An Analytic Study of the NMR Properties for Deformed Polymer Networks Blended with Free Chains

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ABSTRACT: We show that when a network is deformed, the line splitting seen from NMR probe molecules located on the network or on free chains dissolved in the network can be accounted for by considering the effect of isotropic excluded volume interactions. For a uniaxial deformation λ the splitting is proportional to $(\lambda^2 - \lambda^{-1})$ and inversely proportional to the molecular weight of the network chains. The dominant contribution depends linearly on the network fraction and is directly related to the ratio of the Edwards screening length to the length of the statistical segments. Smaller effects are present which also depend on the concentration, molecular weight, and chemical nature of the free chains as well as the molecular weight of the network chains. For chains which show a preference to microphase separate these effects can be strongly enhanced. A variety of specific predictions are made as the phase separation point is approached which reflect the statistical mechanics of the process.

1. Introduction

Deuterium nuclear magnetic resonance is sensitive to anisotropic molecular motion and has been used to investigate the reorientation of probe molecules in strained networks.[1−5] The deuterium probe can be located either on the network or on free molecules dissolved into the network. For undeformed networks a single resonance line is observed in the NMR spectrum, which splits into a well-defined doublet when a uniaxial deformation λ is applied.[5] The intriguing observation is that the magnitude of the splitting is the same for both the free chains and the network chains.[2] This suggests that the origin of the doublet does not arise directly from the presence of cross-links. In fact it is already known[5,6] that for a noninteracting (phantom) network there is no splitting in the NMR spectrum on deformation. This seemed to strongly indicate that molecular interactions played an important role in understanding this phenomena. Previously, Sotta and Deloche[5] had postulated a nematic order parameter to account for their experimental finding on PDMS networks and other systems. In a later paper[6] one of us (M.G.B.) showed that it was sufficient to include only isotropic excluded volume interactions in order to account for the observed splitting. For the network these were treated at the mean field level and it was shown that an anisotropic mean field arises when the network is deformed. Subsequent numerical simulations[7,8] on deformed one component network systems have demonstrated the ability of isotropic excluded volume interactions to produce the experimentally observed splitting.

The idea of a mean field goes a long way to explaining why free chains dissolved in a deformed network also show an NMR splitting of a comparable magnitude to the network chains. The mean field is made up from contributions from both network and free chains. Only the deformed network chains contribute to the anisotropic component of the mean field which, however, acts equally on all the chains in the system.

In a previous paper,[9] where a preliminary account of this work was presented, the deformation of the network was modeled by coupling the chain ends to an external field. In this paper we will deal directly with the network vectors, which are treated as quenched variables in our work. Our intention is to show explicitly how they collectively determine the anisotropy in the mean field. The splitting on either kind of chain (network or free) for a uniaxial extension λ is shown to vary linearly with $(\lambda^2 - (1/\lambda))$, and the magnitude is shown to be determined by the mean field. This can be experimentally controlled by blending the network with free chains. For chains, identical to the network chains, the principal effect is simply to dilute the contribution to the mean field from the network chains, with the chain length playing a minor role. We will show that the magnitude of the line splitting from both kinds of chain is the same.

A more interesting contribution to the mean field arises by choosing free chains of a different chemical nature so that an interaction parameter is introduced. The mean field will now consist of concentration fluctuations which can be made to exhibit critical fluctuations as the system is driven to a microphase separation. Since the mean field contributes directly to the line NMR splitting, it will prove possible to monitor details of the phase separation in a unique way. In this case there are different signals from the NMR probe on the network chains compared to one on the free chains.

In the next section a model for the NMR properties of an interacting network/free chain system is presented. At the level of description of a single chain, the interactions with the rest of the system are shown to be described by an effective screened potential. In section 3 a general expression is derived for the magnitude of the splitting without having to assume any form for the screened potential. In section 4 specific results are obtained using the mean field approach or random phase approximation to calculate the screened potential for polymer blends. The dependence of the splitting on the chain lengths, free chain concentration, and the Flory interaction parameter is derived and discussed in section 5 and compared with available experimental data.

2. NMR Network/Free Chain Model

The NMR probe, either an isolated proton pair or deuterium−carbon interaction, is assumed to be rigidly

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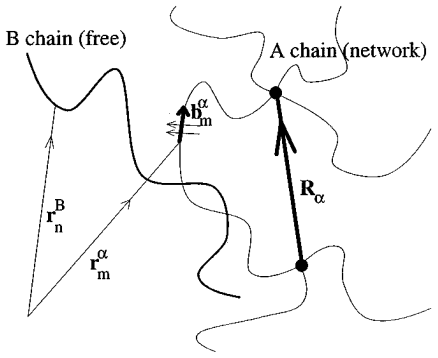

Figure 1. Vector representation of the network blend.

attached to the polymer backbone of either the network chains (labeled A) or the free chains (labeled B). The motion of the probe thus follows that of the chain. The chains, both network (A) and free (B), are represented by a coarse-grained, scale invariant model as a series of bonds $\{\mathbf{b}_i^{A/B}\}$ which obey Gaussian statistics. The NMR probe, which is fixed to an atomic bond, is rescaled to the coarse-grained level described by the $\{\mathbf{b}_i^{A/B}\}$ vectors following the method introduced by Cohen Addad[10,11] and further developed by Brereton.[12,13] The result is that the Zeeman levels of the nuclear spin are dependent on the orientation of the bond vectors through the term

$$\epsilon(\mathbf{b}_j) = \frac{v_0}{b^2}(2b_{j,z}{}^2 - b_{j,x}{}^2 - b_{j,y}{}^2) \qquad (2.1)$$

where v_0 is an interaction constant and b is the average length of the jth bond vector with components $b_{j,x}$, $b_{j,y}$, and $b_{j,z}$. When the dynamics of the bonds $\{\mathbf{b}_i^{A/B}\}$ are considered to be fast compared to the NMR time set by $\hbar/v_0$, the relaxation of the transverse components of the nuclear magnetization, $G(t;\mathbf{b}_j)$, can be written as[13]

$$G(t) = \cos(\langle\epsilon(\mathbf{b}_j)\rangle t) \qquad (2.2)$$

The averaging $\langle ... \rangle$ is over all the available configurations for the bond vectors.

