function:

$$\left(-\frac{d}{d\langle\alpha(\mathbf{r})\rangle} (\Phi(\langle\alpha\rangle) - \Phi_0) - D\nabla^2 \right) \langle\alpha(\mathbf{r}), \alpha(\mathbf{r}')\rangle = k\tau\delta(\mathbf{r} - \mathbf{r}'). \quad (3.11)$$

When

$$-\frac{d}{d\langle\alpha(\mathbf{r})\rangle} (\Phi(\langle\alpha\rangle) - \Phi_0) = \gamma$$

is independent of \mathbf{r} this has the solution

$$\langle\alpha(\mathbf{r}), \alpha(\mathbf{r}')\rangle = \frac{k\tau}{4\pi D} \frac{\exp(-|\mathbf{r} - \mathbf{r}'|/l_c)}{|\mathbf{r} - \mathbf{r}'|} \quad (3.12)$$

where $l_c = (D/\gamma)^{1/2}$. Now since

$$g(\mathbf{r}, \mathbf{r}') = \langle\alpha(\mathbf{r}), \alpha(\mathbf{r}')\rangle = p(\mathbf{r}, \mathbf{r}') - \langle x(\mathbf{r})\rangle\delta(\mathbf{r} - \mathbf{r}') \quad (3.13)$$

this gives us in the molecular number representation

$$p(\mathbf{r}, \mathbf{r}') = \langle x(\mathbf{r})\rangle\delta(\mathbf{r} - \mathbf{r}') + \frac{k\tau}{4\pi D} \frac{\exp(-|\mathbf{r} - \mathbf{r}'|/l_c)}{|\mathbf{r} - \mathbf{r}'|} \quad (3.14)$$

where $l_c = (D/\gamma)^{1/2}$.

This reproduces the form of the result (equation (2.5)) obtained from the stochastic master equation.

4. A chemical reaction exhibiting a second-order phase transition

We shall consider as an example of the foregoing technique a chemical reaction which is known to exhibit a second-order phase transition (Schlögl 1971, McNeil and Walls 1974)



where A , B and C are held constant, and the k_i are the reaction rate constants. The homogeneous macroscopic steady state is given by

$$k_3 C + (K_2 - K_1)x - k_4 x^2 = 0 \quad (4.2)$$

where x is the number of molecules of chemical species X .

A stochastic master equation including diffusion for this reaction was derived by Gardiner *et al* (1976). Because of the non-linearity in the reaction this yields an equation for the second-order correlation function which is coupled to higher-order correlation functions. In order to truncate this hierarchy of coupled equations an approximation assuming the molecular distributions to be Gaussian was made. The equation for the spatial correlation function $g(\mathbf{r})(\mathbf{r} = |\mathbf{r} - \mathbf{r}'|)$ in the steady state obtained in the Gaussian approximation is

$$(D\nabla^2 + K_2 - K_1 - 2k_4\langle x \rangle)g(\mathbf{r}) = -\delta(\mathbf{r})(K_2\langle x \rangle - k_4\langle x \rangle^2) \quad (4.3)$$

where $K_1 = k_1 B$, $K_2 = k_2 A$ and we have neglected $g(0) \ll 1$.

Using the Landau theory described in § 3 we obtain directly from equation (3.11)

$$(D\nabla^2 + K_2 - K_1 - 2k_4(x))g(r) = -\delta(r)k\tau. \quad (4.4)$$

Comparing equations (4.2) and (4.3) there is a one-to-one correspondence with the identification

$$k\tau = (K_2\langle x \rangle - k_4\langle x \rangle^2) = (K_1\langle x \rangle - k_3C) \quad (4.5)$$

with this value of $k\tau$ the result (3.14) for the correlation function is identical to that given by the master equation in the Gaussian approximation.

The steady-state distribution in α space is characterised by a 'generalised temperature' τ

$$f(\alpha) = \exp\left(-\frac{H(\alpha)}{k\tau}\right). \quad (4.6)$$

The τ parameter gives a measure of the fluctuations in excess of equilibrium fluctuations. τ is zero when the system is in equilibrium.

