Entanglements in polymers: II. Networks

1999 J. Phys. A: Math. Gen. 32 3301

(http://iopscience.iop.org/0305-4470/32/18/307)

J. Phys. A: Math. Gen. **32** (1999) 3301–3320. Printed in the UK PII: S0305-4470(99)99740-8

Entanglements in polymers: II. Networks

Sam F Edwards† and Kristian K Müller-Nedebock‡

† Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK
‡ Max-Planck-Institut für Polymerforschung, Postfach 3148, 55021 Mainz, Germany

Received 27 November 1998

Abstract. The effect of the preservation of the topology of the entanglement in systems of polymer loops which are part of a gel is investigated. A simple two-state invariant of this topology is implemented in the preservation of the state of linking of sets of loops. We compute the free energy of a network by making use of a variational principle and thereby to go beyond the limit of phantom chains. We compute the contribution due to entanglements to the reduced stress of the network.

1. Networks with entanglements

When polymer strands are linked to form a network, loops may occur in the process, and these may be classified by their state of knottedness. For permanent looping and linking this classification represents a quenched, disordered topological and geometric state of the system. How do these factors, specifically the knot invariance, influence the network elasticity?

The mathematical formulation of entanglement constraints is rather difficult, and successful treatments have so far generally reverted to the ideas of reptation [1] for dynamics, or to the model of slipping links [2], which have provided a direct and insightful inclusion of some entanglements. However, the idea of the slipping link, modelled as a ring of infinitesimal diameter binding two strands of polymer at a single point and captured between two crosslinks, is still local in nature. This makes redundant the concepts of required closed loops in the network and reduces the problem of entanglement invariance, which is a global function of the system, to the view of only local constraints or interactions in the replica space. The slipping link model has been combined with the tube model for networks, and the Mooney–Rivlin behaviour found [3]. An approach including the global nature of entanglements into an expression for the free energy of a network (using the Gauss invariant) has been made by Iwata [4–6].

Here it is envisaged to build upon the simple ideas already introduced in the previous paper [7] (hereafter referred to as I) for the melt of rings with quenched topology and to present an alternative approach to entanglement in a network. Again the model will be highly idealized and it will have severe limitations caused by the introduction of extraneous parameters such as numbers of loops, the fact that the loop sizes will remain fixed and that a size distribution for loops due to the process of crosslinking will be neglected. As already mentioned, the invariance is imposed strictly upon pairs of such loops and reduces the denumerably infinite number of such states to essentially two classes. Nevertheless, the topology is still maintained even if the calculation is minimally non-phantom. Furthermore, the manner in which the replica problem will be solved, i.e. by the variational ansatz as used by Deam and Edwards [8],

0305-4470/99/183301+20$19.50

already assumes a specific form of the answer, and the fact of topology is not what leads to an harmonic, replica-coupling constraint in the system but rather because this is put in by hand.

Simulations of entanglement on crosslink lattices, which have been performed recently by Everaers and Kremer [9, 10], have probed the fluctuation assumptions of Pearson and Graessley [11]. Here again, though, only pairwise invariance has been considered. Everaers and Kremer, on the basis of their simulations which explicitly compute the Gaussian invariant, argue that the assumptions of Pearson and Graessley do not lead to the correct answer. They also showed how stress is transmitted through a network by entanglements when such strands are forced to make contact. In the present investigations the finite extensibility of the polymer is not taken into account due to the use of a Wiener measure random walk, which ascribes a finite probability to the end-to-end distance of an overstretched chain.

2. The model

Even without the inclusion of any crosslinking a spontaneously generated system of ring-like molecules will have quenched disorder due to the arbitrariness and permanent nature of the entanglement. A given number of rings is generated spontaneously at a certain density. The entanglements thus created are trapped permanently. A deformation of such a system should show an elastic response apart from the fact that the presence of non-phantom chains should decrease the entropy from that of the phantom case.

As in I, it is chosen that the problem of physical topological invariance is most clearly addressed by viewing the system as consisting of a set of rings which will be primary in the identification of the objects between which pairwise invariance is maintained. As a consequence here, the first simplification of the general network (depicted in figure 1) is the fixing of the level, number and type of constraining conditions *a priori*. It is noted, that in comparison to the arbitrary network, where the crosslinking of arbitrarily shaped molecules on its own is responsible for the determination of the distribution and exact placement of loops, the problem will be separated here.