The crucial point for this work is to recognize that there are two principal factors which govern the availablity of the allowed configurations: For the network chains, the network vectors $\{\mathbf{R}_A\}$ impose the constrain

$$\sum_i \mathbf{b}_i^A = \mathbf{R}_A \qquad (2.3)$$

on the reorientation of bond vectors $\{\mathbf{b}_j^A\}$ between cross-link points; see Figure 1. It can readily be shown that for each Cartesian componen

$$\langle b_{j,X}^{A\ 2}\rangle_c = \frac{b^2}{3} + \frac{X_A{}^2}{N^2} \qquad \text{etc.}$$

where (X_A, Y_A, Z_A) are the components of the network vector $\mathbf{R}_A$. The $\{\mathbf{R}_A\}$ are quenched variables and in the deformed state

$$\langle\epsilon(\mathbf{b}_j^A)\rangle_c = \frac{v_0}{N_A}\left(\frac{2Z_A{}^2 - X_A{}^2 - Y_A{}^2}{N_A b^2}\right) \qquad (2.4)$$

and hence $\langle\epsilon(\mathbf{b}_j^A)\rangle_c \neq 0$. The subscript "c" refers to the constraint (2.3). In previous work[6] it was shown that while this gives a splitting for each individual network vector, when all network orientations are averaged only a broadened single line is obtained. For the free chains (B), where there are no network constraints, then it might be anticipated tha

$$\langle b_{j,z}^{B\ 2}\rangle_0 = \langle b_{j,x}^{B\ 2}\rangle_0 = \langle b_{j,y}^{B\ 2}\rangle_0 \qquad \text{and} \qquad \langle\epsilon(\mathbf{b}_j^B)\rangle_0 = 0$$

However this ignores the interactions present in the system between all the chains, both free and the network chains. The effect of interactions in limiting the availability of bond configurations is expressed through the Boltzmann factor.

$$\langle\epsilon(\mathbf{b}_j^B)\rangle = \frac{\left\langle\epsilon(\mathbf{b}_j^B)\exp\left[-\frac{1}{kT}\sum_{\substack{m,n\\ \beta,\beta'=A,B}} V_{\beta\beta'}(r_m^\beta - r_n^{\beta'})\right]\right\rangle_0}{\left\langle\exp\left[-\frac{1}{kT}\sum_{\substack{m,n\\ \beta,\beta'=A,B}} V_{\beta\beta'}(r_m^\beta - r_n^{\beta'})\right]\right\rangle_0} \qquad (2.5)$$

$V_{\beta\beta'}(r_m^\beta - r_n^{\beta'})$ is the excluded volume interaction between a statistical segment m at position r_m^β on the β chain and a statistical segment n at $r_n^{\beta'}$ on the β' chain. The brackets $\langle ... \rangle_0$ represent an average over all possible configurations of all the chains, both network and free. We will assume that the potentials $V_{\beta\beta'} = \{V_{AA}, V_{AB}, V_{BB}\}$ are isotropic interactions and that the anisotropy is introduced by the position of the deformed network chain vectors at $\{\mathbf{r}_n^A\}$ which are included in the sum in (2.5).

The many chain problem posed by (2.5) is reduced to an effective single chain problem by averaging over the configurations of all the chains except for the one carrying the NMR probe (we will label this chain α). This was done for the first time by Edwards[14] for a polymer melt using the random phase approximation. The same approach has also been shown[15,16] to be valid for a network. The result is that if α is the chain carrying the NMR probe, then the many chain expression in (2.5) can be replaced by

$$\left\langle\exp\left[-\frac{1}{kT}\sum_{\substack{m,n\\ \beta,\beta'=A,B}} V_{\beta\beta'}(r_m^\beta - r_n^{\beta'})\right]\right\rangle_{\text{all chains except }\alpha} = \exp\left[-\frac{1}{kT}\sum_{m,n} V_{\alpha\alpha}^*(r_m^\alpha - r_n^\alpha)\right] \qquad (2.6)$$

$V_{\alpha\alpha}^*$ represents the effective self-interaction of a chain in a concentrated blend of chains and is known as a screened potential. When one component of the blend consists of network chains, the screened potential will also depend explicitly on the network vectors $\{\mathbf{R}_A\}$

$$V_{\alpha\alpha}^*(r_m^\alpha - r_n^\alpha) \equiv V_{\alpha\alpha}^*(r_m^\alpha - r_n^\alpha;\{\mathbf{R}_A\})$$

This will be true when α labels a network chain (A) or a free chain (B). Stretching of the network induces anisotropy into this interaction, which we will show leads to anisotropic motion of the NMR bond.

The full problem of incorporating network constraints and interactions can be stated as follows: when the

NMR probe on the α chain is a network chain (A chain), then the interaction energy is given by

$$\langle\epsilon(\mathbf{b}_j^\alpha;\{\mathbf{R}_A\})\rangle_A = \frac{\left\langle \epsilon(\mathbf{b}_j^\alpha)\delta(\sum_i^{N_\alpha}\mathbf{b}_i - \mathbf{R}_\alpha)\exp\left[-\frac{1}{kT}\sum_{m,n}V^*_{AA}(r_m^\alpha - r_n^\alpha;\{\mathbf{R}_A\})\right]\right\rangle_0}{\left\langle \delta(\sum_i^{N_\alpha}\mathbf{b}_i - \mathbf{R}_\alpha)\exp\left[-\frac{1}{kT}\sum_{m,n}V^*_{AA}(r_m^\alpha - r_n^\alpha;\{\mathbf{R}_A\})\right]\right\rangle_0} \quad (2.7)$$

and when the NMR probe is on a free chain (B chain)

$$\langle\epsilon(\mathbf{b}_j^\alpha;\{\mathbf{R}_A\})\rangle_B = \frac{\left\langle \epsilon(\mathbf{b}_j^\alpha)\exp\left[-\frac{1}{kT}\sum_{m,n}V^*_{BB}(r_m^\alpha - r_n^\alpha;\{\mathbf{R}_A\})\right]\right\rangle_0}{\left\langle \exp\left[-\frac{1}{kT}\sum_{m,n}V^*_{BB}(r_m^\alpha - r_n^\alpha;\{\mathbf{R}_A\})\right]\right\rangle_0} \quad (2.8)$$

