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J. Katriel^a; G. F. Kventse^{ab}; G. R. Luckhurst^b; T. J. Sluckin^{ac}

^a Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel ^b Department of Chemistry, University of Southampton, Southampton, England ^c Faculty of Mathematical Studies, University of Southampton, Southampton, England

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Free energies in the Landau and molecular field approaches

by J. KATRIEL†, G. F. KVENTSEL†‡, G. R. LUCKHURST‡
and T. J. SLUCKIN§†

† Department of Chemistry, Technion—Israel Institute of Technology,
32000 Haifa, Israel

‡ Department of Chemistry, University of Southampton,
Southampton SO9 5NH, England

§ Faculty of Mathematical Studies, University of Southampton,
Southampton SO9 5NH, England

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An expression for the entropy as a power series in the order parameter is derived in the context of molecular field theory. The expression is valid both at and away from equilibrium. It is a unique generalization of molecular field theory to non-equilibrium situations. Discrepancies with certain expressions which have appeared in the literature are resolved. Analysis of the radius of convergence of the power series indicates that in certain cases, including the Maier–Saupe model of liquid crystals, molecular field theory and Landau theory cannot be made to agree over the entire range of possible values of the order parameter.

1. Introduction

Students of liquid crystals, when faced with a problem concerning the onset of nematic behaviour, almost always start by attempting to interpret their results in terms of one of two canonical perspectives. Phenomenologists turn to the Landau–de Gennes theory [1] which is based on a power law expansion of the relevant free energy in terms of a nematic order parameter. By contrast those who prefer microscopic theory will begin by seeking to apply the appropriate molecular field theory, first developed by Maier and Saupe [2]. Both models have their limitations, but they have been sufficiently successful to play a powerful role in our understanding of liquid-crystalline behaviour. For some purposes it is interesting to examine the relationship between these two perspectives, and, in particular, to map the parameters of one on to the other. It is this problem which we address in this paper.

Our interest in this problem originates from attempts to interpret results of experiments conducted in part by one of us [3]. These experiments probe, using N.M.R. spectroscopy, the pretransitional regime just above the isotropic–nematic transition. A particular concern was the interpretation of the field-induced Saupe ordering matrix of a biaxial solute in a nematogenic solvent. It became apparent that, if the commonly accepted interpretations of Landau theory and Maier–Saupe theory were applied, contradictory answers were obtained. Clarification of this point demanded further examination of the models for the simpler and more commonly discussed nematic phase composed of uniaxial molecules.

The most fundamental difference between the framework provided by Landau theory and that of molecular field theory is this. The former starts from a postulated

free energy expression in terms of an order parameter, valid at arbitrary temperature and for arbitrary (though in some sense small) order parameter, whereas the latter only provides information about the equilibrium states of the system. The problem of principle we consider is the derivation of the non-equilibrium Landau expansion, given the equilibrium molecular field equations. While the framework of our discussion applies to the derivation of the Landau free energy for a wide range of molecular field theories, we shall stress the application to the simple nematic phase of uniaxial particles. As far as we are aware ours is the first complete and coherent discussion of this problem, although considerations similar in spirit to ours exist in the literature in several statistical mechanical contexts [4].

One of our aims is, by setting up the basic framework in sufficient detail, to sort out the various ambiguous and sometimes erroneous considerations and results which are scattered in the relevant literature. The general (non-equilibrium) expression we derive for the entropy is totally independent of the form of the system hamiltonian, depending only on the nature of the order parameters involved. It is only after the equilibrium values of the order parameter have been substituted, that the entropy becomes an explicit function of the temperature, involving the hamiltonian parameters. Furthermore, our analysis has led to certain intriguing observations concerning the radius of convergence of the power series expansions of the molecular field entropies. In particular, the Maier–Saupe theory results in an expansion whose radius of convergence is approximately 0.49 whereas the range of variation of the second rank order parameter is $0 \leq \bar{P}_2 \leq 1$. This implies that in a certain sense molecular-field and Landau–de Gennes theories cannot agree for situations involving a large value of the nematic order parameter.

This paper is organized as follows. In §2 we describe how a general molecular field theory for an arbitrary system implies the existence of a unique free energy for that system as a function of the parameter defining the order in the system, and how this is related to the Landau expansion for that system. Some relevant but elementary technicalities concerning the inversion of power series are presented in §3. In §4 we describe the nematic liquid crystal composed of uniaxial particles. In §4.1 we define the model employed, and translate the results of §2 into the language of nematic liquid crystals. In §4.2 we explain how these results can be used to generate the Landau–de Gennes expansion of the free energy as a function of a nematic order parameter. In §5 we make some concluding remarks. Appendix A contains an analogous analysis for ferromagnetic systems. In Appendix B we present the general formalism, applicable to a system specified by a set of order parameters. In Appendix C we make a detailed exhaustive comparison between our results and those of other authors who have considered this problem, and explain why they obtain different solutions.

2. Free energies within molecular field theories

The core of our argument lies in this section, which is very general and applies to *all* simple molecular field theories. We suppose that the system under consideration consists of N particles, each of which may take any position, and that at any position each particle may exist in one of M states; these might, for example, correspond to its orientation. For systems with continuous symmetry, such as classical Heisenberg magnets and liquid crystals, M goes to infinity in a particular way, but this is a detail that need not concern us here. We label these states by $i = 1, 2, \dots, M$, and suppose for simplicity that the system remains translationally invariant in all phases, a

condition which is also not essential to the argument. In the high temperature phase the symmetry of the system remains unbroken, and the probability of occurrence of state i is $1/M$. In the low temperature phase this will not be the case and in general state i will have a normalized probability p_i . This phase is marked by the existence of one or more non-zero *order parameters*. At this stage we consider just one of these which we label \bar{Q} ; this is the mean of some molecular quantity Q_i

$$\bar{Q} = \sum_{i=1}^M Q_i p_i, \quad (2.1)$$

with

$$\frac{1}{M} \sum_{i=1}^M Q_i = 0. \quad (2.2)$$

Equation (2.2) merely states that the order parameter vanishes in the high temperature phase. The entropy S of a phase defined by the set of probabilities $\{p_i\}$, neglecting correlation between the particles, is given by $-k \sum_i p_i \ln p_i$; we are interested in the entropy change, ΔS , between the phase with broken symmetry and the isotropic phase

$$\Delta S = -k \sum_i p_i \ln (M p_i), \quad (2.3)$$

where k is the Boltzmann constant.