The Gaussian approximation of the topologically relevant collective variable is again utilized (as this obviously makes the expressions, without having to resum the complete series of the expansion functions like a cosine squared, more tractable).

If two spontaneously created rings are found to have an entanglement described by

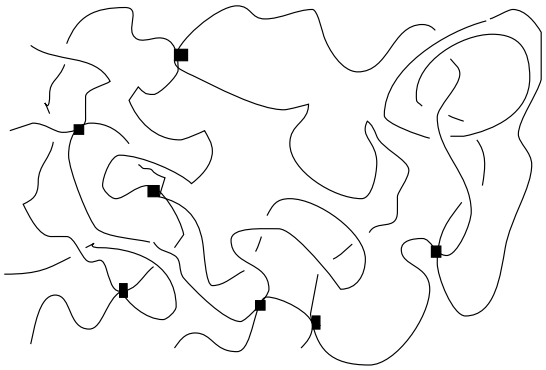

Figure 1. Representation of a network formed by the crosslinking of entangled rings. The black squares indicate crosslink positions. An entanglement of two loops of linking number two can be observed in the uppermost right-hand corner.

$\mathfrak{t}[\boldsymbol{r}_1^{(0)}, \boldsymbol{r}_2^{(0)}]$, given by

$$\begin{aligned}\mathfrak{t}^{\star}[\boldsymbol{R}_1, \boldsymbol{R}_2]_{\hat{\boldsymbol{x}}} &= \int_{0^+}^{\infty} \mathrm{d}\tau \int_0^L \mathrm{d}s \int_0^{L'} \mathrm{d}s' \, |\hat{\boldsymbol{x}} \cdot (\dot{\boldsymbol{R}}_1(s) \times \dot{\boldsymbol{R}}_2(s'))| \delta^{(3)}(\boldsymbol{R}_1(s) - \boldsymbol{R}_2(s') - \hat{\boldsymbol{x}}\tau) \\ \mathfrak{t}[\boldsymbol{R}_1, \boldsymbol{R}_2]_{\hat{\boldsymbol{x}}} &= \int_{0^+}^{\infty} \mathrm{d}\tau \int_0^L \mathrm{d}s \int_0^{L'} \mathrm{d}s' \, \hat{\boldsymbol{x}} \cdot (\dot{\boldsymbol{R}}_1(s) \times \dot{\boldsymbol{R}}_2(s')) \delta^{(3)}(\boldsymbol{R}_1(s) - \boldsymbol{R}_2(s') - \hat{\boldsymbol{x}}\tau)\end{aligned} \tag{2.1}$$

it is required that the condition,

$$\delta^{\star}(\mathfrak{t}[\boldsymbol{r}_1^{(0)}, \boldsymbol{r}_2^{(0)}] - \mathfrak{t}[\boldsymbol{r}_1^{(\alpha)}, \boldsymbol{r}_2^{(\alpha)}]) = 1 \tag{2.2}$$

must hold for all subsequent replicas, $\alpha > 0$. We have used

$$\delta^{\star}(\mathfrak{t}[\boldsymbol{R}_1, \boldsymbol{R}_2]) = \mathfrak{t}_2[\boldsymbol{R}_1, \boldsymbol{R}_2] = |\mathfrak{t}[\boldsymbol{R}_1, \boldsymbol{R}_2] \bmod 2|. \tag{2.3}$$

The condition

$$\text{constraint} = \delta(I_{\text{reference}} - I_{\text{test}}) \tag{2.4}$$

for an invariant I is implemented for all pairs of rings (i.e. excluding considerations like the problem of the Borromean rings). It will be seen that even this simple implementation of the invariant, using a random phase approximation and a variational approach, leads to lengthy analysis.

The crosslinking and entanglement of separate rings also pose the question as to when the system gels. Percolation can appear due to topological effects and in a different manner due to the crosslinking. When does a melt of rings form an infinite cluster under linking and crosslinking? Here reference can be made to the recent works of Zippelius, Goldenfeld and Goldbart on the problem of percolation in networks, and as to when the transition from a liquid-like to gel-like state takes place—an interesting but difficult question [12–14]. Henceforth, it shall be assumed that one is well within the regime where gelation has occured.