Finally, the relaxation function given by (2.2) has to be averaged over the distribution of network vectors $\{\mathbf{R}_A\}$ to give

$$G(t) = \overline{\cos(\langle\epsilon(\mathbf{b}_j^\alpha;\{\mathbf{R}_A\})\rangle_{A/B}t)} \quad (2.9)$$

Equations 2.7−2.9 summarize the main problem to be addressed in this paper. The essential physics which models the interaction of the network and free chains is contained in the screened potentials V^*_{AA} and V^*_{BB}. However, before adopting any specific model for the screened potential, we will show in the next section that the formalism contained in eqs 2.7−2.9 leads quite generally to an oscillating contribution to the relaxation function (2.9), which is equivalent to a resolved doublet in the spectrum.

3. General Expression for the NMR Doublet Splitting

The screened potential can be treated in perturbation theory, and expanding (2.7) or (2.8) up to first-order terms in V^* gives

$$\langle\epsilon(\mathbf{b}_j^\alpha;\{\mathbf{R}_A\})\rangle_{A/B} = \langle\epsilon(\mathbf{b}_j^\alpha)\rangle_{c,0} - [\langle\epsilon(\mathbf{b}_j^\alpha)\sum_{m,n}V^*_{\alpha\alpha}(r_m^\alpha - r_n^\alpha;\{\mathbf{R}_A\})\rangle_{c,0} - \langle\epsilon(\mathbf{b}_j^\alpha)\rangle_{c,0}\langle\sum_{m,n}V^*_{\alpha\alpha}(r_m^\alpha - r_n^\alpha;\{\mathbf{R}_A\})\rangle_{c,0}] \quad (3.1)$$

where the subscript 0 is for the NMR probe on the free chain (B) and the subscript c is for the network chain (A).

$$\langle\ldots\rangle_c = \frac{\langle\ldots\delta(\sum_i^{N_\alpha}\mathbf{b}_i - \mathbf{R}_\alpha)\rangle_0}{\langle\delta(\sum_i^{N_\alpha}\mathbf{b}_i - \mathbf{R}_\alpha)\rangle_0} \quad (3.2)$$

For the free chain case (B chains) $\langle\epsilon(\mathbf{b}_j)\rangle_0 = 0$ and the problem reduces to

$$\langle\epsilon(\mathbf{b}_j^\alpha;\{\mathbf{R}_A\})\rangle_B = -\langle\epsilon(\mathbf{b}_j^\alpha)\sum_{m,n}V^*_{BB}(r_m^\alpha - r_n^\alpha;\{\mathbf{R}_A\})\rangle_0 \quad (3.3)$$

These expressions can be further simplified by writing the screened potential $V^*_{\alpha\alpha}(r_m^\alpha - r_n^\alpha;\{\mathbf{R}_A\})$ in terms of its Fourier components

$$V^*_{\alpha\alpha}(r_m^\alpha - r_n^\alpha;\{\mathbf{R}_A\}) = \frac{1}{\Omega}\sum_{\mathbf{q}}V^*_{\alpha\alpha}(\mathbf{q};\{\mathbf{R}_A\})\exp[i\mathbf{q}(r_m^\alpha - r_n^\alpha)] \quad (3.4)$$

where Ω is the volume of the system. The essential statistical problem is contained in the term on the right hand side of (3.3); this can be written as

$$\frac{v_0}{\Omega b^2}\sum_{\mathbf{q}}V^*_{\alpha\alpha}(\mathbf{q};\{\mathbf{R}_A\})\langle(2b_{jz}^2 - b_{jx}^2 - b_{jy}^2)\times \exp[i\mathbf{q}(r_m^\alpha - r_n^\alpha)]\rangle_{0,c} \quad (3.5)$$

For polymer chains with Gaussian configurational statistics the averages in (3.5) are straightforward to calculate. In the context of another quite separate problem a similar calculation occurred and the details are given in the appendix in ref 17. Keeping terms of the order of $N_{A/B}^{-1}$ and $V^*_{\alpha\alpha}$ but neglecting terms $V^*_{\alpha\alpha}$ $N_{A/B}^{-1}$ gives

$$\langle\epsilon(\mathbf{b}_j^\alpha;\{\mathbf{R}_A\})\rangle_{A/B} = \frac{v_0}{N_A}\left(\frac{2Z_A^{\alpha 2} - X_A^{\alpha 2} - Y_A^{\alpha 2}}{N_A b^2}\right)\delta_{\alpha,A} - \frac{4v_0}{b^2}\frac{1}{\Omega}\sum_{\mathbf{q}}V^*_{\alpha\alpha}(\mathbf{q};\{\mathbf{R}_A\})\frac{(2q_z^2 - q_x^2 - q_y^2)}{q^4} \quad (3.6)$$

when the position j of the probe along the chain is not near an end. The first term is present only when the probe is on an isolated network chain. $(X_A^\alpha, Y_A^\alpha, Z_A^\alpha)$ are the end to end coordinates of the network chain. The second term in (3.6) arises through the monomer−monomer interactions and is common to both network and free chains. It is this term which is of principal interest in this paper. When the network constraint is ignored, the screened potential is isotropic

$$V^*_{\alpha\alpha}(\mathbf{q};\{\mathbf{R}_A\}) = V^*_{\alpha\alpha}(q^2)$$

and if the sum over $\mathbf{q}$ is replaced by an integral

$$\frac{1}{\Omega}\sum_{\mathbf{q}} \rightarrow \frac{1}{(2\pi)^3}\int d\mathbf{q}^3$$

then the second term in (3.6) vanishes by symmetry. For a non-zero result it is vital to have terms involving the network vectors $\{\mathbf{R}_A^\beta\}$. These (see later) occur in the combinations $\{\mathbf{q}\mathbf{R}_A^\beta\}$. Accordingly, we expand the potential as a Taylor series in terms of $(\mathbf{q}\mathbf{R}_A^\beta)^2$ centered on $(\mathbf{q}\mathbf{R}_A^\beta) = 0$. Essentially, the higher terms contain

information about the screened potential for smaller length scales, i.e. greater detail.