There are many hamiltonians consistent with the system thus described. An approximation is adopted which gives the contribution of the broken symmetry to the energy per particle as a functional of the order parameter; we call this $H(\bar{Q})$. In general we do not enquire too closely into the origin of $H(\bar{Q})$, although we note that in principle there may be a consistent scheme of approximation which maps many microscopic hamiltonians onto the same $H(\bar{Q})$. There is a particular case where it has been shown that $H(\bar{Q})$ is exact [5]; this is when the microscopic hamiltonian is

$$\mathcal{H} = -\frac{u}{N} \sum_{\langle m,n \rangle} Q(m) Q(n), \quad (2.4)$$

where the sum is taken over *all* particle pairs $\{mn\}$. The interaction is long-ranged, all particles are equivalent, there are no interparticle correlations, and

$$\mathcal{H} = -\frac{1}{2} \frac{u}{N} \sum_m Q(m) \sum_n Q(n). \quad (2.5)$$

In consequence

$$\begin{aligned} H(\bar{Q}) &= \mathcal{H}/N, \\ &= -\frac{1}{2} u \bar{Q}^2 \end{aligned} \quad (2.6)$$

if the thermodynamic limit is taken on going from equation (2.5) to equation (2.6). Having introduced the order parameter dependent hamiltonian $H(\bar{Q})$ and the entropy difference we write the free energy difference

$$\Delta A = H(\bar{Q}) + kT \sum_i p_i \ln (M p_i), \quad (2.7)$$

subject to the constraints

$$\sum_i p_i = 1$$

and

$$\bar{Q} = \sum_i p_i Q_i.$$

The normal procedure would now be to minimize the free energy difference directly with respect to the order parameter, \bar{Q} . However, we prefer to perform the minimization in two distinct steps; the first of these is to maximize the entropy difference, $\Delta S(\{p_i\})$, with respect to $\{p_i\}$ for a fixed \bar{Q} . This will yield a function $\Delta S(Q)$ and only at this stage do we minimize the free energy difference

$$\Delta A = H(\bar{Q}) - T\Delta S(\bar{Q})$$

directly with respect to \bar{Q} . The reason for this apparently contorted procedure will become apparent as the derivation evolves.

Maximizing $\Delta S(\{p_i\})$ we obtain

$$p_i = (MZ)^{-1} \exp(\eta Q_i), \quad (2.8)$$

where the single particle partition function is

$$Z = M^{-1} \sum_i \exp(\eta Q_i) \quad (2.9)$$

and η is a lagrangian multiplier determined by

$$(MZ)^{-1} \sum_i Q_i \exp(\eta Q_i) = \bar{Q}. \quad (2.10)$$

We note the last equation may be written in the form

$$\bar{Q} = \partial \ln Z / \partial \eta \equiv W(\eta). \quad (2.11)$$

The entropy difference can now be written in terms of η , using equations (2.3) and (2.8),

$$\begin{aligned} \Delta S &= -k \sum_i p_i \ln(M p_i), \\ &= k(\ln Z - \eta \bar{Q}), \end{aligned} \quad (2.12)$$

which is an explicit function of η through equations (2.9) to (2.11).

At this stage we make some further comments about the method which we have adopted. The lagrangian multiplier η has, as yet, no physical significance although from the previous equations it is seen to play a crucial role in the theory. For example, the probability distribution function p_i *always* has the same form, given by equation (2.8). However we have no numerical information about η because we have yet to make any assumptions concerning the hamiltonian $H(\bar{Q})$ appropriate for the system. None the less if we did know η , then we could evaluate from equations (2.11) and (2.12) the values of the order parameter and the entropy difference. The universal form of the distribution function follows from the principle of maximum entropy and ΔS is the maximum entropy difference the system could possess, consistent with a particular value of \bar{Q} . Indeed ΔS is the entropy difference the system would have at equilibrium if by some procedure we could ensure that \bar{Q} was the corresponding order parameter.

The problem, however, is that ΔS is a function of η and not of \bar{Q} , although we could write ΔS as a function of \bar{Q} if we could invert equation (2.11) to produce a function

$$\eta = f(\bar{Q}). \quad (2.13)$$

This can be achieved as we now demonstrate. $W(\eta)$ can be inverted if $\partial W(\eta)/\partial\eta$ has the same sign everywhere; however

$$\begin{aligned}\partial W(\eta)/\partial\eta &= \partial^2 \ln Z / \partial\eta^2, \\ &= \sum_i Q_i^2 p_i - \left(\sum_i Q_i p_i \right)^2\end{aligned}\quad (2.14)$$

and so

$$\begin{aligned}\partial W(\eta)/\partial\eta &= \sum_i (Q_i^2 - \bar{Q}^2) p_i, \\ &= \sum_i (Q_i - \bar{Q})^2 p_i,\end{aligned}\quad (2.15)$$

which is the variance of the variable Q_i ; this is, of course, positive definite. Hence $\partial W/\partial\eta$ is positive everywhere and the inverse function $f(\bar{Q})$ exists. It turns out however that equation (2.12) is not the most convenient form to describe $\Delta S(\bar{Q})$. From equation (2.12) observe that

$$\partial\Delta S/\partial\bar{Q} = k \left[-\eta + \frac{\partial\eta}{\partial\bar{Q}} \left(\frac{\partial \ln Z}{\partial\eta} - \bar{Q} \right) \right], \quad (2.16)$$

which from equation (2.11) implies that

$$\begin{aligned}\partial\Delta S/\partial\bar{Q} &= -k\eta, \\ &= -kf(\bar{Q})\end{aligned}\quad (2.17)$$

and hence that

$$\Delta S(\bar{Q}) = -k \int_0^{\bar{Q}} f(\bar{Q}') d\bar{Q}'. \quad (2.18)$$

At this point we stress that the functional forms of $W(\eta)$, $f(\bar{Q})$ and $\Delta S(\bar{Q})$ are entirely independent of the form of the hamiltonian, but do depend on the magnitude of M and the behaviour of the quantities Q_i associated with the order parameter, \bar{Q} . This is expected if $\Delta S(\bar{Q})$ is to be interpreted as the entropy of a state characterized by the order parameter \bar{Q} , irrespective of whether this is an equilibrium or a non-equilibrium state.

The free energy is now minimized with respect to \bar{Q} , to give

$$\partial A/\partial\bar{Q} = \partial H/\partial\bar{Q} + kTf(\bar{Q}) = 0. \quad (2.19)$$

This equation can now be inverted to obtain the standard molecular field equation for the order parameter

$$\bar{Q} = W \left[-\frac{1}{kT} \frac{\partial H}{\partial\bar{Q}} \right] \quad (2.20)$$

at which stage we can identify the lagrangian multiplier η as $-(1/kT)(\partial H/\partial\bar{Q})$. Now $-\partial H/\partial\bar{Q}$ is what is generally called the mean or molecular field, and so the quantity $-kT\eta$ is essentially that molecular field, required at a given temperature, to impose a particular value of \bar{Q} on the system. Using equations (2.7) and (2.18) we then obtain

$$\Delta A(\bar{Q}) = H(\bar{Q}) + kT \int_0^{\bar{Q}} f(\bar{Q}') d\bar{Q}'. \quad (2.21)$$

This, however, is the most general form of $\Delta A(\bar{Q})$ that we can obtain, because the formula for $Z(\eta)$ varies depending on the type of order parameter, and so no universal formula for $f(\bar{Q})$ can be derived.

The Landau expansion for $\Delta A(Q)$ is the expansion of equation (2.21), or equivalently equation (2.12), in powers of \bar{Q} . This involves the power series expansion of $f(\bar{Q})$, which can be derived using equations (2.9), (2.11) and (2.13) for an expansion of $Z(\eta)$. The general expansion procedure is presented in the following section. The nematic liquid crystal case is treated in detail in §4, and magnetic systems are discussed in Appendix A. In all cases, however, we expect a series of the form [6]

$$\Delta A(\bar{Q}) = \frac{1}{2}a_2(T)\bar{Q}^2 + \frac{1}{3}a_3(T)\bar{Q}^3 + \frac{1}{4}a_4(T)\bar{Q}^4 + \dots, \quad (2.22)$$

where \bar{Q} is a scalar order parameter, and is perhaps the magnitude of some vectorial or tensorial order parameter. The presence or absence of terms of a given order in \bar{Q} is dictated by the existence or otherwise of invariants of the vectorial or tensorial order parameter of that order. The series begins at a_2 so that $\bar{Q} = 0$ corresponds to a minimum of $\Delta A(\bar{Q})$ at high temperatures, and the order and position of a phase transition to non-zero \bar{Q} is governed by the variation of the set $\{a_i(T)\}$.