This we can see from the above example where equilibrium occurs when the separate reactions balance independently which means

$$K_1x = k_3C \quad k_2x = k_4x^2 \quad (4.7)$$

which are equivalent to the vanishing of τ according to equation (4.4). In the case that $\tau = 0$ we see that equation (4.6) predicts $f(\alpha)$ is zero unless $H(\alpha)$ vanishes as is indeed found in the Poisson representation where in equilibrium

$$f(\alpha) = \delta(\alpha - \alpha_{\text{eq}}) \quad (4.8)$$

corresponding to a Poisson distribution in the molecular number

$$P(x) = \exp(-\alpha_{\text{eq}}) \frac{(\alpha_{\text{eq}})^x}{x!}. \quad (4.9)$$

This leads us to the following construction for a non-equilibrium distribution function:

$$P(x) = \int d\alpha \exp(-\alpha) \frac{\alpha^x}{x!} \exp\left(-\frac{H(\alpha)}{k\tau}\right). \quad (4.10)$$

Thus for a one-component system the non-equilibrium distribution function may be simply constructed requiring only one additional parameter, a generalised temperature τ .

5. Limits of validity of the Landau theory and the Gaussian approximation for chemical reactions

To test if the Landau theory is valid for chemical reactions we shall use the Ginsburg criterion (see Kadanoff *et al* 1967). For the Landau theory to be valid fluctuations in the order parameter over distances comparable with the coherence length must be relatively small. In particular they must be small in comparison with the order parameter itself. In chemical reactions, the chemical concentration in the Poisson

representation plays the role of the order parameter and the criterion may be written as

$$\langle \alpha(\mathbf{r}), \alpha(\mathbf{r}') \rangle |_{|\mathbf{r}-\mathbf{r}'|=l_c} \ll \langle \alpha(\mathbf{r}) \rangle^2. \quad (5.1)$$

For the chemical reaction considered in § 4 this yields

$$\frac{K_1 \langle \alpha \rangle}{l_c} \ll \langle \alpha \rangle^2. \quad (5.2)$$

Re-arranging we require the inequality

$$\left(\frac{K_2 - K_1}{K_1} \right)^{1/2} \gg \frac{l_{NL}}{l_L} \quad (5.3)$$

where

$$l_L = \left(\frac{D}{K_1} \right)^{1/2} \quad l_{NL} = \frac{k_4}{D}.$$

That is, as long as the distance from the critical point $K_1 = K_2$ is much greater than l_{NL}/l_L the Landau theory is valid. On the right-hand side we have the ratio of two lengths, l_L pertains to the linear reaction and gives a measure of the distance over which the molecule diffuses before undergoing a spontaneous decay, l_{NL} pertains to the non-linear reaction. As long as l_{NL} is small the Landau theory should be valid for systems not too close to the critical point.

Higher-order corrections to the Gaussian approximation to the master equation have been calculated by Gardiner and Chaturvedi (1977). They find that the Gaussian approximation is valid under exactly the same condition (5.3). Taken with the result of § 4 this leads us to conclude that our generalised Landau theory and the Gaussian approximation to the master equation are equivalent.

An order of magnitude estimate of l_L and l_{NL} may be given for gaseous reactions:

$$D \propto v_{\text{therm}}[(\text{molecular radius})^2 \times \text{number density}]^{-1} \sim 0.1 \text{ cm}^2 \text{ s}^{-1}$$

$$k_4 \propto qv_{\text{therm}}(\text{molecular radius})^2 \sim q \times 10^{-11} \text{ molecules}^{-1} \text{ s}^{-1} \text{ cm}^3$$

where q is the quantum efficiency of the reaction

$$K_1 \sim 10^{13} \text{ molecules s}^{-1}$$

$$l_{NL} = k_4/D \sim q \times 10^{-10} \text{ cm}$$

$$l_L = (D/K_1)^{1/2} \sim 10^{-7} \text{ cm}.$$

Therefore

$$\frac{l_{NL}}{l_L} \sim q \times 10^{-3}.$$

Because of the extremely small value normally assumed by l_{NL} we conclude that the Landau theory should be valid for chemical reactions. This is in keeping with the results obtained for non-equilibrium phase transitions in other systems, e.g. the laser and hydrodynamic instabilities. In non-equilibrium systems only a finite number of degrees of freedom is crucial and a mean field theory such as the master equation in the Gaussian approximation or the Landau theory has so far proved adequate for singularities (Martin 1976).

6. Generalisation to multicomponent systems

It has been shown (Gardiner and Chaturvedi 1977) that a general chemical system may be described by a multivariate Fokker-Planck equation in the Poisson representation, and the multivariate distribution function be written

$$P(\{x_a\}) = \int d\alpha \prod_a \frac{\exp(-\alpha_a) \alpha_a^{x_a}}{x_a!} f(\{\alpha_a\}). \quad (6.1)$$

Here, the index a has a two-fold significance: more precisely we should write x_{ai} where a refers to the chemical species and i refers to the label of a cell in a spatially extended system; but for simplicity we shall combine both of these into the single index a , except when we wish to talk explicitly about the spatial dependence.