$$V^*_{\alpha\alpha}(\mathbf{q};\{\mathbf{R}_A\}) = V^*_{\alpha\alpha,0}(\mathbf{q}^2) + \frac{1}{N_{net}}\sum_{\beta}(\mathbf{q}\mathbf{R}_A^{\beta})^2 V^*_{\alpha\alpha,1}(\mathbf{q}^2) + \ldots \quad (3.7)$$

where N_{net} is the number of network vectors and

$$\frac{V^*_{\alpha\alpha,1}(\mathbf{q}^2)}{N_{net}} = \left.\frac{\partial V^*_{\alpha\alpha}(\mathbf{q},\{\mathbf{R}_A\})}{\partial((\mathbf{q}\mathbf{R}_A^{\beta})^2)}\right|_{(\mathbf{q}\text{-}\mathbf{R}_A^{\beta})^2=0} \quad (3.8)$$

The resultant second term in (3.6) is now given by

$$-\frac{4\nu_0}{b^2}\frac{1}{(2\pi)^3}\int \mathrm{d}q^3 V^*_{\alpha\alpha,1}(\mathbf{q}^2)\frac{1}{N_{net}} \times \sum_{\beta=1}^{N_{net}}(\mathbf{q}\mathbf{R}_A^{\beta})^2\frac{(2q_z^2 - q_x^2 - q_y^2)}{q^4} \quad (3.9)$$

The angular **q** integrations can be done without specifying the form of $V^*_{\alpha\alpha,1}(\mathbf{q}^2)$ to give

$$-\frac{4\nu_0}{15\pi^2 b^2}\int_0^\infty q^2\,\mathrm{d}q\; V^*_{\alpha\alpha,1}(\mathbf{q}^2)\frac{1}{N_{net}}\sum_{\beta=1}^{N_{net}}(2Z_A^{\beta 2} - X_A^{\beta 2} - Y_A^{\beta 2}) \quad (3.10)$$

The term in expression 3.10 explicitly involving the network vectors ($X_A^{\beta 2}$, $Y_A^{\beta 2}$, $Z_A^{\beta 2}$) is **self-averaging** and can be replaced by

$$\frac{1}{N_{net}}\sum_{\beta=1}^{N_{net}}(2Z_A^{\beta 2} - X_A^{\beta 2} - Y_A^{\beta 2}) = 2\bar{Z}_A{}^2 - \bar{X}_A{}^2 - \bar{Y}_A{}^2 = 2(\lambda^2 - \lambda^{-1})\frac{N_A b^2}{3} \quad (3.11)$$

for an affine uniaxial deformation. The result is that the orientation dependent interaction of the NMR probe can be written as

$$\langle \epsilon(\mathbf{b}_j^{\alpha};\{\mathbf{R}_A\})\rangle = \frac{\nu_0}{N_A}\left(\frac{2Z^{\alpha 2} - X^{\alpha 2} - Y^{\alpha 2}}{N^2}\right)\delta_{\alpha,A} - \Delta_\alpha(\lambda^2 - \lambda^{-1}) \quad (3.12)$$

where

$$\Delta_\alpha = \frac{8\nu_0 N_A}{45\pi^2}\int_0^\infty V^*_{\alpha\alpha,1}(\mathbf{q}^2)q^2\,\mathrm{d}q \quad (3.13)$$

For the free chains (α = B) dissolved in the network the first term of (3.12) is absent and the NMR signal is a split doublet given in the time domain directly from (2.9) as

$$G(t)|_{free} = \cos\left[\left(\lambda^2 - \frac{1}{\lambda}\right)\Delta_B t\right] \quad (3.14)$$

This result gives two sharp doublet lines because we have assumed that the dynamics of the free chains is very fast. If, for example, the Rouse model was used for the chain dynamics, then in the NMR signal there would be an additional factor of[18]

$$\exp\left(-\frac{t}{T_2}\right) \equiv \exp\left(-\frac{8\nu_0^2\tau\ln(N_B)}{3\pi}t\right) \quad (3.15)$$

where τ is the Rouse time given in terms of the monomer friction coefficient ν by

$$\tau = \frac{\nu b^2}{12kT}$$

We will not consider the dynamics of the chains any further in this present paper. The important feature for this work is that the oscillation of the transverse decay of nuclear magnetization for the free chain can now be seen to originate from the anisotropy of the network vectors without the need to assume any nematic interactions.

For the probe on the network chain (α = A) there is an additional contribution coming from the network constraint. This is given using (3.12) and (2.9)

$$G(t)|_{network} = \overline{\cos\left[\left(\frac{2Z^{\alpha 2} - X^{\alpha 2} - Y^{\alpha 2}}{N_A b^2}\right)\frac{\nu_0}{N_A}t - \left(\lambda^2 - \frac{1}{\lambda}\right)\Delta_A t\right]} \quad (3.16)$$

The quenched averaging $\overline{(\ldots)}$ must be taken over all orientations of the network end to end vector $\mathbf{R}_A^{\alpha}$ of the chains α that the probe is attached to. The other network vectors $\{\mathbf{R}_A{}^{\beta}\}$ are self-averaging, as shown in (3.11). Again, assuming Gaussian statistics and a uniaxial affine deformation, this is readily done[6] to give

$$G(t)|_{network} = \mathrm{Real}\left[\frac{\exp\left(\mathrm{i}\left(\lambda^2 - \frac{1}{\lambda}\right)\Delta_{AA}t\right)}{\sqrt{1 + \mathrm{i}\frac{2\nu_0 t}{N_A}}\left(1 - \mathrm{i}\frac{\nu_0 t}{N_A}\right)}\right] \quad (3.17)$$

The exponential term in (3.17) gives rise to the splitting, while the algebraic part gives rise to a line shape dependent on the deformation. These two factors will be discussed in detail in section 5 after an expression for $\Delta_{A/B}$ has been derived in section 4. Equations 3.14 and 3.17 for the NMR relaxation function are major results of this paper together with the splitting given by (3.13).