The generalization of the considerations of this section to the case where there are several order parameters is relatively straightforward, though we postpone the mathematical details to Appendix B. If there are a set of P order parameters $\{\bar{Q}^\alpha\}$ corresponding to molecular quantities $\{Q_i^\alpha\}$ in state i , then there will be P lagrangian multipliers $\{\eta^\alpha\}$. By analogy with equations (2.9) and (2.11)

$$Z = M^{-1} \sum_i \exp(\eta^\alpha Q_i^\alpha), \quad (2.23)$$

where we adopt a summation convention over repeated Greek indices. There is a set of functions $\{W_\alpha(\{\eta^\beta\})\}$, which satisfy

$$\begin{aligned} \bar{Q}^\alpha &= W_\alpha(\{\eta^\beta\}), \\ &= \partial \ln Z / \partial \eta^\alpha. \end{aligned} \quad (2.24)$$

An inverse set of functions to $W_\alpha(\{\eta^\beta\})$ exists, so that

$$\eta^\alpha = f_\alpha(\{\bar{Q}^\beta\}). \quad (2.25)$$

By analogy with equation (2.12)

$$\Delta S(\{\bar{Q}^\alpha\}) = k(\ln Z - \eta^\alpha \bar{Q}^\alpha), \quad (2.26)$$

$$\Delta A(\{\bar{Q}^\alpha\}) = H(\{\bar{Q}^\alpha\}) - T\Delta S(\{\bar{Q}^\alpha\}) \quad (2.27)$$

and an analogous form to equation (2.18) also exists.

One particular feature of this generalization is of some interest. Consider a low temperature phase in which the set of order parameters $\{\bar{Q}^\alpha\}$ is non-zero. One of these, however, \bar{Q}^1 , say, is generally regarded as being the most important, indeed $H = H(\bar{Q}^1)$, and for many purposes it suffices to carry through the analysis of the earlier part of this section to construct the free energy difference functional

$$\Delta A(\bar{Q}^1) = H(\bar{Q}^1) - T\Delta S(\bar{Q}^1). \quad (2.28)$$

We now ask what the relationship is between the functions $\Delta A[\{\bar{Q}^\alpha\}]$ defined in equation (2.27) and $\Delta A(\bar{Q}^1)$ defined in equation (2.28). It can be shown rather easily, and is intuitively clear that

$$\Delta A(\bar{Q}^1) = \text{Min}_{\{\bar{Q}^\alpha, \alpha \neq 1\}} \Delta A(\{\bar{Q}^\alpha\}). \quad (2.29)$$

In this situation

$$\partial \Delta A / \partial \bar{Q}^\alpha = 0, \quad \alpha \neq 1,$$

which corresponds to all lagrangian multipliers $\eta^\alpha = 0$ for $\alpha \neq 1$, and thus

$$p_i = Z^{-1} \exp(\eta^1 \bar{Q}^1), \quad (2.30)$$

as in equation (2.8). In general when this occurs $\bar{Q}^\alpha \neq 0$ for $\alpha \neq 1$; rather the values of $\{\bar{Q}^\alpha\}$ will be prescribed by the value of η^1 and thus by \bar{Q}^1 . One experimental test of the assumption that $H = H(\bar{Q}^1)$, is whether or not $\{\bar{Q}^\alpha\}$ show the expected functional dependence on \bar{Q}^1 .

We return to a discussion of the many-order parameter case in Appendix C in the particular context of nematic liquid crystals.

3. Power series expansion of the molecular field entropy

For a system specified by means of a single order parameter, \bar{Q} , molecular field theory results in the self-consistency equation $\bar{Q} = W(\eta)$, (cf. equation (2.11)). The resulting expression for the entropy difference is equation (2.16). In order to obtain the power series expansion for the entropy difference in terms of the order parameter \bar{Q} we write

$$\bar{Q} = W(\eta) = \sum_{i=1}^{\infty} \alpha_i \eta^i \quad (3.1)$$

and invert this series into

$$\eta = f(\bar{Q}) = \sum_{j=1}^{\infty} \beta_j \bar{Q}^j. \quad (3.2)$$

Equation (3.2) can now be substituted in equation (2.16) to obtain a power series expansion for the entropy difference between the ordered and isotropic phase.

The inversion of equation (3.1) into equation (3.2) is carried out by substituting the former in the latter and obtaining

$$\begin{aligned} \eta &= \sum_{j=1}^{\infty} \beta_j \left(\sum_{i=1}^{\infty} \alpha_i \eta^i \right)^j, \\ &= \sum_{p=1}^{\infty} \eta^p \sum_{j=1}^p \beta_j \sum_{\{j_i\}} \binom{j}{j_1 \ j_2 \ \dots \ j_p} \prod_i \alpha_i^{j_i}, \\ &\quad \left(\sum_i j_i = j; \quad \sum_i i j_i = p \right), \end{aligned} \quad (3.3)$$

or

$$\begin{aligned} \beta_p &= \left\{ \delta_{p,1} - \sum_{j=1}^{p-1} \beta_j \sum_{\{j_i\}} \binom{j}{j_1 \ j_2 \ \dots \ j_p} \prod_{i=1}^p \alpha_i^{j_i} \right\} \alpha_1^{-p}, \\ &\quad \left(\sum_i j_i = j; \quad \sum_i i j_i = p \right), \quad p = 1, 2, 3, \dots, \end{aligned} \quad (3.4)$$

where

$$\binom{j}{j_1 \ j_2 \ \dots \ j_p} = j! / \prod_{i=1}^p (j_i!)$$

is the multinomial coefficient. Thus

$$\begin{aligned}\beta_1 &= \alpha_1^{-1}, \\ \beta_2 &= -\alpha_2\alpha_1^{-3}, \\ \beta_3 &= -\alpha_3\alpha_1^{-4} + 2\alpha_2^2\alpha_1^{-5},\end{aligned}$$

etc. Explicit expressions for β_i ($i = 1, 2, \dots, 7$) are given in Abramowitz and Stegun [7].

