

# The free energy of a deforming Lodge rubber-like liquid<sup>1</sup>

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## Abstract

The Lodge network model for concentrated polymer solutions is used to develop a free energy expression in the limit of small deformation rate. Departing from the previous practice of postulating an ad hoc expression analogous to that for a single Gaussian chain with a fixed end-to-end vector, we derive an expression which is consistent with the mechanical picture of the concentrated solution as a network of Hookean springs. By doing this we show that the expression currently in use is actually the internal energy change upon deformation of the network segments. In the case of steady shear and elongational flows the entropic contribution of the springs to the solution free energy is shown to be as large as 50% of the internal energy contribution. For these flows the procedure adopted in this paper, enables us to have a unified treatment of dilute and concentrated polymer solutions and leads to identical free energy expressions in both these limiting cases.

*Keywords:* deformation; free energy; Lodge network model; polymer solutions; rubber-like liquid

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## 1. Introduction

The estimation of free energy in a deforming polymeric fluid assumes importance in a number of situations. Although the free energy expression for a deforming dilute polymer solution has been known for some time [1–4], the question of developing an expression for a deforming concentrated polymer solution is just beginning to be addressed [5–7]. While there appear to be diverse modelling approaches, both continuum and

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molecular, by which a free energy expression may be derived, there seem to be some situations where the use of a transient network model for a concentrated polymer solution is particularly appropriate. In this paper, we use the Lodge network model [4] to develop an expression for the free energy of a deforming concentrated polymer solution. We begin by giving some examples of situations where the use of such a model seems highly relevant.

Experimental observations of the phenomenon of flow-induced crystallization [8–10] suggest that a concentrated amorphous liquid-like phase forms prior to crystal growth. McHugh and coworkers [8–11] propose that in an analogy with strain-induced crystallization of cross-linked polymers, this precursor phase can be viewed as an amorphous network structure with physical entanglements taking the place of chemical cross-links. The process of entanglement formation is seen as the source of the thermodynamic force that governs crystallization, namely, reduced entropy due to chain stretching. Gilbert and McHugh [12,13] have developed a thermodynamic formalism to model this situation by considering the stressed chains to be equivalent to a system of chains with reduced flexibility. However, the notion of temporary physical junctions is the very basis behind the development of transient network models of concentrated polymer solutions. It seems highly desirable, therefore, to use this framework to describe the thermodynamics of flow-induced crystallization.

Another instance where information on the free energy is important is that of stress-induced phase separation. It has been observed that the precipitation temperature of polymer solutions is increased by several degrees on the imposition of simple shear [14,15]. This phenomenon is observed to occur in solutions with a wide range of polymer concentrations (see Ref. 14 for a table of several specific instances). Rangel-Nafaile et al. [14] have modelled this behaviour by assuming that the free energy of the flowing polymer solution is increased due to the stretching of the macromolecules. They calculated the free energy change by using Marrucci's expression [1] for a dilute solution of elastic dumbbells even though the individual phase composition may be in the concentrated solution domain. They justified this by arguing that the expression may be applicable to a broader class of materials, just as the convected Maxwell model is an acceptable constitutive equation in many cases. In this paper, we show that by using the Lodge network model it is possible to develop a common framework wherein the thermodynamics of stress-induced phase separation in both the dilute and concentrated solution limits can be described.

In recent years it has become increasingly clear that diffusion phenomena in polymeric systems are coupled with molecular deformation, both in dilute solutions and in glassy polymers close to their glass transition temperature.

In the case of dilute solutions, a number of anomalous experimental observations have been explained by proposing that the macromolecules migrate across streamlines in non-homogeneous flows [16–21]. It has been argued that such migration is a consequence of an ‘entropic’ driving force, which arises due to the non-uniform departure of the configuration of the macromolecules from their equilibrium configuration [16,22,23]. In glassy polymers, anomalous effects arise because the time-scale of molecular rearrangements due to the diffusion of the solvent is of the same order as the time-scale of the diffusion process itself. This observation has been quantified by Vrentas et al. [24] in terms of a diffusion Deborah number. The physical picture proposed is that the solvent induces a deformation of the entanglement network, which leads to a build up of internal stress. This stress then modifies the driving force for the process [6,7,25–27]. Thus in both dilute and concentrated solutions, the diffusion process needs to be described by a generalized chemical potential which takes into account local changes in the macromolecular configuration.

Durning and Tabor [6] have recently obtained a free energy expression for a deforming concentrated polymer solution by using the transient network model. Basically, they have postulated an expression which is analogous to the free energy expression for a single Gaussian chain, which has a fixed end-to-end vector, and which is suspended in a quiescent solution. Here we adopt a different procedure, which is consistent with the mechanical picture of the concentrated polymer solution as a network of Hookean springs [4]. By doing this, we show that the expression of Durning and Tabor can be viewed as the internal energy change upon deformation of the Hookean springs. Further, we show that in some cases the entropic contribution of the springs to the solution free energy can be as large as 50% of the internal energy contribution. Clearly these results have important implications for the situations discussed above. We also find that for the special cases of steady shear and steady elongational flow, a dilute polymer solution (with the macromolecule modelled as a Hookean dumbbell), and a Lodge rubber-like liquid have identical free energy expressions, albeit in the limit of slow flow. For slow, steady, homogeneous, potential flows the expressions are similar in form.