In the next section analytic expressions are given for the screened potentials, defined by eq 2.6, which are similar to those used in polymer blends. The NMR splitting as given by eq 3.13 can be explicitly calculated.

4. Screened Potentials and Doublet Splitting

We consider the general situation where the network chains (A) and the free chains (B) interact with each other through short range excluded volume interactions V_{AA}, V_{BB}, and V_{AB}. For the case of A/B blends expressions for the screened interactions were derived in ref 19 using the random phase approximation. Before writing down the result it is worth noting that in the present case one of the components is a network which effectively removes the translational degree of freedom of the chains. The loss of the translational degree of freedom dramatically alters the conditions for the usual application of the RPA. This aspect has been examined in refs 15 and 16 where techniques were developed to

use the RPA in network situations. The full results are rather complicated, but for the purposes of calculating the NMR properties it is sufficient to use the blend result given in ref 19 with modified network chain structure factors to account for the constraint imposed by the network vectors $\{\mathbf{R}_A^\beta\}$. The screened potentials V^*_{AA} and V^*_{BB} can be written as

$$V^*_{AA} = \frac{V_{AA} + c_B(V_{AA}V_{BB} - V_{AB}^2)g_B^0(\mathbf{q})}{1 + c_A V_{AA} g_A^0(\mathbf{q};\{\mathbf{R}_A^\beta\}) + c_B V_{BB} g_B^0(\mathbf{q}) + c_A c_B (V_{AA}V_{BB} - V_{AB}^2) g_B^0(\mathbf{q}) g_A^0(\mathbf{q};\{\mathbf{R}_A^\beta\})} \tag{4.1a}$$

$$V^*_{BB} = \frac{V_{BB} + c_A(V_{AA}V_{BB} - V_{AB}^2)g_B^0(\mathbf{q};\{\mathbf{R}_A^\beta\})}{1 + c_A V_{AA} g_A^0(\mathbf{q};\{\mathbf{R}_A^\beta\}) + c_B V_{BB} g_B^0(\mathbf{q}) + c_A c_B (V_{AA}V_{BB} - V_{AB}^2) g_B^0(\mathbf{q}) g_A^0(\mathbf{q};\{\mathbf{R}_A^\beta\})} \tag{4.1b}$$

where

$$g_A^0(\mathbf{q};\{\mathbf{R}_A^\beta\}) = \frac{1}{N_{net}} \sum_{\beta=1}^{N_{met}} g^0_{A,\beta}(\mathbf{q};\mathbf{R}_A^\beta)$$

and $g^0_{A,\beta}(\mathbf{q};\mathbf{R}_A{}^\beta)$ is the structure factor for a noninteracting network chain (A) with the end to end distance constrained by the network vector $\mathbf{R}_A{}^\beta$.

$$g^0_{A,\beta}(\mathbf{q};\mathbf{R}_A^\beta) = \frac{1}{N_A} \sum_{m,n=0}^{N_A} \langle \exp[i\mathbf{q}(\mathbf{r}^\beta_{qm} - \mathbf{r}^\beta_n)]\rangle_c \tag{4.2}$$

The constrained average $\langle ... \rangle_c$ is defined by eq 3.2. $g_B^0(\mathbf{q})$ is the structure factor for a noninteracting free chain (B)

$$g_\beta^0(\mathbf{q}) = \frac{1}{N_B} \sum_{m,n=0}^{N_B} \langle \exp[i\mathbf{q}(\mathbf{r}^B_m - \mathbf{r}^B_n)]\rangle_0 \tag{4.3}$$

$c_{A/B}$ are the monomer concentrations of the network/free chains, and N_{net} is the number of network chains in the system. It is important to note that each network chain is different due to the individual network vectors $\mathbf{R}_A{}^\beta$, which are treated as quenched variables in this work. For the purpose of conducting an analytic calculation of the splitting, the above structure factors can be well approximated by the following form:

$$g^0_{A,\beta}(\mathbf{q};\mathbf{R}_A^\beta) = \frac{g_A^0(\mathbf{q})}{\left(1 + g_A^0(\mathbf{q})^2 \frac{(\mathbf{q}\mathbf{R}_A^\beta)^2}{4N_A{}^2}\right)} \tag{4.4}$$

with

$$g^0_{A/B}(\mathbf{q}) = \left(\frac{\mathbf{q}^2\mathbf{b}^2}{12} + \frac{1}{N_{A/B}}\right)^{-1}$$

The NMR splitting $\Delta_{A/B}$ from a probe on the network (A) or free chains (B) is determined from (3.13) by

$$\Delta_\alpha = \frac{8 v_0 N_A}{45\pi^2} \int_0^\infty V^*_{\alpha\alpha,1}(\mathbf{q}^2) q^2 \, dq \qquad (\alpha = \text{A or B})$$

with

$$V^*_{\alpha\alpha,1}(\mathbf{q}^2) = N_{net} \left.\frac{\partial V^*_{\alpha\alpha}(\mathbf{q},\{\mathbf{R}_A\})}{\partial((\mathbf{q}\mathbf{R}_A^\beta)^2)}\right|_{(\mathbf{q}\text{-}\mathbf{R}_A^\beta)^2=0} \tag{4.5}$$

Since the screened potential is different for the network and free chains, we will consider each case separately.