For vectorial order parameters, such as the magnetization, the power series for \bar{Q} involves odd order terms only. The same must be true for the power series for the associated η . Thus, given

$$\bar{Q} = \sum_{i=1}^{\infty} \alpha_{2i-1} \eta^{2i-1}, \quad (3.5)$$

we obtain

$$\eta = \sum_{j=1}^{\infty} \beta_{2j-1} \bar{Q}^{2j-1}, \quad (3.6)$$

with

$$\begin{aligned}\beta_{2p-1} &= \left\{ \delta_{p,1} - \sum_{j=1}^{p-1} \beta_{2j-1} \sum_{\{j_i\}} \binom{2j-1}{j_1 \ j_2 \ \dots \ j_p} \prod_{i=1}^p \alpha_{2i-1}^{j_i} \right\} \alpha_1^{-(2p-1)}, \\ &\left(\sum_{i=1}^p j_i = 2j-1; \sum_{i=1}^p (2i-1)j_i = 2p-1 \right).\end{aligned} \quad (3.7)$$

4. Nematic liquid crystals

4.1. The molecular field equations

In this section we concentrate on the free energy difference functional in nematic liquid crystals. We do so by interpreting the results of §2 in a liquid crystal context. We first specify the model. The molecules are uniaxial. The axis of each molecule may point in a direction $\hat{\mathbf{l}}(\omega)$ where the solid angle ω is defined by two Euler angles θ, ϕ which take their conventional meaning, so that the unit vector has components

$$\hat{\mathbf{l}}(\omega) = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta). \quad (4.1)$$

The state of the material is defined by the singlet, orientational distribution function $f(\omega)$, which is the analogue of the probabilities $\{p_i\}$ in §2. In the high temperature isotropic phase all molecular orientations are equally likely and $f(\omega) = 1/4\pi$. In the low temperature nematic phase some orientations are preferred, and the entropy change per particle associated with this is

$$\Delta S = -k \int f(\omega) \ln [4\pi f(\omega)] d\omega, \quad (4.2)$$

which is the continuum analogue of equation (2.3). We observe that the sum has become an integral, and the factor M , the number of possible states, is replaced by the normalizing factor 4π .

We shall suppose the low temperature phase to be distinguished by an axis of symmetry, the director $\hat{\mathbf{n}}$, which conventionally lies along the z axis, and an infinite

set of order parameters

$$\bar{P}_{2n} = \int P_{2n}(\cos \theta) f(\omega) d\omega, \quad n = 1, 2, \dots, \quad (4.3)$$

where the $P_l(\cos \theta)$ are the Legendre polynomials of order l . Of these, \bar{P}_2 is by far the most important both from a theoretical and experimental point of view, and is often referred to as *the* nematic order parameter. In so far as is possible we shall also follow this convention, and identify \bar{P}_2 with the quantity \bar{Q} in equation (2.1). Finally, we require the anisotropic contribution to the energy per particle $H = H(\bar{P}_2)$ which in the classical Maier–Saupe theory is taken to be

$$H = -\frac{1}{2}u\bar{P}_2^2. \quad (4.4)$$

Thus

$$\Delta A(\bar{P}_2) = -\frac{1}{2}u\bar{P}_2^2 + kT \int f(\omega) \ln [4\pi f(\omega)] d\omega. \quad (4.5)$$

In the spirit of §2 we merely postulate the form of $H(\bar{P}_2)$ without inquiring into its origin.

The theory encompassed in the functional given by equation (4.5) can now be regarded as an example of the archetypal molecular field theory whose properties we have enunciated in §2. Thus if \bar{P}_2 is identified with \bar{Q} , then $P_2(\cos \theta)$ plays the role of Q_i , and carrying over the results of equations (2.9) to (2.19) we obtain, for the molecular field equations,

$$f(\omega) = (4\pi Z)^{-1} \exp[\eta_2 P_2(\cos \theta)], \quad (4.6 a)$$

$$Z(\eta_2) = (4\pi)^{-1} \int \exp[\eta_2 P_2(\cos \theta)] d\omega, \quad (4.6 b)$$

$$\bar{P}_2 = W_{\text{MS}}(\eta_2) = \partial \ln Z / \partial \eta_2, \quad (4.6 c)$$

where the Maier–Saupe function [2, 8] $W_{\text{MS}}(\eta_2)$ is given by

$$W_{\text{MS}}(\eta_2) = -\frac{1}{2\eta_2} - \frac{1}{2} + \frac{3}{4yD(y)} \Big|_{y=\sqrt{(3\eta_2/2)}} \quad (4.7)$$

and

$$D(y) = \exp(-y^2) \int_0^y \exp(z^2) dz = \frac{i\sqrt{\pi}}{2} \exp(y^2) \operatorname{erf}(iy)$$

is the Dawson integral [7]. As we have described in §2 an inverse function $f_{\text{MS}}(P_2)$ to the function $W_{\text{MS}}(\eta_2)$ exists, and

$$\Delta S = -k \int_0^{\bar{P}_2} f_{\text{MS}}(\bar{Q}) d\bar{Q}. \quad (4.8)$$

The free energy difference is, from equation (2.21),

$$\Delta A(\bar{P}_2) = H(\bar{P}_2) + kT \int_0^{\bar{P}_2} f_{\text{MS}}(\bar{Q}) d\bar{Q}, \quad (4.9)$$

or from equation (2.12)

$$\Delta A(\bar{P}_2) = H(\bar{P}_2) + kT(\eta_2 \bar{P}_2 - \ln Z), \quad (4.10)$$

where we recall, from equation (2.20), that in equilibrium, but only in equilibrium,

$$\eta_2 = -\frac{1}{kT} \frac{\partial H}{\partial \bar{P}_2}.$$

4.2. The Landau–de Gennes expansion

As has been discussed extensively elsewhere [1, 9, 10] the simplest non-trivial order parameter characterizing the nematic phase composed of uniaxial particles, under discussion here, is

$$\bar{Q}_{ij} = \frac{1}{2} \langle 3\hat{l}_i \hat{l}_j - \delta_{ij} \rangle, \quad (4.11)$$

where $\hat{\mathbf{l}}$ denotes the molecular orientation of a molecule and \hat{l}_i is its component in direction i for an arbitrary laboratory frame; the angular brackets indicate an average over all molecules. In the nematic phase this may be written in a suitable principal axis system as

$$\bar{Q}_{ij} = \frac{1}{2} \bar{Q} (3\hat{n}_i \hat{n}_j - \delta_{ij}), \quad (4.12)$$

where $\hat{\mathbf{n}}$ is identified as the nematic director and

$$\bar{Q} = \bar{P}_2. \quad (4.13)$$

Now the Landau–de Gennes expansion of the free energy difference for a uniform fluid is constructed from polynomial invariants of \bar{Q}_{ij} as

$$\Delta A(\bar{Q}_{ij}) = f_2 \bar{Q}_{ij} \bar{Q}_{ij} + f_3 \bar{Q}_{ij} \bar{Q}_{jk} \bar{Q}_{ki} + f_4 (\bar{Q}_{ij} \bar{Q}_{ij})^2 + \dots, \quad (4.14)$$

where the f_i are functions of temperature. When equation (4.12) is substituted into equation (4.14), we obtain, as usual, equation (2.22)

$$\Delta A(\bar{P}_2) = \frac{1}{2} a_2(T) \bar{P}_2^2 + \frac{1}{3} a_3(T) \bar{P}_2^3 + \frac{1}{4} a_4(T) \bar{P}_2^4 + \dots \quad (4.15)$$

We now proceed to analyse equations (4.6) to (4.8) in order to compare the formula for $\Delta A(\bar{P}_2)$ given in equation (4.9) with the Landau–de Gennes expansion given by equation (4.15).