In the next section, we will briefly review the Lodge network model in order to recall the salient features that are useful for the subsequent development. In Section 3 we derive the free energy expression. Section 4 considers the special cases of steady shear, elongational and irrotational flow. In Appendix A, an integral identity required to derive the free energy expression is obtained. Finally, in Appendix B, the free energy expressions for various flows of a dilute solution of elastic dumbbells are tabulated for ease of comparison.

## 2. The Lodge network model

The transient network model envisions the concentrated polymer solution as being composed of strands of polymer molecules joined together at temporary junctions, which continuously break and reform. These junctions are the only means through which the macromolecules interact with each other, and it is assumed that the deformation of the macroscopic sample is transmitted into an affine deformation of the junction points. It is also usually assumed that the individual chains between two junction points exhibit Gaussian statistics. Thus the end-to-end vector  $\mathbf{Q}$  for a typical segment is a stochastic variable. It is consequently described by the distribution function  $\Psi_{iN}(\mathbf{Q}, t)$ , such that  $\Psi_{iN} d\mathbf{Q}$  is the number of  $iN$ -segments per unit volume at time  $t$  that have end-to-end vector in the range  $d\mathbf{Q}$  about  $\mathbf{Q}$ . The symbols  $i$  and  $N$  are used to characterize a typical segment;  $i$  represents the segment complexity, or degree of permanence of the junction knots, and  $(N - 1)$  represents the number of rods of length  $a$  in the Gaussian chain segment. The distribution function satisfies the normalization condition  $\int \Psi_{iN} d\mathbf{Q} = n_{iN}$ , where  $n_{iN}$  is the number of  $iN$ -segments per unit volume.

By combining the equation of motion for a segment with the conservation condition for segments in configuration space, the following 'convection' equation for the distribution function is obtained [4]:

$$\frac{\partial \Psi_{iN}}{\partial t} = - \frac{\partial}{\partial \mathbf{Q}} \cdot [\boldsymbol{\kappa} \cdot \mathbf{Q}] \Psi_{iN} + L_{iN}(\mathbf{Q}, t) - \frac{\Psi_{iN}}{\lambda_{iN}(\mathbf{Q}, t)}. \quad (1)$$

Here,  $L_{iN}(\mathbf{Q}, t)$  is the number of  $iN$ -segments of length  $Q$  (per unit volume) that are created per unit time at time  $t$ ,  $\lambda_{iN}^{-1}(\mathbf{Q}, t)$  is the probability per unit time that an  $iN$ -segment will be destroyed, and  $\boldsymbol{\kappa}$  is the velocity gradient of the homogeneous flow field.

In the Lodge network model, two additional assumptions are made. First, the segments are assumed to be produced at a constant rate and with a distribution of configurations identical to an unconstrained bead-rod chain at equilibrium. That is,

$$L_{iN}(Q) = \hat{L}_{iN} \Psi_{iN,eq}(Q), \quad (2)$$

where,  $\hat{L}_{iN}$  is the constant creation rate of all  $iN$ -segments independent of segment length, and

$$\Psi_{iN,eq} = \left( \frac{H_N}{2\pi kT} \right)^{3/2} \exp\left( - \frac{H_N}{2kT} Q^2 \right). \quad (3)$$

Here,  $H_N = 3kT/(N - 1)a^2$ ,  $k$  is Boltzmann's constant and  $T$  is the absolute temperature. The second assumption is that the loss rates  $\lambda_{iN}$  are constants.

On making these assumptions, the convection equation (eqn. (1)) may be solved for the segment distribution function, which is found to be given by [4]

$$\Psi_{iN}(\mathbf{Q}, t) = \hat{L}_{iN} \left( \frac{H_N}{2\pi kT} \right)^{3/2} \int_{-\infty}^t e^{-(t-t')/\lambda_{iN}} e^{-(H_N/2kT)\mathbf{B}^{-1}:\mathbf{Q}\mathbf{Q}} dt', \quad (4)$$

where  $\mathbf{B}^{-1}(t', t)$  is the Cauchy strain tensor [28]. It is also found [4] that the number density of  $iN$ -segments satisfies the relation

$$n_{iN} = \hat{L}_{iN} \lambda_{iN}. \quad (5)$$

These results are used in the next section for evaluating the Helmholtz free energy change upon deformation.

### 3. Helmholtz free energy

#### 3.1. The governing equation

In the random walk approximation, the Helmholtz free energy of a polymer chain with a fixed end-to-end vector  $\mathbf{Q}$ , suspended in a quiescent solvent at temperature  $T$  is [4]

$$A(\mathbf{Q}) = \frac{H}{2} \text{tr} \mathbf{Q}\mathbf{Q} + \text{constant}, \quad (6)$$

where  $\text{tr}$  is the trace of the dyadic product  $\mathbf{Q}\mathbf{Q}$ , and  $H = 3kT/(N-1)a^2$ . Durning and Tabor [6] postulate that for an assembly of flexible  $iN$ -segments, the configurational quantity  $\mathbf{Q}\mathbf{Q}$  must be replaced with an average over the segment distribution function. Thus they suggest that the  $iN$ -segment free energy change on flow is

$$A_{iN} = \frac{H_N}{2} \text{tr} \langle \mathbf{Q}\mathbf{Q} \rangle_{iN}. \quad (7)$$

Here, the angular brackets  $\langle \rangle$  denote an average over all configurations, that is, for any arbitrary quantity  $B(\mathbf{Q}, t)$ ,  $\langle B \rangle_{iN} = \int B \Psi_{iN} d\mathbf{Q}$ , where  $\Psi_{iN}(\mathbf{Q}, t)$  is a solution of the convection equation (eqn. (1)). The total free energy is then assumed to be the sum of contributions from all segments existing at the present time. Therefore,  $A = \sum_i \sum_N A_{iN}$ . Here, we adopt a different procedure to obtain the free energy, the reasons for which are elaborated below.