4.1. Splitting from the Network Probe. The term $V^*_{\alpha\alpha,1}(\mathbf{q}^2)$ is readily obtained from (4.1a) with the forms (4.2) and (4.3) for the structure factors. It can be written as

$$V^*_{AA,1}q^2 = c_A \frac{q^2 g_A^0(\mathbf{q})}{4N_A{}^2} \times \left[\frac{g_A^0(\mathbf{q})(V_{AA} + c_B g_B^0(\mathbf{q})(V_{AA}V_{BB} - V_{AB}{}^2))}{1 + c_A V_{AA} g_A^0(\mathbf{q}) + c_B V_{BB} g_B^0(\mathbf{q}) + c_A c_B g_A^0(\mathbf{q}) g_B^0(\mathbf{q})(V_{AA}V_{BB} - V_{AB}{}^2)}\right]^2 \tag{4.6}$$

It is convenient to write the excluded volume potentials as

$$V_{AA} = V + \epsilon_{AA}, \qquad V_{BB} = V + \epsilon_{BB}, \qquad V_{AB} = V + \epsilon_{AB}$$

where the V is much larger than any of the ϵ's. For the phase behavior of polymer blends it is normally sufficient to consider the incompressible limit. This is achieved in the limit $V \to \infty$; however care must be exercized in the present problem since, as we will show, the leading contribution to the splitting goes as $\sqrt{V}$. To find this term, it is sufficient to set the ϵ's equal to 0. Furthermore since V is considered as an excluded volume, then $c_{A/B}V \sim 1$, so that terms $N_{A/B}^{-1}$ can also be neglected. Under these conditions

$$V^*_{AA,1} = c_A \frac{3V^2}{N_A{}^2}\left[\frac{1}{q^2b^2 + 12cV}\right]^2 \tag{4.7}$$

and the integral in (4.6) can be done to give

$$\int_0^\infty V_{AA,1}{}^2 q^2 \, dq = \frac{3\pi}{4} \frac{c_A}{c^2} \frac{1}{N_A{}^2} \frac{1}{b^3} \sqrt{12Vc}$$

where c is the total monomer concentration ($c = c_A + c_B$). The interaction term V can be eliminated in favor of the Edwards screening length[14] ξ given by

$$\xi = b/\sqrt{12Vc} \tag{4.8}$$

The contribution of the (smaller) terms dependent on the ϵ's can be obtained by looking at the limit $V \to \infty$. From (4.7) this limit is given by

$$V^*_{AA,1}q^2 = c_A \frac{q^2 g_A^0(\mathbf{q})}{4N_A{}^2} \times \left[\frac{g_A^0(\mathbf{q})(1 - 2\chi_F c_B g_B^0(\mathbf{q}))}{c_A g_A^0(\mathbf{q}) + c_B g_B^0(\mathbf{q}) - 2\chi_F c_A c_B g_A^0(\mathbf{q}) g_B^0(\mathbf{q})}\right]^2 \tag{4.9}$$

where

$$2\chi_F = 2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}$$

χ_F can be identified with the Flory interaction parameter, except our definition has the dimensions of a volume. The integral $\int_0^\infty V^*_{AA,1}q^2 \, dq$ now contains a

divergent part corresponding to the simplification $V \rightarrow \infty$. The integral can be written as

$$\int_0^\infty V^*_{AA,1} q^2 \, dq = \frac{c_A}{c^2} \frac{3}{{N_A}^2 b^2} [\int_0^{\text{cutoff}} dq + \text{finite term}]$$

The first term then corresponds to the $\sqrt{V}$ dependence found in (4.10). The second term is readily found after lengthy but straightforward algebra, and the complete result can be written as

$$\int_0^\infty V^*_{AA,1} q^2 \, dq = \frac{3\pi}{4} \frac{c_A}{c^2} \frac{1}{{N_A}^2} \frac{1}{b^3} \left[\frac{b}{\xi} + \frac{c_B}{c} F_A(\chi_F, N_A, N_B, c_A, c_B) \right] \quad (4.10)$$

with

$$F_A(\chi_F, N_A, N_B, c_A, c_B) = \frac{\sqrt{12} \left(\frac{1}{N_B} - \frac{1}{N_A} - 2c_B\chi_F \right) \left(\frac{1}{N_B} + 6 \left(\frac{c_A c_B}{c} (\chi_0 - \chi_F) \right) - 2c_B\chi_F \right)}{\left[\frac{2c_A c_B}{c} (\chi_0 - \chi_F) \right]^{3/2}} \quad (4.11)$$

where

$$2\chi_0 = \frac{1}{c_A N_A} + \frac{1}{c_B N_B}$$

Finally, the term Δ_A, from (4.5) can be written as

$$\Delta_A = \frac{2}{15\pi} \frac{\nu_0}{N_A} \frac{c_A}{c} \frac{1}{cb^3} \left[\frac{b}{\xi} + \frac{c_B}{c} F_A(\chi_F, N_A, N_B, c_A, c_B) \right] \quad (4.12)$$

4.2. Splitting from a Probe on the Free Chains. The screened potential for the NMR probe on a free chain (B) is given by (4.1b), and the calculation of $V^*_{BB,1}$ and the subsequent integration proceed in the same way as before. The term dependent on V is the same and the, and the $V \rightarrow \infty$ limit for the term $V^*_{BB,1}$ is given by

$$V^*_{BB,1} q^2 = c_A \frac{q^2 g^0_A(\mathbf{q})}{4{N_A}^2} \times \left[\frac{g^0_A(\mathbf{q})}{c_A g^0_A(\mathbf{q}) + c_B g^0_B(\mathbf{q}) - 2\chi_F c_A c_B g^0_A(\mathbf{q}) g^0_B(\mathbf{q})} \right]^2 \quad (4.13)$$