The Maier–Saupe function can be written in the form

$$W_{\text{MS}}(\eta_2) = -\frac{1}{2\eta_2} - \frac{1}{2} + \frac{1}{2\eta_2 \sum_{n=0}^{\infty} [(-3\eta_2)^n / (2n+1)!!]}. \quad (4.16)$$

To write this as a power series in η_2 we set

$$\left(\sum_{n=0}^{\infty} a_n \eta_2^n \right)^{-1} = \sum_{m=0}^{\infty} b_m \eta_2^m, \quad (4.17)$$

which results in

$$\sum_{m=0}^p a_{p-m} b_m = \delta_{p,0},$$

that is

$$b_p = \left(\delta_{p,0} - \sum_{m=0}^{p-1} a_{p-m} b_m \right) / a_0. \quad (4.18)$$

Since

$$a_n = (-3)^n / (2n + 1)!!,$$

we obtain

$$b_0 = 1; \quad b_1 = -1; \quad b_2 = \frac{2}{5}; \quad b_3 = -\frac{2}{35}; \quad \dots \quad (4.19)$$

Substituting in equation (4.16) we obtain

$$\begin{aligned} W_{\text{MS}}(\eta_2) = & \frac{1}{5} \eta_2 + \frac{1}{5 \cdot 7} \eta_2^2 - \frac{1}{5^2 \cdot 7} \eta_2^3 - \frac{1}{5 \cdot 7 \cdot 11} \eta_2^4 + \frac{23}{5^3 \cdot 7^2 \cdot 11 \cdot 13} \eta_2^5 \\ & + \frac{23}{5^3 \cdot 7 \cdot 11 \cdot 13} \eta_2^6 + \frac{157}{5^4 \cdot 7^2 \cdot 13 \cdot 17} \eta_2^7 - \frac{37 \cdot 43 \cdot 61}{5^4 \cdot 7^3 \cdot 11 \cdot 13 \cdot 17 \cdot 19} \eta_2^8 \\ & - \frac{1614583}{5^5 \cdot 7^3 \cdot 11^2 \cdot 13 \cdot 17 \cdot 19} \eta_2^9. \end{aligned} \quad (4.20)$$

Using equations (4.18) and (4.19) the coefficients of the power series for $W_{\text{MS}}(\eta_2)$ were evaluated to order 67. Applying the root test [16] for the radius of convergence of the power series we note that the series $|b_n|^{-1/n}$ exhibits an oscillatory convergence towards $R \simeq 3.75$. The value of the order parameter at the radius of convergence is $\bar{P}_2 \simeq W(3.75) \simeq 0.69$. This observation is of minor significance because there seems to be no context in which the use of the power series for the Maier–Saupe function has any advantage over the closed form expression. Note, however, that the situation is entirely different with respect to the power series expansion of the inverse Maier–Saupe function, which from equations (2.18) and (4.8), determines the power series for the entropy change associated with the nematic ordering, which enters into the Landau power series for the free energy difference. Recalling that the radius of convergence of a power series is unaffected by term-by-term integration we proceed to study the inverse Maier–Saupe function.

Inverting the power series for the Maier–Saupe function, equation (4.20), by using equation (3.4), we obtain

$$\begin{aligned} \eta_2 = f(\bar{P}_2) = & 5\bar{P}_2 - \frac{25}{7} \bar{P}_2^2 + \frac{17 \cdot 25}{49} \bar{P}_2^3 - \frac{83 \cdot 5^4}{7^3 \cdot 11} \bar{P}_2^4 + \frac{5^3 \cdot 277 \cdot 41}{7^3 \cdot 11 \cdot 13} \bar{P}_2^5 \\ & - \frac{5^5 \cdot 19 \cdot 29}{7^4 \cdot 13} \bar{P}_2^6 + C_7 \bar{P}_2^7 + C_8 \bar{P}_2^8 + C_9 \bar{P}_2^9 + \dots, \end{aligned} \quad (4.21)$$

where

$$C_7 = 113.27866, \quad C_8 = -227.42967, \quad C_9 = 465.98831.$$

The last three coefficients have been obtained numerically. The radius of convergence of this expansion is estimated in figure 1 and is very close to $R \simeq 0.49 \pm 0.01$. This means, of course, that a Landau type expansion can usually be used to study the system in the vicinity of the first order phase transition, at which $\bar{P}_2 \sim 0.4$, but cannot be used over the whole nematic range. In particular it is unlikely that a unified Landau treatment of transitions from the nematic to more ordered phases, such as smectic and biaxial nematic, is valid.

It follows, using equations (2.18) and (4.8), that the entropy reduction in the nematic phase relative to the isotropic phase is given by

$$\Delta S = -\frac{5}{2} \bar{P}_2^2 + \frac{25}{21} \bar{P}_2^3 - \frac{17 \cdot 25}{196} \bar{P}_2^4 + \dots \quad (4.22)$$

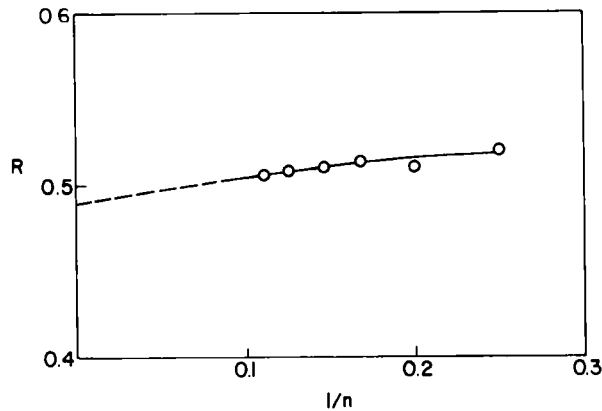


Figure 1. In the root test the radius of convergence R of a series $f(z) = \sum_n a_n z^n$ is given by $R = \lim_{n \rightarrow \infty} x_n$, where $x_n = a_n^{-1/n}$. In this figure we plot x_n against $1/n$ for the inverse Maier–Saupe function. The dotted line indicates our extrapolation of x as $n \rightarrow \infty$ and thus our estimate of R .

Hence, using equation (4.20), we obtain an equation of the form of equation (4.13), but with explicit parameters

$$\Delta A(\bar{P}_2) = \frac{5}{2} k(T - T^*) \bar{P}_2^2 - \frac{25}{21} kT \bar{P}_2^3 + \frac{425}{196} kT \bar{P}_2^4 + \dots, \quad (4.23)$$

where

$$kT^* = u/5.$$

This expression is not in accord with results obtained by other authors [9, 13, 14] and so in Appendix C we proceed to analyse the origin of these differences.

5. Conclusions

We have established that it is feasible to construct, within the framework of molecular field theory, an expression for the entropy difference which depends on the order parameter only and consequently is valid both at and away from equilibrium. The procedure employed depends on the monotonicity of the molecular field function, $W_0(x)$, which follows from its defining equation. The power series expansion obtained for the entropy (and thus the free energy) difference established the equivalence of this framework to Landau theory. It is interesting to observe that this equivalence is of limited validity because the radius of convergence of the power series expansion of the entropy difference in terms of the order parameter is sometimes smaller than the range of physically relevant values of the order parameter in question. The derivation of a generalized Landau free energy corresponding to a lattice gas model of a system exhibiting an isotropic, a nematic, a smectic A and a smectic C phase was very recently presented by Drossinos and Ronis [17]. The system and approach they present are too different from ours to enable a detailed comparison. However, the observation they make concerning the inadequacy of a truncation into 4 to 8 terms, and, in particular, the fact that increasing the order of truncation (within the above range) does not necessarily improve its agreement with the molecular field free energy, is consistent with our results concerning the radius of convergence of the Landau series corresponding to the Maier–Saupe model. On the other hand, the derivation of the entropy difference expansion from the molecular field equations reduces the problem of

specifying the free energy coefficients within the Landau model, to that of specifying the internal energy. The latter is typically represented by means of one or two independent coefficients only.