The linear elastic dumbbell model of polymer rheology is motivated by considering the change in free energy that occurs when the end-to-end vector of a Gaussian chain is changed by a small amount. Noting that this change is identical to the change in free energy accompanying a small change in the length of a Hookean spring, it is postulated that a macromolecule may be

represented by a Hookean dumbbell [4]. In a similar manner, a network of Gaussian chains may be replaced by a network of Hookean springs [4]. Once this identification is made, all microscopic and macroscopic properties are obtained by using this mechanical picture. For example, the equilibrium configurational distribution function of an  $iN$ -segment (eqn. (3)) can be obtained from the expression given by statistical mechanics for a linear spring with spring constant  $H_N$  [4]. Likewise, the stress tensor is obtained by summing up the forces in the springs cutting a plane arbitrarily drawn in the material [4]. Here, we argue that for reasons of consistency, the free energy must also be obtained from this mechanical picture. This is the philosophy that has motivated the subsequent development.

Based on the discussion above, it follows that the internal energy contribution to the flowing solution arising from the presence of network segments is given by the sum of the potential energies associated with the springs. Thus,

$$U_{\text{flow}} = \sum_i \sum_N U_{iN} = \sum_i \sum_N \int \frac{1}{2} H_N Q^2 \Psi_{iN} d\mathbf{Q}. \quad (8)$$

Here,  $U_{iN}$  refers to the internal energy contribution (per unit volume) due to all  $iN$ -segments, and  $\frac{1}{2} H_N Q^2$  is the potential energy of an  $iN$ -segment whose end-to-end vector is given by  $\mathbf{Q}$ . The entropy change (per unit volume) is taken to be given by

$$S_{\text{flow}} = \sum_i \sum_N S_{iN} = \sum_i \sum_N -k \int \Psi_{iN} \ln \Psi_{iN} d\mathbf{Q}. \quad (9)$$

It follows that the Helmholtz free energy  $A = U - TS$ , is obtained from

$$A_{\text{flow}} = \sum_i \sum_N A_{iN} = \sum_i \sum_N \int \left( \frac{1}{2} H_N Q^2 + kT \ln \Psi_{iN} \right) \Psi_{iN} d\mathbf{Q}. \quad (10)$$

The complex nature of the segment distribution function (eqn. (4)) makes it difficult to obtain an exact analytical expression for the free energy. We now discuss the development of an approximate expression.

### 3.2. An approximate expression

In this section, we shall use the governing equation (eqn. (10)) to obtain an approximate expression for the free energy change, correct to second order in velocity gradients. On substituting eqn. (4) for the distribution function into eqn. (8) and interchanging the order of the time and  $\mathbf{Q}$ -integrations, leads to

$$U_{iN} = \frac{1}{2} \hat{L}_{iN} kT \int_{-\infty}^t e^{-(t-t')/\lambda_{iN}} \text{tr} \mathbf{B} dt'. \quad (11)$$

Here, we have used the fact that  $\det \mathbf{B}^{-1} = 1$  for an incompressible fluid [28]. The quantity  $\mathbf{B}$  is the Finger strain tensor. It can be shown that the mean square end-to-end distance for an  $iN$ -segment is [4]

$$\langle Q^2 \rangle_{iN} = \text{tr} \langle \mathbf{Q}\mathbf{Q} \rangle_{iN} = \frac{\hat{L}_{iN} kT}{H_N} \int_{-\infty}^t e^{-(t-t')/\lambda_{iN}} \text{tr} \mathbf{B} \, dt'. \quad (12)$$

It follows from eqns. (11) and (12) that

$$U_{iN} = \frac{H_N}{2} \text{tr} \langle \mathbf{Q}\mathbf{Q} \rangle_{iN}. \quad (13)$$

This result can be shown to be valid even without making the additional assumptions of the Lodge network model. Comparison with eqn. (7) shows that the procedure followed by Durning and Tabor [6] leads to the internal energy of all  $iN$ -segments idealized as Hookean springs, rather than to the free energy.

It is convenient to introduce the tensor  $\alpha_{iN}$  defined as follows:

$$\alpha_{iN} = \frac{1}{\lambda_{iN}} \int_{-\infty}^t e^{-(t-t')/\lambda_{iN}} \mathbf{B} \, dt'. \quad (14)$$

Noting that  $\alpha_{iN} = \delta$  at equilibrium, (where  $\delta$  is the unit tensor) the internal energy change upon deformation of an  $iN$ -segment can then be written as

$$\Delta U_{iN} = \frac{1}{2} n_{iN} kT \text{tr}(\alpha_{iN} - \delta), \quad (15)$$

where we have used eqn. (5) for the  $iN$ -segment density.

It is more difficult to obtain the entropy, since the logarithm of the distribution function (eqn. (4)) must be calculated. Indeed the approximate nature of the subsequent development arises because of this difficulty.