3. Partition function

The model system consists of N monodisperse rings of length L such that the total length is $\mathcal{L} = NL$. These rings are crosslinked with each other at their *melt* contact points, in, for the sake of simplicity, the same density and temperature conditions as the deformed network, N_c times. The crosslinks are modelled as Dirac delta functions in the manner which has become established convention throughout theoretical treatments aimed at treating network properties in the direct manner. The product of crosslink constraints is exponentiated by the integration of a variable μ, which will form part of a steepest descents and variational solution. Both the entanglements and the crosslinks represent quenched disorder. This means that the free energy of such a system needs to be computed using the quenched average, and again the replica trick in invoked [15, 16]. By denoting a generic disorder-dependent Hamiltonian by $H = H(x, [D])$, with disorder distribution $\mathcal{P}[D]$, the averaged free energy is given by $F = \int \mathrm{d}D \, \mathcal{P}[D] \ln \int \mathrm{d}x \, \exp -H(x, [D])$. This can be computed by noting the identity $\lim_{n\to 0}(Z^n - 1)/n = \ln Z$. For a network the probablity of disorder is given by the Hamiltonian itself, and n replicas of the system itself are used for the calculations. The replica trick involves making n copies of the system and then computing the disorder and thermodynamic averages. Analytic continuation of the resulting free energy as a function of n is then used to calculate the replica limit above.

The statistical measure of the rings is given by a Wiener measure with a loop closure condition:

$$\mathfrak{Dm}\{\boldsymbol{r}_j\} = \left\{ \prod_{j=1}^{N} \mathfrak{D}\boldsymbol{r}_j(s) \right\} \exp\left(- \sum_{j=1}^{N} \frac{3}{2\ell} \int_0^L \mathrm{d}s \, \dot{\boldsymbol{r}}_j^2(s) \right)$$

$$\times \prod_{j=1}^{N} \delta[\boldsymbol{r}_j(0) - \boldsymbol{r}_j(L)]\delta[\dot{\boldsymbol{r}}_j(0) - \dot{\boldsymbol{r}}_j(L)]. \tag{3.1}$$

This is included in the replicated partition function with pairwise $\delta^\star$-topological invariance constraints for all pairs of rings.

$$Z_n = \int \prod_{\alpha}^{n} \mathfrak{Dm}\{\boldsymbol{r}_j^\alpha\} \frac{N_c! \mathrm{d}\mu}{2\pi \mathrm{i}} \left[\prod_{i\neq j} \prod_{\alpha=1}^{n} \delta^\star(\mathfrak{t}[\boldsymbol{r}_i^0, \boldsymbol{r}_j^0] - \mathfrak{t}[\boldsymbol{r}_i^\alpha, \boldsymbol{r}_j^\alpha]) \right]$$
$$\times \exp\left\{ + \mu \sum_{i\neq j}^{N,N} \int\int \mathrm{d}s\, \mathrm{d}s' \prod_{\alpha=0}^{n} \delta(\boldsymbol{r}_i^\alpha(s) - \boldsymbol{r}_j^\alpha(s')) - N_c \ln \mu \right\}. \tag{3.2}$$

The replicated free energy, F_n, is defined through the definitions and the order $\mathcal{O}(n)$ term in analytic continuation to $n \in \mathbb{R}$,

$$\mathrm{e}^{-\beta F_n} = Z_n \tag{3.3}$$

$$F = \frac{\partial}{\partial n} F_n \bigg|_{n=0}. \tag{3.4}$$

The expression in braces of equation (3.2) representing the crosslinking is denoted by X,

$$X = +\mu \sum_{i\neq j}^{N,N} \int_0^L \int_0^L \mathrm{d}s\, \mathrm{d}s' \prod_{\alpha=0}^{n} \delta(\boldsymbol{r}_i^\alpha(s) - \boldsymbol{r}_j^\alpha(s')) - N_c \ln \mu. \tag{3.5}$$

Here the summation excludes the possibility of crosslinkage of a ring to itself. This is to prevent, at least, the formation of additional loops out of a single loop. Nevertheless, the act of crosslinking can cause the situation of more loops to occur as a set of subpaths from several individual strands of polymer. These will be ignored.