The Fokker-Planck equation can be written (we use a repeated index summation convention)

$$\frac{\partial f(\{\alpha\})}{\partial t} = \frac{\partial}{\partial \alpha_a} \left([J_a(\{\alpha\}) + \frac{1}{2} \frac{\partial}{\partial \alpha_b} B_{ab}(\{\alpha\})] f \right). \quad (6.2)$$

In order to relate this to a generalised Landau theory we linearise equation (6.2) as follows. Defining

$$\delta \alpha_a = \alpha_a - \alpha_a^{ss} \quad (6.3)$$

we assume $J_a(\{\alpha\}) = J_{ab} \delta \alpha_b$ and B_{ab} is independent of α . Under these assumptions by following the methods of Lax (1960, see § 5) a Gaussian solution of equation (6.2) can be derived of the form

$$f(\{\alpha\}) = \exp(-\frac{1}{2} \sigma_{ab}^{-1} \delta \alpha_a \delta \alpha_b) |\det \sigma|^{-1/2} (2\pi)^{-n/2} \quad (6.4)$$

where

$$J_{ab} \sigma_{bc} + \sigma_{ab} J_{cb} = B_{ac} \quad (6.5)$$

and σ_{bc} is the correlation function

$$\sigma_{bc} = \langle \alpha_b, \alpha_c \rangle \quad (6.6)$$

or in a matrix notation

$$\mathbf{J}\sigma + \sigma\mathbf{J}^T = \mathbf{B}. \quad (6.7)$$

For an explicit spatial dependence the equations become

$$(D\nabla^2 + \mathbf{J})\sigma(\mathbf{r}-\mathbf{r}') + \sigma(\mathbf{r}-\mathbf{r}')(D\nabla'^2 + \mathbf{J}^T) = \mathbf{B}\delta(\mathbf{r}-\mathbf{r}'). \quad (6.8)$$

Now in a one-variable situation the matrices become one dimensional, so we may simplify equation (6.8) to the form

$$(D\nabla^2 + \mathbf{j})\sigma(\mathbf{r}-\mathbf{r}') = \frac{1}{2}\mathbf{b}\delta(\mathbf{r}-\mathbf{r}') \quad (6.9)$$

which is of the form of equation (4.2).

In the multidimensional situation however, the appropriate equation (6.8) cannot easily arise as the result of procedures developed in § 3. In fact, all that the Landau procedure amounts to is to say that for a one-variable space-dependent situation, the correlation function is proportional to $(D\nabla^2 + \mathbf{j})^{-1}$ and the only correct multivariate analogue of this is obtained by solving equation (6.8).

The equation (6.8) gives a non-equilibrium distribution which is characterised by the linearised time development operator, $D\nabla^2 + \mathbf{J}$, and by the noise matrix \mathbf{B} , so that if there are n chemical species, there are $\frac{1}{2}n(n+1)$ different noise parameters or generalised temperatures. The equilibrium state is characterised by $\mathbf{B} = 0$ and $\mathbf{f}(\{\alpha\})$ becomes a multivariate delta function. Thus deviation from equilibrium is measured by a generalised temperature matrix $k\mathbf{T} = \mathbf{B}$. One sees that in general the non-equilibrium situation is much more complicated than the equilibrium situation.

7. Conclusions

A generalised Landau theory for chemical instabilities has been formulated. Our theory modifies the generalised free energy chosen by Pimpale and Landsberg to one which just describes the fluctuations in excess of equilibrium. This is most easily accomplished in the Poisson representation. The results for the spatial correlation function predicted by this generalised Landau theory are shown to be in exact agreement with the predictions of the stochastic master equation in the Gaussian approximation. The range of validity of the generalised Landau theory and the Gaussian approximation to the master equation are found to be the same. Both are expected to be valid for non-equilibrium phase transitions in chemical reactions. In equilibrium the fluctuations in chemical reactions are Poissonian. For a one-component chemical system the additional fluctuations may be described by the introduction of one additional parameter: a 'generalised temperature'.

However in general the extension to non-equilibrium systems is not so simple. A system with n components would require $\frac{1}{2}n(n+1)$ additional parameters to describe non-equilibrium fluctuations. Thus while in the special case of a one-component system non-equilibrium transitions may be treated by a simple generalisation of equilibrium techniques, in general non-equilibrium systems are considerably more complicated and though a procedure is clear its application except in special cases would appear to be limited.