We first expand the distribution function as a power series in velocity gradients. This is achieved by repeatedly using the technique of integration by parts to perform the time integration in eqn. (4). Carrying out this procedure upto second-order terms in velocity gradients leads to

$$\Psi_{iN} = n_{iN} \Psi_{iN, \text{eq}} \phi_{\text{fl}} = n_{iN} \Psi_{iN, \text{eq}} \{1 + \phi_1 + \phi_2 + \cdots\}, \quad (16)$$

where,  $\Psi_{iN, \text{eq}}$  is the equilibrium distribution function given by eqn. (3), and

$$\phi_1 = \frac{\lambda_{iN} H_N}{2kT} \gamma^{(1)} : \mathbf{Q}\mathbf{Q}, \quad (17)$$

$$\phi_2 = \frac{\lambda_{iN}^2 H_N}{2kT} \left\{ \frac{H_N}{2kT} [\gamma^{(1)} : \mathbf{Q}\mathbf{Q}]^2 - (\gamma^{(2)} : \mathbf{Q}\mathbf{Q}) \right\}. \quad (18)$$

Here,  $\gamma^{(1)}$  is the rate of strain tensor and  $\gamma^{(2)}$  is the covariant convected derivative of  $\gamma^{(1)}$  [28]. The terms  $\phi_k$  in eqn. (16) are clearly of  $k$ th order in the velocity gradients. It is interesting to note that the first three terms of the

distribution function (eqn. (16)) obtained in this manner satisfy the normalization condition for  $\Psi_{iN}$ . In other words, we find that

$$\int n_{iN} \Psi_{iN,eq} \phi_k d\mathbf{Q} = 0 \quad (k = 1, 2) \quad (19)$$

The integral identity given in Appendix A has been used in order to prove eqn. (19) for  $k = 2$ .

Taking the logarithm of the approximate distribution function (eqn. (16)), and using the Taylor series to expand  $\ln \phi_{\Pi}$  upto second-order terms in velocity gradient leads to

$$\begin{aligned} \ln \Psi_{iN} = & \frac{3}{2} \ln \left( \frac{n_{iN}^{2/3} H_N}{2\pi kT} \right) - \frac{H_N}{2kT} Q^2 + \frac{\lambda_{iN} H_N}{2kT} \gamma^{(1)} : \mathbf{Q}\mathbf{Q} + \frac{\lambda_{iN}^2 H_N^2}{8k^2 T^2} (\gamma^{(1)} : \mathbf{Q}\mathbf{Q})^2 \\ & - \frac{\lambda_{iN}^2 H_N}{2kT} \gamma^{(2)} : \mathbf{Q}\mathbf{Q}. \end{aligned} \quad (20)$$

On substituting eqn. (4) and eqn. (20) into eqn. (9), interchanging the time and  $\mathbf{Q}$ -integrations, and subtracting the equilibrium contribution, we finally obtain the entropy change upon deformation of an  $iN$ -segment, correct to second order in velocity gradients:

$$\begin{aligned} \Delta S_{iN} = & \frac{n_{iN} k}{2} \text{tr}(\alpha_{iN} - \delta) - \frac{\lambda_{iN} n_{iN} k}{2} \gamma^{(1)} : \alpha_{iN} + \frac{\lambda_{iN}^2 n_{iN} k}{2} \gamma^{(2)} : \alpha_{iN} \\ & - \frac{\lambda_{iN}^2 n_{iN} k}{4} \gamma^{(1)} : \gamma^{(1)}. \end{aligned} \quad (21)$$

In order to obtain eqn. (21), we have used the table of integrals in Appendix E of Bird et al. [4], and the integral identity derived in Appendix A. We have also dropped terms of order greater than 2 in the velocity gradient when carrying out the time integration of the penultimate term in eqn. (20).

The Helmholtz free energy change upon deformation of an  $iN$ -segment correct to second order in velocity gradients is consequently given by

$$\Delta A_{iN} = \frac{\lambda_{iN} n_{iN} kT}{2} \gamma^{(1)} : \alpha_{iN} - \frac{\lambda_{iN}^2 n_{iN} kT}{2} \gamma^{(2)} : \alpha_{iN} + \frac{\lambda_{iN}^2 n_{iN} kT}{4} \gamma^{(1)} : \gamma^{(1)}. \quad (22)$$

Equation (22) is the principal result of this work. In contrast to a solution of Hookean dumbbells, for which it is possible to obtain an exact expression, we have succeeded here in getting an analytical expression which is correct only upto terms quadratic in the velocity gradients. Consequently, eqn. (22) is valid only in the small deformation rate limit. It is necessary to keep in mind however, that while the free energy expression for a dilute solution of Hookean dumbbells may be mathematically valid at high deformation rates,



there are physical limitations to its validity. This is evident from the unrealistic behaviour, such as infinite elongational viscosity, that is predicted because the Hookean dumbbell model permits infinite extension.

Let us assume that the  $iN$ -segments' free energy change is defined by the expression

$$\Delta A_{iN} = kT \langle \ln(\Psi_{iN}/\Psi_{iN,eq}) \rangle_{iN}. \quad (23)$$

Equation (23) may be derived by considering an  $iN$ -segment to be an ideal chain, and adopting the expression for entropy change on deformation from the theory of rubber elasticity [29]. On substituting the approximate distribution function (eqn. (16)), it turns out that eqn. (23) leads to an expression which is identical to eqn. (22). Thus, both eqns. (10) and (23) may be used to define the free energy. However, as we have remarked earlier, eqn. (10) is consistent with the mechanical picture of the concentrated solution as a network of Hookean springs.