The approach now follows closely to that of the previous sections in that it is fortuitously helpful to transform the variables into collective variables, to enable the utilization of a Gaussian/random phase approximation (RPA). Once again, one can define collective variables,

$$\vec{\Psi}^\alpha(\boldsymbol{k}) = \sum_{i=1}^{N} \int_0^L \mathrm{d}s\, \dot{\boldsymbol{r}}_i^\alpha \exp(+\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}_i^\alpha(s)) \tag{3.6}$$

such that the invariant can be expressed in the form,

$$\mathfrak{t}_{ij} = \sum_{\boldsymbol{k}} \mathbb{E}(\boldsymbol{k}) \cdot \boldsymbol{u}_i(\boldsymbol{k}) \times \boldsymbol{u}_j(-\boldsymbol{k}) = \sum_{\boldsymbol{k}} \mathbb{E}(\boldsymbol{k}) \cdot \vec{\Psi}_i(\boldsymbol{k}) \times \vec{\Psi}_j(-\boldsymbol{k}) \tag{3.7}$$

with

$$\mathbb{E}(\boldsymbol{k}) = \int_0^\infty \mathrm{d}\tau\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\hat{\boldsymbol{p}}\tau} \epsilon_{abc} \hat{\boldsymbol{p}}_c. \tag{3.8}$$

The complete system, subjected to crosslinking and to the topological constraints is modelled variationally by means of the variational parameter q (of [8]) which localizes all fluctuations in a harmonic manner.

3.1. Variational approach

In a crosslinked system the assumption that replica-to-replica monomer fluctuations are harmonically localized, works very well. There is the an additional degree of freedom here that uncrosslinked rings possess. In figure 2 a pair is shown. The tubes indicate the localization. The polymer ring can still move along its length bringing an additional contribution L^{Nn} to the replicated partition function.

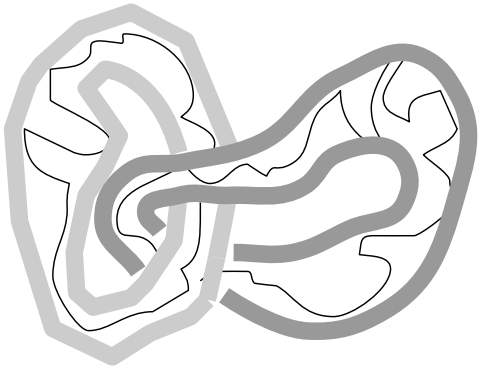

Figure 2. A schematic representation of two entangled polymer rings in their tubes.

Since the crosslinks and the entanglements both provide an extremely difficult integral for the partition function, it is helpful to model the constrained system by a variational Hamiltonian, $H_{\rm var}(q)$, with q representing some set of parameters which have to be determined by minimization of the variational free energy,

$$F \leqslant \tilde{F}_{\rm var}(q) = F_{\rm var} + \langle H_0 - H_{\rm var}\rangle_0 \tag{3.9}$$

where,

$$-\beta F_{\rm var} = \ln \int {\rm e}^{-\beta H_{\rm var}} \tag{3.10}$$

and

$$\langle \ldots \rangle_0 = \mathcal{N} \int \ldots {\rm e}^{-\beta H_{\rm var}} \tag{3.11}$$

with the inverse temperature $\beta = 1/\kappa_B T$, for Boltzmann's constant κ_B and normalized such that $\mathcal{N} = \int {\rm e}^{-\beta H_{\rm var}}$. The familiar Hamiltonian is used, where the effects of the constraints upon the molecules is calculated as an average over the variational replica-fluctuation localizing Hamiltonian:

$$\begin{aligned} -\beta H_{\rm eff} = \sum_{i,a}^{N,3} \int_0^L {\rm d}s \Bigg(& -\frac{3}{2\ell}\dot{\boldsymbol{X}}_{0ia}^2 - \frac{3}{2\ell}\dot{\boldsymbol{X}}_{1ia}^2 \\ & - \sum_m \frac{3}{2\ell}|\dot{\boldsymbol{Y}}_{mia}|^2 - \frac{q_a^2\ell}{6}\boldsymbol{X}_{1ia}^2 - \frac{q_a^2\ell}{6}\sum_m |\boldsymbol{Y}_{mia}|^2 \Bigg) \\ = & -W - Q \end{aligned} \tag{3.12}$$