The complete result can be written as

$$\int_0^\infty V^*_{BB,1} q^2 \, dq = \frac{3\pi}{4} \frac{c_A}{c^2} \frac{1}{{N_A}^2} \frac{1}{b^3} \left[\frac{b}{\xi} + \frac{c_B}{c} F_B(\chi_F, N_A, N_B, c_A, c_B) \right]$$

where

$$F_B(\chi_F, N_A, N_B, c_A, c_B) = \frac{\sqrt{12} \left(\frac{1}{N_B} - \frac{1}{N_A} + 2c_A\chi_F \right) \left(\frac{1}{N_B} + 6 \left(\frac{c_A c_B}{c} (\chi_0 - \chi_F) \right) \right)}{\left[\frac{2c_A c_B}{c} (\chi_0 - \chi_F) \right]^{3/2}} \quad (4.14)$$

Finally, the splitting from the free chains Δ_B can be written as

$$\Delta_B = \frac{2}{15\pi} \frac{\nu_0}{N_A} \frac{c_A}{c} \frac{1}{cb^3} \left[\frac{b}{\xi} + \frac{c_B}{c} F_B(\chi_F, N_A, N_B, c_A, c_B) \right] \quad (4.15)$$

In both cases the dominant contribution to the splitting from the network or free chains comes from the first term. This involves only the excluded volume interaction V through the term $b/\xi \sim \sqrt{V}$and is linearly dependent on the monomer concentration of network chains c_A. In the next section we consider the detailed features of these results and the extent to which they can be compared with experimental data.

5. Molecular Weight, Concentration, and Temperature Dependence of the Deformation-Induced Line Splitting: Comparison with Experiment

The line splitting $\Delta\nu_{A/B}$ from either the network or free chains can be written as

$$2\pi\Delta\nu_{A/B} = 2(\lambda^2 - \lambda^{-1})\Delta_{A/B}(\chi_F, N_A, N_B, c_A, c_B) \quad (5.1)$$

The deformation dependence is entirely contained in the prefactor, whereas the molecular weight, concentration, and temperature dependences are contained in the term $\Delta_{A/B}$.

$$\Delta_{A/B} = \frac{2}{15\pi} \frac{1}{cb^3} \frac{\nu_0}{N_A} \frac{c_A}{c} \left[\frac{b}{\xi} + \frac{c_B}{c} F_{A/B}(\chi_F, N_A, N_B, c_A, c_B) \right] \quad (5.2)$$

where $F_{A/B}$ is given by (4.11) or (4.14).

We have assumed fast dynamics for the polymer chains. For the free chains this leads to narrow lines independent of the deformation. However, for the network chains there is a contribution to the line shape which comes from the constraint on the end to end vector. For the network chains the deformation also affects the line shape in a manner which has been previously discussed[6] and is given in the result (3.17). In this section we restrict our attention to the splitting given by (5.1) and (5.2).

For both network and free chains the splitting is inversely proportional to N_A, the molecular weight between cross-links. This has been confirmed experimentally for networks by the work of Gronski et al.[20] on a variety of deuterated elastomers. To date we have not found any data to test the prediction for the splitting from free chains dissolved in the network.

There are two contributions to the splitting given by (5.2). The first term b/ξ (the ratio of the segment length to the screening length) can be found from the case where the free chains and the network chains are identical, i.e. $N_A = N_B = N$ and $\chi_F = 0$. From (4.11) or (4.14) it can be seen that $F_{A/B}(0,N,N,c_A,c_B) = 0$ and hence

$$\Delta_{A/B} = \left(\frac{2}{15\pi} \frac{1}{cb^3} \frac{\nu_0}{N_A} \right) \frac{c_A}{c} \frac{b}{\xi} \quad (5.3)$$

The free chains act as a dilutant, and the splitting is determined by the ratio of the Edward's screening length ξ to the statistical monomer length b.

A comparison with experiment can be made on the data of Deloche et al.[3] on a dry PDMS network. Under a uniaxial deformation λ the splitting was measured to

be

$$\Delta\nu_{\text{exptal}} = (\lambda^2 - \lambda^2)37.7 \text{ Hz}$$

where the strain is at right angles to the applied magnetic field. The molecular weight of the chains between cross-links was 10 500. Computer modeling at the University of Leeds found that to obtain Gaussian statistics, eight monomers need to be connected together. From this the number of statistical segments between cross-links can be determined as $N_A \sim 15$. Further modeling determined how the bare carbon−deuterium interaction rescaled onto the representative Rouse chain. The eight monomers that form the Rouse unit reduce the magnitude of this interaction, by fast reorientations, to $\nu_0 = 21.0$ kHz. Finally, we set $c_A = c$ with $cb^3 = 1$.

The screening length ξ can be calculated from (5.1) and (5.3) as

$$\xi \sim b/4 \tag{5.4}$$

The smallness of this length compared to the segment statistical length b can be explained in terms of the near incompressibility of the dry network. In the random phase approximation the Fourier components ϕ_q. of the monomer volume fraction fluctuations for an interacting system are given by a well-known result of de Gennes as

$$\langle|\phi_q|^2\rangle = \frac{\langle|\phi_q|^2\rangle_0}{1 + V\langle|\phi_q|^2\rangle_0} = \frac{1}{V} \quad \text{as} \quad q \rightarrow 0 \tag{5.5}$$

The Edwards screening length ξ is related to the interaction V by eq 4.8. Using $b/\xi \sim 33$ gives $V \sim 90$ (the units of V are in terms of kT).

In the same paper[3] a system consisting of free PDMS chains of varying molecular weights dissolved in the network was considered. Results were reported of the NMR signal from the free chains and the network chains separately. In this case the chains are chemically identical but of different molecular weights. The first term in (5.2) predicts a linear dependence on the network fraction c_A and the second term $F_{A/B}$ is given from (4.11) and (4.14) by

$$F_{A/B}(\chi_F{=}0, N_A, N_B, c_A, c_B) = \sqrt{12}\frac{\left(\frac{1}{N_B} - \frac{1}{N_A}\right)\left(\frac{1}{N_B} + 6\left(\frac{c_A c_B}{c}(\chi_0)\right)_F\right)}{\left[\frac{2c_A c_B}{c}(\chi_0)\right]^{3/2}} \tag{5.6}$$

and is the same for both kinds of chains.