It must be mentioned here that Durning and Tabor [6] have also derived a free energy expression using the reptation model. They base their analysis on an expression similar in form to eqn. (23), which had been derived earlier by Marrucci and Grizzuti [5] using the Doi-Edwards theory and the independent alignment approximation. However, the relevant distribution function is the orientational distribution function, and the average has a different meaning [6].

At first sight, the form of eqn. (22) appears quite intractable for practical purposes. In section 4 we show, by considering the special cases of steady shear and elongational flow, that eqn. (22) actually leads to an expression that is similar to the well known Marrucci [1] expression. Furthermore, for slow, steady, homogeneous, potential flows, we find that even a dilute solution of elastic dumbbells has a free energy expression similar to eqn. (22). However, before deriving these results, it is worth digressing for a moment to note that striking parallels to the present development of the free energy expression exist in the case of a dilute solution of elastic dumbbells.

### 3.3. A dilute solution of Hookean dumbbells

Marrucci [1] has calculated the free energy for a dilute solution of elastic dumbbells by suggesting that analogous to the expression (eqn. (6)) for the free energy of a Gaussian chain with a fixed end-to-end vector, the free energy of a dilute solution of Hookean dumbbells should be

$$A = \frac{nH}{2} \text{tr} \langle \mathbf{Q}\mathbf{Q} \rangle + \text{constant}, \quad (24)$$

where,  $n$  is the number of dumbbells per unit volume, and angular brackets

represent an average over all internal configurations. It can then be shown that the free energy change on flow is given by

$$\Delta A = -\frac{1}{2} \text{tr} \tau, \quad (25)$$

where  $\tau$  is the polymer stress tensor defined in the compressive sense [28]. Subsequently, Sarti and Marrucci [2] and Booij [3] postulated that the free energy expression for a Rouse chain is given by

$$\Delta A = nkT \langle \ln(\psi/\psi_{\text{eq}}) \rangle, \quad (26)$$

where,  $\psi$  and  $\psi_{\text{eq}}$  are the non-equilibrium and equilibrium configurational distribution functions, respectively. Sarti and Marrucci obtained eqn. (26) by noting that the elastic forces of the spring acting on a bead, and the Brownian forces on a bead sum up to a force that admits a potential of the form  $kT \ln(\psi/\psi_{\text{eq}})$ . On the other hand, Booij derived eqn. (26) by using the familiar expression for entropy change on deformation from the theory of rubber elasticity [29], and by neglecting the internal energy contribution to the free energy on account of the ideality of the chains. More recently, Bird et al. [4] obtained the following expression for a dilute solution of elastic dumbbells:

$$\Delta A = n \int \left\{ \left[ \phi^{(c)}(\psi - \psi_{\text{eq}}) \right] + T \left[ k(\psi \ln \psi - \psi_{\text{eq}} \ln \psi_{\text{eq}}) \right] \right\} d\mathbf{Q}, \quad (27)$$

where  $\phi^{(c)}$  is the spring potential energy. The first term in the integrand is considered to represent the internal energy change, stored as potential energy in the springs, and the second term is considered to be proportional to the entropy change. Bird et al. have justified this formalism in their reply to the review of their book by McLeish [30]. A similar physical interpretation of these terms has been given by King [31]. It is worth noting that the definition of free energy in eqn. (27) is similar to the concept of the dynamical-free energy of a polymer solution introduced by Doi [32].

By using the relation between  $\psi_{\text{eq}}$  and  $\phi^{(c)}$  [4], and the normalization conditions  $\int \psi d\mathbf{Q} = \int \psi_{\text{eq}} d\mathbf{Q} = 1$ , it can be shown that eqn. (27) reduces to eqn. (26). Consequently, they lead to the same expression for the free energy (see eqn. (B3)). In other words, both eqns. (26) and (27) may be used to define the free energy. This result is consistent with replacing the Gaussian chain with a Hookean dumbbell. The purely 'entropic' free energy change of the ideal chain has been partitioned into an internal energy contribution and an entropy contribution of the artificial object that has replaced it. Nevertheless, this internal energy change remains 'entropic' in nature since it vanishes at  $T = 0$  [33].

The first term in the integrand of eqn. (27) namely, the internal energy contribution of the spring to the free energy change upon deformation, can

be shown to be equal to  $-(1/2)\text{tr}\tau$ . Thus the original procedure of Marrucci [1] of postulating the free energy in analogy with that of a single Gaussian chain leads to the neglect of the entropic contribution of the spring to the free energy change upon deformation. As we have seen in Section 3.2 above, this is also the case for a deforming concentrated polymer solution. However, one may note that while the term that represents the entropic contribution of the spring is important at low flow rates, it becomes negligible at high flow rates as has been correctly pointed out earlier by Sarti and Marrucci [2] and Booij [3].