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Appendix A

Magnetic systems

For a magnetic system consisting of elementary constituents with spin σ the molecular field equation involves Brillouin's function

$$\begin{aligned} s &= \sigma B_{\sigma}(\sigma x) \equiv (\sigma + \frac{1}{2}) \coth[(\sigma + \frac{1}{2})x] - \frac{1}{2} \coth(\frac{1}{2}x) \\ &= \sum_{n=1}^{\infty} \frac{B_{2n}}{(2n)!} [(2\sigma + 1)^{2n} - 1] x^{2n-1}, \end{aligned} \quad (\text{A } 1)$$

where B_{2n} are the Bernoulli numbers [8]. Defining $\Sigma = (2\sigma + 1)^2$ we obtain the inverse expansion

$$x = \sum_{n=1}^{\infty} b_{2n-1} s^{2n-1}, \quad (\text{A } 2)$$

with

$$\begin{aligned} b_1 &= \frac{12}{\Sigma - 1}, \\ b_3 &= \frac{12^2 \Sigma + 1}{5 (\Sigma - 1)^3}, \\ b_5 &= \frac{12^3}{5^2 \cdot 7} \frac{11(\Sigma^2 + 1) + 32\Sigma}{(\Sigma - 1)^5}, \\ b_7 &= \frac{12^4}{5^3 \cdot 7} \frac{19(\Sigma^3 + 1) + 107(\Sigma^2 + \Sigma)}{(\Sigma - 1)^7}, \\ b_9 &= \frac{12^5 \cdot 3}{5^3 \cdot 7^2 \cdot 11} \frac{173(\Sigma^4 + 1) + 8 \cdot 199(\Sigma^3 + \Sigma) + 16 \cdot 193\Sigma^2}{(\Sigma - 1)^9}. \end{aligned} \quad (\text{A } 3)$$

For $\sigma = \frac{1}{2}$ the Brillouin function takes the particularly simple form

$$s = \frac{1}{2} B_{1/2}(\frac{1}{2}x) = \frac{1}{2} \tanh(\frac{1}{2}x), \quad (\text{A } 4)$$

which can be inverted explicitly to give

$$x = \ln \frac{1 + 2s}{1 - 2s} = \sum_{n=1}^{\infty} s^{2n-1} \frac{2^{2n}}{2n - 1}. \quad (\text{A } 5)$$

Using the root test the radius of convergence of this series is

$$R = \lim_{n \rightarrow \infty} \left(\frac{2^{2n}}{2n - 1} \right)^{-1/(2n-1)} = \frac{1}{2}. \quad (\text{A } 6)$$

The same result is obtained using the ratio test

$$R = \lim_{n \rightarrow \infty} \sqrt{\left(\frac{2^{2n}}{2n-1} / \frac{2^{2(n+1)}}{2n+1} \right)} = \frac{1}{2}. \quad (\text{A } 7)$$

For $\sigma > \frac{1}{2}$ we can only estimate the radius of convergence of $f(s)$ on the basis of the coefficients available. The estimates are presented in figure 2; they suggest that $R \geq \sigma$. If this is true for arbitrary σ it implies that the power series expansion, that is a Landau type theory of sufficiently high order, can be used to obtain the magnetization curve over its complete range.

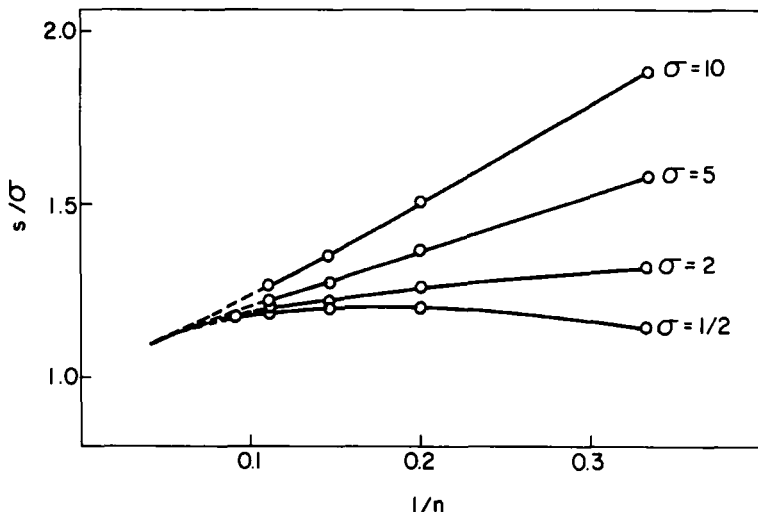


Figure 2. The radius of convergence of the power series expansion of the inverse Brillouin function, using the root test, as explained in the caption to figure 1.

Situations in which higher order terms in the Landau expansion are of crucial relevance have been discussed by Galam and Birman [11]. Furthermore, anisotropic spin systems can undergo phase transitions among ordered phases involving finite values of some components of the magnetization. The result which we have obtained concerning the radius of convergence of the Landau expansion guarantees that an appropriate Landau series can account for these situations, as well as for first order magnetic phase transitions involving arbitrarily high jumps in the magnetization. It is perhaps of some interest to mention that the radius of convergence of the power series for the Brillouin function itself can be determined by noting that $\coth[(\sigma + \frac{1}{2})x]$ has a singularity at $x = i2\pi/(2\sigma + 1)$ which means that the radius of convergence is $R = 2\pi/(2\sigma + 1)$. Note that the singularity of $\coth[(\sigma + \frac{1}{2})x]$ at $x = 0$ is cancelled by that of $\coth(x/2)$, in consequence the Brillouin function is not singular at this point.

The maximum value of s/σ which can be obtained by means of the power series for the Brillouin function is given by

$$s/\sigma = 1 + \left(2 + \frac{1}{\sigma}\right) / \left[\exp(2\pi) - 1\right] - \left\{\sigma[\exp[2\pi/(2\sigma + 1)] - 1]\right\}^{-1}. \quad (\text{A } 8)$$

A plot of s/σ versus σ is presented in figure 3. We note

$$\left. \frac{s}{\sigma} \right|_{\sigma=1/2} = [\exp(\pi) - 1] / [\exp(\pi) + 1] \approx 0.91715 < 1,$$

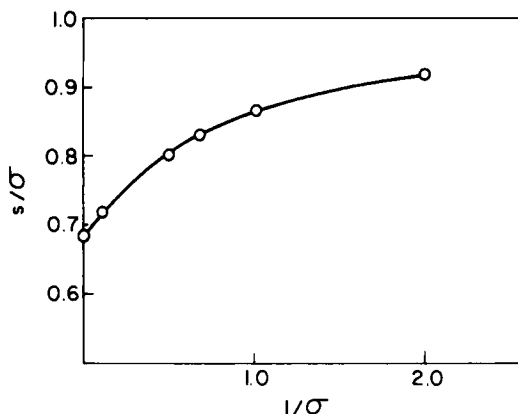


Figure 3. The maximum value of the magnetization which can be evaluated from the power series expansion of Brillouin's function, at the radius of convergence of the latter.

where s/σ is a monotonically decreasing function of σ , with

$$\lim_{\sigma \rightarrow \infty} s/\sigma = 1 + 2/[\exp(2\pi) - 1] - \pi^{-1} \simeq 0.685.$$

Thus, as σ increases, the fraction of the physical range of magnetizations covered by the power series decreases.