The contribution of this term is of order $1/\sqrt{N_{A/B}}$ compared to the first term, .i.e. b/ξ, which is of the order of 1. It will be important for shorter chains either as a network or free chains, and the sign is determined entirely as to whether $N_B < N_A$ (+) or $N_B > N_A$ (−).

For the case of free PDMS chains of molecular weight 450 ($N_B \sim 6$) dissolved in the network ($N_A \sim 130$) the data presented in ref 3 were too limited to make a complete comparison. However the sign of the deviation from a linear dependence on c_A was positive in accordance with our result.

Although in general the value of the term $F_{A/B}$ is intrinsically small ($1/\sqrt{N_{A/B}}$), its value can be greatly enhanced for interacting systems by the denominator term $[(\chi_0 - \chi_F)]^{3/2}$ in eq 4.11 or 4.14. At some temperature represented by the interaction parameter χ_F reaching the critical value $\chi_F = \chi_0$, the system will become unstable and phase separate. Concentration fluctuations in the mean field become unstable, which are reflected in the contribution of $F_{A/B}$ to the overall splitting. For the case $N_A = N_B = N$ the behavior of $F_{A/B}$ is quite different depending on whether the probes on the free or network chains. For the free chains

$$F_B = \sqrt{12}\frac{8c_B\chi_F\left(\frac{1}{N} - \frac{3}{2}\chi_F\frac{c_A c_B}{c}\right)}{\left(\frac{1}{N} - 2\chi_F\frac{c_A c_B}{c}\right)^{3/2}} \tag{5.7}$$

This is positive for all values of $\chi_F < \chi_0$. However for the probe on a network chain the contribution from F_A is predominantly negative, yet it can change sign dependent on χ_F increasing and for a range of concentrations.

$$F_A = \sqrt{12}\frac{(-2c_B\chi_F)\left(\frac{4}{N} - 2\chi_F c_B\left(4 - \frac{3c_B}{c}\right)\right)}{\left(\frac{1}{N} - 2\chi_F\frac{c_A c_B}{c}\right)^{3/2}} \tag{5.8}$$

The second factor in the numerator of (5.8) changes sign when

$$\frac{c_B}{c} = \frac{2}{3}(1 \pm \sqrt{1 - {}_3}2N\chi_F \tag{5.9}$$

i.e. when $Nc\chi_F \geq {}^3/_2$, whereas the instability or phase separation occurs when the denominator changes sign a

$$\frac{c_B}{c} = \frac{1}{2}(1 \pm \sqrt{1 - {}_2}Nc\chi_F \tag{5.10}$$

i.e. when $Nc\chi_F \geq 2$. The contribution of F_A to the observed splitting can therefore change sign before the phase separation point.

The behavior of $F_{A/B}$ is shown as a function of the free chain fraction c_B/c for a range of values of the Flory interaction parameter χF in Figure 2a−c. For χ_F sufficiently close to χ_0 this term should compete with the first term dependent on b/ξ. In an NMR experiment this will be revealed as a significant increase in the magnitude of splitting. To date we have not found any experimental data to compare with these predictions.

6. Conclusions

In this paper we have shown how isotropic excluded volume interactions are sufficient to account for the line splitting seen on deformation from NMR probe molecules located on network chains or on free chains dissolved in the network. For a uniaxial deformation λ the splitting is proportional to $(\lambda^2 - \lambda^{-1})$ and inversely proportional to the molecular weight of the network chains. These results have been well established in the literature for many years. In this work we show that the dominant contribution to the magnitude of the splitting is linearly dependent on the network fraction

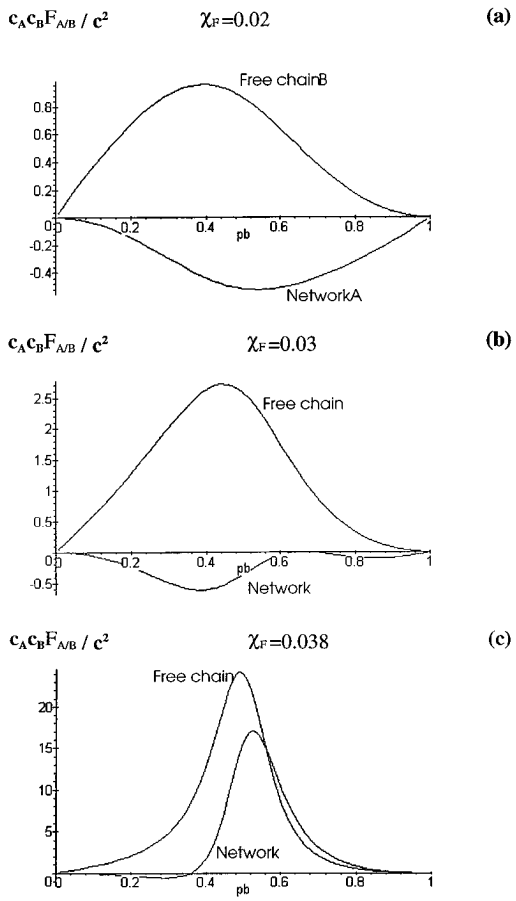

Figure 2. Contribution of the second term of eq 5.2 to the NMR line splitting plotted against the monomer fraction of free chains $pb = c_B/c$ for three values of the Flory interaction parameter χ_F. In each case the chain lengths of the network (A) and free chains (B) are the same with $N_A = N_B = 100$. For these parameters microphase separation will occur at $\chi_F = 0.04$.

and determined by the excluded volume interaction as expressed by the ratio of the Edwards screening length ξ to the chain segment length b. For the case of a dry PDMS network we found $b/\xi \sim 4$. Smaller, secondary contributions to the splitting are also present which do depend on the molecular weight, concentration, and chemical nature of the dissolved chains. Detailed predictions were made for the dependence on the parameters involved. For chains which show a preference to microphase separate the secondary effects can be strongly enhanced. A variety of specific predictions are made as the phase separation point is approached which reflect the statistical mechanics of the process.

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