#### 4. Some standard flows

We now use eqns. (15), (21) and (22) to calculate the relevant thermodynamic quantities for some standard flows of a concentrated polymer solution. However, before doing so, it is convenient to express the tensor  $\alpha_{iN}$  as a power series in velocity gradients. In terms of the relative finite strain tensor  $\gamma_{[0]}$ , eqn. (14) may be written as

$$\alpha_{iN} = \delta - \frac{1}{\lambda_{iN}} \int_{-\infty}^t e^{-(t-t')/\lambda_{iN}} \gamma_{[0]} dt'. \quad (28)$$

The relative strain tensor may be expanded in a Taylor series about  $t' = t$ , to give [28]

$$\gamma_{[0]} = \sum_{p=1}^{\infty} (p!)^{-1} \gamma_{(p)} (t' - t)^p, \quad (29)$$

where  $\gamma_{(p)}$  is the  $(p-1)$ th contravariant convected derivative of  $\gamma_{(1)}$ . Substituting eqn. (29) into eqn. (28) and carrying out the time integration leads to

$$\alpha_{iN} = \delta - \sum_{p=1}^{\infty} (-1)^p \lambda_{iN}^p \gamma_{(p)}. \quad (30)$$

Another useful result is the relation between the contribution to the stress tensor from the  $iN$ -segments  $\tau_{iN}$  and the tensor  $\alpha_{iN}$ . Using the single-integral constitutive equation for  $\tau_{iN}$  derived using the Lodge network model [4], we can show that

$$\alpha_{iN} = \delta - \tau_{iN}/n_{iN}kT. \quad (31)$$

Equations (30) and (31) are used repeatedly in the discussion below.

##### 4.1. Steady shear flows

A steady shear flow is given by the velocity field

$$v_x = \dot{\gamma}y; v_y = 0; v_z = 0, \quad (32)$$

where  $\dot{\gamma}$  is the constant shear rate. For these flows,  $\gamma_{(p)} = 0$ , for  $p \geq 3$  [28]. Therefore, from eqn. (30)

$$\alpha_{iN} = \delta + \lambda_{iN} \gamma_{(1)} - \lambda_{iN}^2 \gamma_{(2)}. \quad (33)$$

Using the table of kinematic tensors given in Appendix C of Bird et al. [28], and eqn. (33), it can be shown that

$$\gamma^{(1)} : \alpha_{iN} = \lambda_{iN} \gamma^{(2)} : \alpha_{iN}; \text{tr}(\alpha_{iN} - \delta) = \lambda_{iN}^2 \gamma^{(1)} : \gamma^{(1)}. \quad (34)$$

It follows from eqns. (15), (21), (22), (31) and (34) that the internal energy ( $\Delta U$ ), the entropy ( $\Delta S$ ) and the free energy ( $\Delta A$ ) changes for a concentrated polymer solution undergoing a slow steady shear flow are

$$\Delta U = -\frac{1}{2} \text{tr} \tau; \Delta S = -\frac{1}{4T} \text{tr} \tau; \Delta A = -\frac{1}{4} \text{tr} \tau. \quad (35)$$

It is clear from eqn. (35) that, in these circumstances the entropic contribution of the springs to the free energy is as large as 50% of the contribution due to the internal energy. These relations are identical to those that obtain for the slow shear flow of a dilute solution of elastic dumbbells (see eqn. (B5)).

In terms of the relative strain tensor, the free energy change in a steady shear flow is given by

$$\Delta A = -\frac{1}{4} \int_{-\infty}^t M(t-t') \text{tr} \gamma_{[0]} dt', \quad (36)$$

in which, the memory function is given by

$$M(t-t') = \sum_i \sum_N kT \hat{L}_{iN} e^{-(t-t')/\lambda_{iN}}.$$

The memory integral in eqn. (36) is consistent with the rheological description of viscoelastic materials. When used to obtain a constitutive equation for the diffusive flux, it will lead to a coupling between mechanical and transport processes; the source of much that is anomalous in the behaviour of polymeric systems.

#### 4.2. Steady elongational flows

Steady elongational flows are given by the velocity field

$$v_x = -\frac{\dot{\epsilon}}{2} x; v_y = -\frac{\dot{\epsilon}}{2} y; v_z = \dot{\epsilon} z, \quad (37)$$

where  $\dot{\epsilon}$  is the constant elongation rate. For steady, homogeneous, irrotational flows  $\gamma_{(p)} = (-1)^{p+1} \gamma_{(1)}^p$  [28]. Therefore, from eqn. (30)

$$\alpha_{iN} = \sum_{p=0}^{\infty} (\lambda_{iN} \gamma_{(1)})^p. \quad (38)$$

Since elongational flows are irrotational flows, eqn. (38) may be used here. From the table in Appendix C of Bird et al. [28], and eqn. (38) upto second-order terms in  $\dot{\epsilon}$ , it can be shown that eqn. (34) is satisfied in this instance also. This implies that in terms of the stress tensor, the internal energy, entropy and free energy changes for the slow, steady, elongational flow of a concentrated polymer solution are also given by eqn. (35). Consequently, the neglect of the entropic contribution of the springs to the solution free energy is equally serious in this case. From eqn. (B5) of Appendix B, it is evident that for this flow too, the free energy expressions for dilute and concentrated polymer solutions (within the limitations of the models used here) are identical.

#### 4.3. Steady, homogeneous, irrotational flows

In Appendix B, we have considered the steady, homogeneous potential flow of a dilute solution of elastic dumbbells. Using the well-known distribution function for such flows [4], we have shown that the free energy, correct to second order in velocity gradients, is

$$\Delta A = \frac{1}{2}\lambda_H n k T \gamma^{(1)} : \alpha - \frac{1}{4}\lambda_H^2 n k T \gamma^{(1)} : \gamma^{(1)}, \quad (39)$$

where  $\alpha$  is defined by eqn. (B2). Steady, homogeneous, potential flows are irrotational flows. For irrotational flows, it can be shown from eqn. (38) that, correct to second order in velocity gradients,  $\gamma^{(2)} : \alpha_{iN} = \gamma^{(1)} : \gamma^{(1)}$ . Substituting this result into eqn. (22), we find that for a concentrated polymer solution

$$\Delta A_{iN} = \frac{1}{2}\lambda_{iN} n_{iN} k T \gamma^{(1)} : \alpha_{iN} - \frac{1}{4}\lambda_{iN}^2 n_{iN} k T \gamma^{(1)} : \gamma^{(1)}. \quad (40)$$

Clearly eqn. (39) and (40) are similar in form.