The value of s/σ ($\sigma \rightarrow \infty$) obtained is remarkably close to that found for \bar{P}_2 at the radius of convergence of the power series for the Maier-Saupe function. Whether or not this has any deep significance remains to be seen.

Appendix B

Molecular field entropies for systems with several order parameters

In this Appendix we present the mathematical details of the extension of the argument of §2 to systems with several order parameters. We start with a set of P molecular quantities which take values $\{Q_i^\alpha\}$ in state i of the system, and to which are associated a set of order parameters $\{\bar{Q}^\alpha\}$, such that

$$\bar{Q}^\alpha = \sum_i Q_i^\alpha p_i. \quad (\text{B } 1)$$

The entropy difference

$$\Delta S = -k \sum_i p_i \ln(M p_i) \quad (\text{B } 2)$$

is to be maximized subject to the P constraints in equation (B 1) and the normalization condition. By the usual argument

$$p_i = (MZ)^{-1} \exp(\eta^\alpha Q_i^\alpha), \quad (\text{B } 3)$$

where, as before, a summation convention is assumed over repeated Greek indices, $\{\eta^\alpha\}$ is a set of lagrangian multipliers, the single particle partition function is

$$Z = M^{-1} \sum_i \exp(\eta^\alpha Q_i^\alpha) \quad (\text{B } 4)$$

and hence

$$\bar{Q}^\alpha = \partial \ln Z(\{\eta^\alpha\}) / \partial \eta^\alpha \equiv W_\alpha(\{\eta^\alpha\}), \quad (\text{B } 5)$$

by exact analogy with equations (2.9) and (2.11). We observe that an elegant way of writing equation (B 5) is to suppose that the set $\{\eta^\alpha\}$ form a vector $\boldsymbol{\eta} = (\eta^1, \eta^2, \dots, \eta^p)$ and that similarly the set $\{\bar{Q}^\alpha\}$ form a vector $\bar{\mathbf{Q}}$, in which case equation (B 5) takes the form

$$\bar{\mathbf{Q}} = \nabla_{\boldsymbol{\eta}} \ln Z(\boldsymbol{\eta}) \equiv \mathbf{W}(\boldsymbol{\eta}), \quad (\text{B } 6)$$

using conventional vector notation. We now assert that the equations (B 5) and (B 6) can be inverted, under suitable rather sensible conditions, giving

$$\eta^\alpha = f_\alpha(\{\bar{Q}^\alpha\}), \quad (\text{B } 7a)$$

or

$$\boldsymbol{\eta} = \mathbf{f}(\bar{\mathbf{Q}}). \quad (\text{B } 7b)$$

The proof of this assertion is as follows. The inverse function theorem [12] states that equation (B 5) can be inverted within a region of parameter space in which $\det(\partial W_\alpha / \partial \eta^\beta)$ does not change sign. Now

$$\partial W_\alpha / \partial \eta^\beta \equiv M_{\alpha\beta} = \frac{\partial^2 \ln Z}{\partial \eta^\alpha \partial \eta^\beta}, \quad (\text{B } 8)$$

$$= \sum_i p_i (Q_i^\alpha - \bar{Q}^\alpha)(Q_i^\beta - \bar{Q}^\beta) = \langle (Q^\alpha - \bar{Q}^\alpha)(Q^\beta - \bar{Q}^\beta) \rangle. \quad (\text{B } 9)$$

Suppose there is a certain $\boldsymbol{\eta}$ for which $\det(M_{\alpha\beta}) = 0$. Then at this point there exists a set of numbers $\{C_\alpha \neq 0\}$, such that

$$C_\alpha M_{\alpha\beta} = \langle C_\alpha (Q^\alpha - \bar{Q}^\alpha)(Q^\beta - \bar{Q}^\beta) \rangle = 0. \quad (\text{B } 10)$$

Hence, in this case

$$\begin{aligned} C_\alpha C_\beta M_{\alpha\beta} &= 0 = \langle C_\alpha (Q^\alpha - \bar{Q}^\alpha) C_\beta (Q^\beta - \bar{Q}^\beta) \rangle, \\ &= \langle [C_\alpha (Q^\alpha - \bar{Q}^\alpha)]^2 \rangle. \end{aligned} \quad (\text{B } 11)$$

However the quantity $\langle [C_\alpha (Q^\alpha - \bar{Q}^\alpha)]^2 \rangle$ is the mean of a positive quantity, which must itself be positive unless in each state i

$$C_\alpha (Q_i^\alpha - \bar{Q}^\alpha) = 0. \quad (\text{B } 12)$$

However, if equation (B 12) is true, then for each i, j

$$C_\alpha Q_i^\alpha = C_\alpha Q_j^\alpha = C_\alpha \bar{Q}^\alpha, \quad (\text{B } 13)$$

$$= \frac{C_\alpha}{M} \sum_i Q_i^\alpha, \quad (\text{B } 14)$$

$$= 0, \quad (\text{B } 15)$$

by the hypothesis that the average of the order parameter is zero when the system is in the high temperature phase. Thus $\det(M_{\alpha\beta}) = 0$ can only occur at a point $\boldsymbol{\eta}$ when there exists a set $\{C_\alpha\}$ such that in every state of the system i

$$C_\alpha Q_i^\alpha = 0, \quad (\text{B } 16)$$

or equivalently, if the set $\{\bar{Q}^\alpha\}$ are not *independent* molecular variables. If, however, this is the case $\det(M_{\alpha\beta}) = 0$ for *all* values of $\boldsymbol{\eta}$. Thus, as long as we insist that the set $\{\bar{Q}^\alpha\}$ is a set of independent molecular variables, $\det(M_{\alpha\beta})$ is non-zero everywhere,

and hence cannot change sign anywhere, and equations (B 5) and (B 6) can be inverted to give equations (B 7). Now we may substitute the form (B 3) for p_i into the entropy difference equation (B 2) to yield

$$\begin{aligned}\Delta S &= \bar{Q}^\alpha \eta^\alpha - \ln Z, \\ &= \bar{\mathbf{Q}} \cdot \boldsymbol{\eta} - \ln Z,\end{aligned}\tag{B 17}$$

which is directly analogous to equation (2.12).