with the new variables for each loop,

$$\begin{aligned} \boldsymbol{X}_{0ai}(s) &= \frac{\boldsymbol{R}_{ai}^0(s) + \lambda_a \sum{}' \boldsymbol{R}_{ai}^\alpha(s)}{(1+\lambda_a^2 n)^{\frac{1}{2}}} \\ \boldsymbol{X}_{1ai}(s) &= \frac{\lambda_a n^{\frac{1}{2}} \boldsymbol{R}_{0ai}(s) - n^{-\frac{1}{2}} \sum{}' \boldsymbol{R}_{ai}^\alpha(s)}{(1+\lambda_a^2 n)^{\frac{1}{2}}} \\ \boldsymbol{Y}_{mi}(s) &= n^{-\frac{1}{2}} \sum{}' {\rm e}^{2\pi {\rm i}\alpha m/n} \boldsymbol{R}_i^\alpha(s) \end{aligned} \tag{3.13}$$

for which the Jacobian of the coordinate transformation is equal to one. The function W is the abbreviation for the Wiener terms in the Hamiltonian of new variables and Q represents the harmonic terms. A primed sum omits the replica $\alpha = 0$.

The closed paths in the replica space lead to closed paths in the transformed space individually. The non-entanglement contributions for closed chains can be calculated as shown by Deam and Edwards [8] by writing the Green function, derived from a differential equation for a random walk, for example,

$$G_0(x,x',s,s') = \frac{1}{V\prod_a \sqrt{1+n\lambda_a^2}} + \left(\frac{3}{2\ell\pi|s-s'|}\right)^{\frac{3}{2}} \mathrm{e}^{-\frac{3}{2\ell}\frac{(x-x')^2}{|s-s'|}} \tag{3.14}$$

$$G_\alpha(x,x',s,s') = \prod_a \left(\frac{q_a}{2\pi\sinh\frac{\ell q_a(s-s')}{3}}\right)^{\frac{1}{2}} \exp\left(-\frac{q_a}{2}\frac{[(x_a^2+(x_a')^2]\cosh\frac{\ell q_a(s-s')}{3} - 2x_a x_a'}{\sinh\frac{\ell q_a(s-s')}{3}}\right) \tag{3.15}$$

where $\alpha > 0$, for which the additional condition that rings be described means that the Green function must be modified as follows,

$$G_{\mathrm{ring}}(x,x';s,s') = G(x,x';s-s)\times G(x,x';L-s+s'). \tag{3.16}$$

Sometimes the lowest eigenfunction for large $q_a(s-s)\ell$ in equation (3.15) can be used:

$$G_\alpha \simeq \prod_a \sqrt{\frac{q_a}{\pi}}\mathrm{e}^{-\frac{1}{2}q_a(x_a^2+(x_a')^2)-\ell q_a|s-s'|/6}. \tag{3.17}$$

The variational partition functions for crosslinked and uncrosslinked entangled melts consisting of $\frac{1}{2}N(N-1)$ distinct loop-pairs, respectively, are given by:

$$Z_{n\,\mathrm{crossl}} = \int \mathrm{e}^{-W-Q+\langle Q\rangle_0}\left\langle \sum_{\tau=0,1}\prod_{\alpha=0}^{n}\delta^\star(\mathfrak{t}^\alpha-\tau)\right\rangle_0^{N(N-1)/2} \mathrm{e}^{\langle X\rangle_0} \tag{3.18}$$

$$Z_{n\,\mathrm{melt}} = \int \mathrm{e}^{-W-Q+\langle Q\rangle_0}\left\langle \sum_{\tau=0,1}\prod_{\alpha=0}^{n}\delta^\star(\mathfrak{t}^\alpha-\tau)\right\rangle_0^{N(N-1)/2} L^{nN}. \tag{3.19}$$