In all the three special flows considered above, we have found that in the limit of small deformation rates, the Lodge network model for concentrated solutions and the Hookean dumbbell model for dilute solutions lead to the same expression for the free energy. It is not clear at present whether the coincidence of the free energy expressions extends in general to arbitrary deformation rates. It is interesting to note however, that as far as their respective constitutive equations are concerned, Lodge [34] has demonstrated analytically that they must have the same form.

## 5. Conclusions

We have derived a free energy expression for a deforming concentrated polymer solution by using the Lodge network model. Examples of many different phenomena have been given where this expression could prove

useful. However, it is appropriate to strike a cautionary note. The expression (eqn. (22)) is strictly valid only for small deformation rates. Indeed the Lodge network model is known to give good predictions of rheological properties only in the limit of small strains. Like the Hookean dumbbell model, it does not predict the shear rate dependence of the viscosity and first normal stress coefficient. As far as the description of anomalous diffusion is concerned, where the deformation rates are small and the capacity of the rubber-like liquid to store elastic energy is the dominant feature, perhaps these shortcomings are not so important. However, it would be incorrect to use the present expression for modelling the phase separation that occurs at high shear rates. The same caveat also applies to expressions based on the Hookean dumbbell model, such as the ones derived by Marrucci [1,2]. Rangel-Nafaile et al. [14] have assumed Marrucci's expression (25) to be generally valid because of the lack of alternative expressions.

By adopting a general definition for the free energy that unifies the approach to dilute and concentrated polymer solutions, we have obtained a number of interesting results. The most important one is that the earlier expression of Durning and Tabor [6], which has been assumed to be applicable in the description of anomalous diffusion [35,36], is actually the internal energy change of the network structure modelled as Hookean springs. It remains to be seen if the expression derived here is able to describe the processes of diffusion and relaxation that simultaneously takes place in these systems satisfactorily.

The other result obtained here, namely, the similarity of the free energy expressions for steady shear and steady elongational flows of dilute and concentrated polymer solutions, suggests that the same framework may safely be adopted for the description of stress-induced phase separation in both these limiting cases. However, Rangel-Nafaile et al. [14] have adopted the original expression due to Marrucci [1] for the description of this phenomenon. We have seen here that in the case of small deformation rates, this may lead to a large error in the predicted free energy change. There appear to be, therefore, a number of unresolved issues that could be usefully tackled with the approach presented here.

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## Appendix A: An integral identity

Here we are concerned with evaluating the integral

$$\int (\gamma^{(1)} : \mathbf{Q}\mathbf{Q})^2 e^{-\mathbf{C} : \mathbf{Q}\mathbf{Q}} d\mathbf{Q},$$

where  $\mathbf{C}$  is an arbitrary second-order tensor. In regular Cartesian tensor

notation and using the Einstein summation convention, this integral may be written as

$$\int (\gamma^{(1)} : \mathbf{Q}\mathbf{Q})^2 e^{-\mathbf{C} : \mathbf{Q}\mathbf{Q}} d\mathbf{Q} = \gamma_{ji}^{(1)} \gamma_{nm}^{(1)} I_{ijnm}, \quad (\text{A1})$$

where

$$I_{ijnm} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} Q_i Q_j Q_m Q_n e^{-C_{pq} Q_p Q_q} dQ_1 dQ_2 dQ_3. \quad (\text{A2})$$

Consider the integral

$$I_{ms}^* = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} Q_m Q_s e^{-C_{pq} Q_p Q_q} dQ_1 dQ_2 dQ_3. \quad (\text{A3})$$

Then

$$\frac{\partial I_{ij}^*}{\partial C_{nm}} = -I_{ijnm}, \quad (\text{A4})$$

since  $\partial C_{ps}/\partial C_{mn} = \delta_{pm}\delta_{sn}$ , where  $\delta_{ij}$  is the Kronecker delta. We already know that (see Appendix E of Bird et al. [4])

$$I_{pq}^* = \frac{\pi^{3/2} C_{pq}^{-1}}{2\sqrt{\det(C_{st})}}, \quad (\text{A5})$$

where  $\det(C_{st})$  is the determinant of  $\mathbf{C}$ . It can be shown that

$$\frac{\partial C_{pq}^{-1}}{\partial C_{nm}} = -C_{pn}^{-1} C_{mq}^{-1}; \quad \frac{\partial}{\partial C_{nm}} [\det(C_{st})] = A_{mn},$$

where  $A_{mi} = \frac{1}{2} e_{mnp} e_{ijk} C_{jn} C_{kp}$  is called the co-factor [37] of the element  $C_{im}$  in the determinant  $\det(C_{st})$  and  $e_{ijk}$  is the permutation symbol. It follows therefore that

$$\frac{\partial I_{pq}^*}{\partial C_{nm}} = -\frac{\pi^{3/2}}{2\sqrt{\det(C_{st})}} \left[ C_{pn}^{-1} C_{mq}^{-1} + \frac{1}{2} C_{pq}^{-1} C_{mn}^{-1} \right], \quad (\text{A6})$$

where, we have used the result [37]  $C_{mn}^{-1} = A_{mn}/\det(C_{st})$ . From eqns. (A1), (A4) and (A6), we have

$$\int (\gamma^{(1)} : \mathbf{Q}\mathbf{Q})^2 e^{-\mathbf{C} : \mathbf{Q}\mathbf{Q}} d\mathbf{Q} = \frac{\pi^{3/2} \gamma_{ji}^{(1)} \gamma_{nm}^{(1)}}{2\sqrt{\det(C_{st})}} \left( C_{in}^{-1} C_{mj}^{-1} + \frac{1}{2} C_{ij}^{-1} C_{mn}^{-1} \right). \quad (\text{A7})$$