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Appendix. The Landau theory for chemical reactions in equilibrium

The Landau theory for chemical equilibrium provides a useful illustration of the effect of using a correct free energy. From equilibrium statistical mechanics, it may be shown that the distribution function is Poissonian. More precisely, if the system is divided into cells, labelled by an index i , and the number of molecules of component A in cell i is $x_a(i)$, the ideal solution limit gives the form

$$P(\{x_a(i)\}) = \prod_{a,i} \frac{e^{-\langle x_a \rangle} \langle x_a \rangle^{x_a(i)}}{x_a(i)!} \quad (\text{A.1})$$

This result has been demonstrated by Gardiner and Chaturvedi (1977), and van Kampen (1976a)†. The quantities $\langle x_a \rangle$ are the mean numbers in the cells in equilibrium, and are the steady-state solutions of the reaction diffusion equations

$$\frac{\partial x_a(\mathbf{r}, t)}{\partial t} = D_a \nabla^2 x_a(\mathbf{r}, t) + \Phi_a(x_1(\mathbf{r}) \dots x_n(\mathbf{r})). \quad (\text{A.2})$$

However the free energy which corresponds to the distribution (2.8) is given by‡

$$P(\{x_a(i)\}) = C \exp\left(-\frac{A(\{x_a(i)\})}{kT}\right) \quad (\text{A.3})$$

and using Stirling's approximation, we find

$$A(\{x_a(i)\}) \approx kT \ln C + kT \sum_{a,i} \left[\langle x_a \rangle - x_a(i) + x_a(i) \ln \left(\frac{x_a(i)}{\langle x_a \rangle} \right) \right]. \quad (\text{A.4})$$

If we take $x_a(i)$ to be a small deviation from equilibrium, and use a continuum notation, so that

$$x_a(\mathbf{r}) = \langle x_a \rangle + \delta x_a(\mathbf{r}) \quad (\text{A.5})$$

we find

$$A(\{x_a(\mathbf{r})\}) = kT \ln C + kT \sum_a \int d\mathbf{r} \frac{(\delta x_a(\mathbf{r}))^2}{2\langle x_a \rangle}. \quad (\text{A.6})$$

Thus, even though the system diffuses, *there is no gradient dependent term in the free energy*. The free energy is strictly local. The free energy (A.4) is of course also the exact form usually assumed in ideal solution theory.

If we apply the usual Landau procedure to the free energy (A.4) or (A.6) we find that minimising it gives the macroscopic equation

$$\delta x_a(\mathbf{r}) = \frac{x_a(\mathbf{r}) - \langle x_a \rangle}{\langle x_a \rangle} = 0 \quad (\text{A.7})$$

which is not the same *equation* as obtained by taking the steady-state form of the reaction diffusion equation. If we now carry out the Landau procedure to calculate the correlation function, using the free energy (A.4) we obtain

$$\langle x_a(\mathbf{r}), x_b(\mathbf{r}') \rangle = \delta_{ab} \langle x_a \rangle \delta(\mathbf{r} - \mathbf{r}') \quad (\text{A.8})$$

as required. From this we draw the following conclusions.

(i) The reaction diffusion equations themselves give no information about the free energy function, other than through their steady-state *solutions* $\langle x_a \rangle$. Thus, an attempt to generalise the Landau procedure on the basis that the reaction diffusion equations are known is unjustified.

(ii) The Landau procedure can give a description of local fluctuations, in the case where there are no long-range correlations. The failure of the usual Landau procedure at short range arises from the approximate form of the free energy, in which a

† The canonical ensemble result is obtained by multiplying by delta functions of the stoichiometric constraints. Since the number of these is of the same order of magnitude as the number of components, in the limit of a macroscopic system these constraints can be ignored, a result demonstrated more rigorously by Gardiner and Chaturvedi (1977). Thus, we need only consider the grand canonical ensemble.

‡ A thorough investigation of the basis for this free energy is carried out in Gardiner (1977).

$(\nabla x(r))^2$ term is added, an exact form of free energy would have higher-order terms, and a local part of the correlation function would be predicted. This term takes care of correlations, but is not the only part of the free energy which enforces homogeneity. If the local part of the free energy has a minimum, this will also enforce homogeneity.

(iii) In cases where the Landau theory is normally used (ferromagnets, ferro-electrics, liquid-gas) the $(\nabla x(r))^2$ term is a surface energy term, which can be seen to arise from the forces involved. For chemical reactions, the free energy (in ideal solution theory) arises entirely from entropy. Diffusion is itself an entropy effect, not an energy effect, and has no $(\nabla x(r))^2$ term in the corresponding free energy.

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