A comparable equation to equation (2.21) can be derived by observing in equation (B 17) that

$$\begin{aligned}[\nabla_{\bar{\mathbf{Q}}}(\Delta S)]_\alpha &= \frac{\partial \Delta S}{\partial \bar{Q}^\alpha} = \eta^\alpha + \left(\bar{Q}^\beta - \frac{\partial \ln Z}{\partial \eta^\beta} \right) \frac{\partial \eta^\beta}{\partial \bar{Q}^\alpha} \\ &= \eta^\alpha = f_\alpha(\bar{\mathbf{Q}}) = [\mathbf{f}(\bar{\mathbf{Q}})]_\alpha.\end{aligned}\tag{B 18}$$

This equation can be integrated directly to yield ΔS in terms of a line integral in $\bar{\mathbf{Q}}$ space

$$\Delta S(\bar{\mathbf{Q}}) = \int_L \mathbf{dl} \cdot \mathbf{f}(\bar{\mathbf{Q}}'),\tag{B 19}$$

where L is any line in $\bar{\mathbf{Q}}$ space starting at $\bar{\mathbf{Q}}' = 0$ and finishing at $\bar{\mathbf{Q}} = \bar{\mathbf{Q}}$. Equation (B 19) may then be evaluated over whatever is the most convenient path.

Appendix C

Some sources of error in derivations of molecular field free energies

Since the free energy difference expansion derived in this paper does not agree with certain expressions appearing in the literature, we now discuss the sources of these discrepancies.

Method 1

This argument is used either explicitly or implicitly by Stephen and Straley [13], Chandrasekhar [9] and Palfy-Muhoray and Dunmur [14]. We start with the formula in equation (4.10)

$$\Delta A(\bar{P}_2) = H(\bar{P}_2) + kT(\eta_2 \bar{P}_2 - \ln Z).\tag{4.10}$$

In the Maier-Saupe model $H = -\frac{1}{2}u\bar{P}_2^2$ and so at equilibrium we have the relationship

$$\eta_2 = -\frac{1}{kT} \frac{\partial H}{\partial \bar{P}_2} = u\bar{P}_2/kT.\tag{C 1}$$

Hence, substituting for η_2 in equation (4.10), gives

$$\Delta A(\bar{P}_2) = \frac{1}{2}u\bar{P}_2^2 - kT \ln Z,\tag{C 2}$$

where from equations (4.6 a) and (C 1), Z is given explicitly in terms of P_2 as

$$Z = (4\pi)^{-1} \int \exp \left[\frac{1}{kT} u\bar{P}_2 P_2(\cos \theta) \right] d\omega.\tag{C 3}$$

Equations (C 2) and (C 3) are commonly used convenient expressions for the equilibrium free energy difference.

A Landau–de Gennes expansion in \bar{P}_2 is derived by treating $\Delta A(\bar{P}_2)$, as defined in equations (C 2) and (C 3), as a functional expansion in \bar{P}_2 , obtaining

$$\Delta A(\bar{P}_2) = \frac{1}{2} \frac{u}{T} (T - T^*) \bar{P}_2^2 - \frac{1}{105} \frac{u^3}{(kT)^2} \bar{P}_2^3 + \frac{1}{700} \frac{u^4}{(kT)^3} \bar{P}_2^4 + \dots, \quad (\text{C } 4)$$

where $T^* = u/5k$ has the usual significance. It can be shown generally [14] that at $T = T^*$ the coefficients of the quadratic and cubic terms in \bar{P}_2 in equation (C 4) are identical to those of the expansion in equation (4.23), although the \bar{P}_2^4 term is different, and hence that for T close to T^* the use of this free energy difference to compute linear response to an ordering field gives results numerically close to those of the molecular field theory.

Despite this partial success this approach should be treated with caution because it is formally incorrect. This can be seen in a number of different ways. First we note from equation (C 1) that equation (C 4) implies that the entropy associated with the configuration characterised by \bar{P}_2 is given as

$$\Delta S = \frac{u\bar{P}_2^2}{T} - \frac{u^2}{10kT^2} \bar{P}_2^2 + \dots \quad (\text{C } 5)$$

However, the assumptions of molecular field theory imply that this is the single particle configurational entropy which should be *independent* of u . Equation (B 6) must therefore be incorrect. The error has arisen by taking $\Delta A(\bar{P}_2)$ as derived in equation (C 1), which is a *result*, true only at equilibrium, and treating it as a *functional* true for *all* \bar{P}_2 and which can then be differentiated to give the equilibrium value of \bar{P}_2 . It is essential to take the correct functional: equations (4.9) or (4.10).

Method 2

This has been employed by Palffy-Muhoray and Dunmur [14] who specifically noted the difference in predictions between Methods 1 and 2, and by one of us in a previous erroneous analysis [15]. One starts with the correct formula in equation (4.5)

$$\Delta A[f(\omega)] = kT \int f(\omega) \ln [4\pi f(\omega)] d\omega - \frac{1}{2} u \bar{P}_2^2$$

and notes that

$$f(\omega) = (4\pi)^{-1} \sum_l \frac{\bar{P}_{2l}}{4l + 1} P_{2l}(\cos \theta); \quad (\text{C } 6)$$

hence

$$4\pi f(\omega) = 1 + \frac{1}{5} \bar{P}_2 P_2(\cos \theta) + \frac{1}{9} \bar{P}_4 P_4(\cos \theta) + \dots \quad (\text{C } 7)$$

However, as the free energy difference is to be expanded in powers of \bar{P}_2 , all terms in \bar{P}_{2l} for $l \geq 2$ are dropped, and $\ln [4\pi f(\omega)] = \ln [1 + \frac{1}{5} \bar{P}_2 P_2(\cos \theta)]$ is expanded in a power series in \bar{P}_2 . Equation (4.5) can now be written as a power series in \bar{P}_2 , yielding

$$\Delta A(\bar{P}_2) = \frac{5}{2} k(T - T^*) \bar{P}_2^2 - \frac{25}{21} kT \bar{P}_2^3 + \frac{125}{28} kT \bar{P}_2^4 + \dots \quad (\text{C } 8)$$

This also differs from the true result in equation (4.23), although in this case only in the \bar{P}_2^4 term. The problem here is the truncation of equation (C 7) at the \bar{P}_2 stage. This is equivalent to calculating $\Delta A(P_2)$ subject to the constraint that \bar{P}_4, \bar{P}_6 , etc., will all be zero. We have discussed just such a problem in §2, in which \bar{P}_2 corresponds to the

principal order parameter \bar{Q}^1 , and the other $\{\bar{P}_{2l}\}$ corresponds to the other $\{\bar{Q}^a\}$. From the analysis of Appendix B

$$\Delta A(\bar{P}_2) = \text{Min}_{\{\bar{P}_{2l}\}} \Delta A(P_2, \{\bar{P}_{2l}\}), \quad (\text{C } 9)$$

which requires the true distribution function

$$f(\omega) = (4\pi Z)^{-1} \exp[\eta_2 P_2(\cos \theta)] \quad (\text{C } 10)$$

for its evaluation. In contrast the free energy difference $\Delta A(\bar{P}_2, \bar{P}_{2l} = 0; l > 1)$ with its vanishing order parameters is only consistent with the simple distribution function

$$f(\omega) = (4\pi)^{-1} \{1 + \frac{1}{3} \bar{P}_2 P_2(\cos \theta)\}. \quad (\text{C } 11)$$

It is clear that the two distribution functions and hence the free energy differences are not the same.

In fact there is only a minor difference between equations (C 8) and (4.23), which is equivalent to the observation that the higher rank order parameters \bar{P}_4 , etc., are rather small. However, because equation (C 8) is the result of a constrained minimization, we expect that the free energy calculated in equation (C 8) is greater than the true free energy, and this can be seen explicitly by a comparison of the coefficients of the \bar{P}_2^4 terms in the two expansions.

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