## Appendix B: Free energy for standard flows of Hookean dumbbell solutions

For ease of comparison with the results in Section 4, we tabulate here the relevant thermodynamic quantities for some standard flows of Hookean



dumbbell solutions. The configurational distribution function for arbitrary homogeneous flow is found to be [4]

$$\psi(\mathbf{Q}, t) = \left[ \left( \frac{2\pi kT}{H} \right)^3 \det \boldsymbol{\alpha} \right]^{-1/2} \exp \left[ \frac{-H}{2kT} (\boldsymbol{\alpha}^{-1} : \mathbf{Q}\mathbf{Q}) \right], \quad (\text{B1})$$

where

$$\boldsymbol{\alpha}(t) = \frac{1}{\lambda_H} \int_{-\infty}^t e^{-(t-t')/\lambda_H} \mathbf{B} \, dt' \quad (\text{B2})$$

and in which,  $\mathbf{Q}$  is the connector vector,  $\lambda_H$  is the time constant and  $H$  is the spring constant. Substituting eqn. (B1) into the expression for the free energy change of a dilute polymer solution (eqn. (27)), leads to [4]

$$\Delta A = \frac{1}{2} nkT [\text{tr}(\boldsymbol{\alpha} - \boldsymbol{\delta}) - \ln(\det \boldsymbol{\alpha})], \quad (\text{B3})$$

where the first term is proportional to the internal energy change, and the second term is proportional to the entropy change.

For steady shear flows [4]

$$\Delta U = nkT \lambda_H^2 \dot{\gamma}^2; \quad \Delta S = nk \ln \sqrt{1 + \lambda_H^2 \dot{\gamma}^2}. \quad (\text{B4})$$

Expanding the logarithmic term in a Taylor series, retaining only terms upto second order in  $\dot{\gamma}$ , and using the result [4]  $\text{tr} \boldsymbol{\tau} = -2nkT \lambda_H^2 \dot{\gamma}^2$ , we have correct to second order in velocity gradients

$$\Delta U = -\frac{1}{2} \text{tr} \boldsymbol{\tau}; \quad \Delta S = -\frac{1}{4T} \text{tr} \boldsymbol{\tau}; \quad \Delta A = -\frac{1}{4} \text{tr} \boldsymbol{\tau}. \quad (\text{B5})$$

For steady elongational flows, it can be shown that correct to second order in  $\dot{\epsilon}$ ,

$$\Delta U = 3nkT \lambda_H^2 \dot{\epsilon}^2; \quad \Delta S = \frac{3}{2} nk \lambda_H^2 \dot{\epsilon}^2. \quad (\text{B6})$$

Since  $\text{tr} \boldsymbol{\tau} = -6nkT \lambda_H^2 \dot{\epsilon}^2$  (correct to second order in  $\dot{\epsilon}$ ), it follows that eqn. (B5) represents the thermodynamic quantities in this case also.

For the steady-state, homogeneous, potential flow of a dilute solution of dumbbells with a Hookean or a FENE spring force law, the configurational distribution function is given by [4]

$$\psi = \psi_{\text{eq}} \left( \frac{J_{\text{eq}}}{J} e^{(H\lambda_H/2kT)\boldsymbol{\gamma}^{(1)} : \mathbf{Q}\mathbf{Q}} \right), \quad (\text{B7})$$

where  $J_{\text{eq}}$  is the normalization constant for the equilibrium distribution function, and  $J$  is that for the non-equilibrium distribution function. Substituting eqn. (B7) in eqn. (27) leads to

$$\Delta A = \frac{1}{2} n \lambda_H \boldsymbol{\gamma}^{(1)} : H \langle \mathbf{Q}\mathbf{Q} \rangle - nkT \ln(J/J_{\text{eq}}). \quad (\text{B8})$$

The ratio ( $J/J_{\text{eq}}$ ), correct to second order in velocity gradients is [4]

$$\frac{J}{J_{\text{eq}}} = 1 + \frac{1}{15} \left( \frac{H\lambda_H}{2kT} \right)^2 \langle Q^4 \rangle_{\text{eq}} \boldsymbol{\gamma}^{(1)} : \boldsymbol{\gamma}^{(1)}. \quad (\text{B9})$$

For Hookean dumbbells,  $H\langle \boldsymbol{Q}\boldsymbol{Q} \rangle = kT\boldsymbol{\alpha}$  and  $\langle Q^4 \rangle_{\text{eq}} = 15(kT/H)^2$ . Therefore, correct to second order in velocity gradients

$$\Delta A = \frac{1}{2}\lambda_H nkT \boldsymbol{\gamma}^{(1)} : \boldsymbol{\alpha} - \frac{1}{4}\lambda_H^2 nkT \boldsymbol{\gamma}^{(1)} : \boldsymbol{\gamma}^{(1)}. \quad (\text{B10})$$