The exponential term in X is the crosslink contribution, with μ the chemical potential for crosslinks of number N_c. For equation (3.18) to hold one assumes a sufficiently high density of crosslinks such that $N_c > N(N-1)/2$. As a consequence, in the limit when $\tilde{q}_a \gg 1$, the equations,

$$L^{nN}\int \mathrm{e}^{-W-Q} = \mathrm{e}^{-2nN\sum_a \tilde{q}_a - nN\ln L} \tag{3.20}$$

$$\langle Q\rangle_0 = nN\sum_a \tilde{q}_a \tag{3.21}$$

$$\langle X\rangle_0 = \mu\prod_a\left(\frac{q_a}{2\pi}\right)^{n/2}\left(\frac{L^2N(N-1)}{V\sqrt{1+n\lambda_a^2}}\right) - N_c\ln\mu \tag{3.22}$$

and

$$\mathcal{E}_{\mathrm{ent}} = \left\langle \sum_{\tau=0,1}\prod_{\alpha=0}^{n}\delta^\star(\mathfrak{t}^\alpha-\tau)\right\rangle_0 \tag{3.23}$$

are the expressions which hold from previously well-established results. The contributions from the conventional terms of the free energy are adapted for loops (from those computed in the paper of Deam and Edwards [8] using a lowest eigenfunction approach) and recorded here only to the relevant physical orders having terms linear in the replica number, n. The equations

above can be derived using the full expression for $G_{\rm ring}$ and then written in the large $\tilde{q}$ limit. For example,

$$\int G_{\rm ring} = \prod_{\alpha a i} \operatorname{cosech} 2\tilde{q}_a \to \exp\left(-2nN \sum_a \tilde{q}_a \right) \tag{3.24}$$

$$n\mathcal{N} \int_0^L \mathrm{d}s \, \frac{q_a^2 \ell}{6} X^2(s) G_{\rm ring} = n \sum_a \tilde{q}_a (\coth 4\tilde{q}_a - \operatorname{cosech} 4\tilde{q}_a) \to n \sum_a \tilde{q}_a. \tag{3.25}$$

What remains to be determined is the average of the topological constraint, equation (3.23).

3.2. The entanglement contribution

The RPA is computed in this framework in appendix A and is then combined with the replica product of the entanglement constraint, equation (3.23) (see appendix B).

In a network one is not interested in the exact state or value of the invariant in each replica, but only concerned that this state does not differ between the replicas. Again the RPA consists of two non-overlapping sets of rings upon which is imposed on the closed loop condition. A high number density of rings is required to assure the accuracy of the Gaussian approximation.

We rewrite the entanglement contribution as follows:

$$\mathcal{E}_{\rm ent} = \left\langle \sum_{\tau=0,1} \frac{1}{4^{n+1}} \sum_{\{c_\alpha\}} \exp\left[\mathrm{i}\pi \sum_{\alpha=0}^{n} (\mathrm{t}_\alpha c_\alpha - \tau c_\alpha) \right] \right\rangle_0 \tag{3.26}$$

with each $c_\alpha = 0, 0, \pm 1$. This has to be evaluated in the complete replica space and yields a determinant under the RPA as described in appendix B:

$$\mathcal{E}_{\rm ent} = \frac{1}{4^{n+1}} \sum_{\tau=0,1} \sum_{\{c_\alpha\}} \exp[-\operatorname{Tr} \ln \det(\mathbf{1}\delta_{\alpha\beta} + \pi^2 c_\alpha c_\gamma \Delta^T \mathbb{A}_{\alpha\gamma;1} \Delta \mathbb{A}_{\gamma\beta;2})] \times \mathrm{e}^{\mathrm{i}\pi \sum_\alpha c_\alpha \tau}. \tag{3.27}$$

The trace represents the sums:

$$\operatorname{Tr} \mathcal{Q} = \sum_{\boldsymbol{k}>0} \sum_{\alpha} \sum_{a \perp \boldsymbol{k}} \mathcal{Q} \frac{(2\pi)^3}{V}. \tag{3.28}$$

The notation $a \perp \boldsymbol{k}$ means that the trace is taken in the transverse space of the matrix $\mathcal{Q}$ only. This determinant has to be evaluated in the space of $2(n+1) \times 2(n+1)$ dimensions in addition to which there is a summation over a product of terms in c_α. It is useful to factorize the determinant, such that individual rows of the two factored matrices only contain terms in one c_α. Also, in the RPA the two matrices $\mathbb{A}_{\alpha\gamma;1}$ and $\mathbb{A}_{\alpha\gamma;2}$ are the same up to a proportionality factor, and

$$\Delta^T(\boldsymbol{k}) = \Delta_S(\boldsymbol{k}) \tilde{\sigma} \tag{3.29}$$

is related the Pauli matrix, τ_2,

$$\tilde{\sigma} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \mathrm{i}\tau_2. \tag{3.30}$$

The function of $\boldsymbol{k}$ was derived previously as,

$$\Delta_S(\boldsymbol{k}) = |\boldsymbol{k}|^{-1}. \tag{3.31}$$

Factorization in this notation then gives the expression,

$$\mathcal{E}_{\rm ent} = \frac{1}{4^{n+1}} \sum_{\tau=0,1} \sum_{\{c_\alpha\}} \exp\{-\operatorname{Tr} \ln \det[(\mathbf{1}\delta_{\alpha\beta} + \varrho \Delta_S c_\alpha \tilde{\sigma} \mathbb{A}_{\alpha\beta})(\mathbf{1}\delta_{\alpha\beta} - \varrho \Delta_S c_\alpha \tilde{\sigma} \mathbb{A}_{\alpha\beta})]\}$$
$$\times \exp\left(-\mathrm{i}\pi \sum_\alpha c_\alpha \tau \right) \tag{3.32}$$

by using the fact that $\tilde{\sigma}^T = -\tilde{\sigma}$. Here

$$\varrho = \frac{N\pi}{2V} \tag{3.33}$$

is proportional to the number density of rings and it is used because in the RPA $\mathbb{A}_{\alpha\gamma;1} \propto \mathbb{A}_{\alpha\gamma;2}$; additionally, from the replica symmetry imposed by the RPA we define,

$$\mathbb{A}_1 = \mathbb{A}_{11} \tag{3.34}$$

$$\mathbb{A}_2 = \mathbb{A}_{1\alpha} \tag{3.35}$$

$$\mathbb{A}_3 = \mathbb{A}_{\alpha\alpha} \tag{3.36}$$

$$\mathbb{A}_4 = \mathbb{A}_{\alpha\beta} \tag{3.37}$$

where it is given that $\alpha, \beta \in \{1, \ldots, n\}$ and $\alpha \neq \beta$.

Appendix B shows how the replica space determinant can be evaluated to give,

$$\det(\mathbf{1}\delta_{\alpha\beta} + \varrho\Delta_S c_\alpha \tilde{\sigma}\mathbb{A}_{\alpha\beta}) = |\mathbf{1} + \varrho\Delta_S c_0\tilde{\sigma}\mathbb{A}_1|\left\{\prod_{\alpha=1}^{n}|\mathbf{1} + \varrho\Delta_S c_\alpha\tilde{\sigma}\mathbb{D}_5|\right\}$$
$$\times\left|\mathbf{1} + \sum_{\beta=1}^{n}\varrho\Delta_S c_\beta\tilde{\sigma}\mathbb{D}_4(\mathbf{1} + \varrho\Delta_S c_\beta\tilde{\sigma}\mathbb{D}_5)^{-1}\right| \tag{3.38}$$

where the remaining determinants indicated by $|\ldots|$ are over the transverse coordinate space only, and new matrices have been introduced:

$$\mathbb{D}_5 = \mathbb{A}_3 - \mathbb{A}_4 \tag{3.39}$$

$$\mathbb{D}_4 = \mathbb{A}_4 - \mathbb{A}_2(\mathbf{1} + \varrho\Delta_S c_0\tilde{\sigma}\mathbb{A}_1)^{-1}\varrho\Delta_S c_0\mathbb{A}_2. \tag{3.40}$$

The second matrix above couples the zeroth replica to the deformed ones and depends on the 'conjugate' field for the coupling to τ in the constraint $\prod\delta^\star(\mathrm{t}_\alpha - \tau)$.

At this point it is helpful to introduce some additional notation. Let the sum over all the entanglement invariant labels, with the appropriate weighting be denoted by double angular brackets:

$$\langle\langle\mathcal{Q}\rangle\rangle = \mathcal{N}\sum_{\tau=0,1}\sum_{\{c^\alpha\}}\frac{1}{4^{n+1}}\mathcal{Q}\prod_{\alpha=1}^{n}\mathrm{e}^{-\operatorname{Tr}\ln|\mathbf{1}+c_\alpha\varrho\tilde{\sigma}\Delta_S\mathbb{D}_5|+\mathrm{i}\pi c_\alpha\tau}. \tag{3.41}$$

and $\mathcal{N}$ be the correct normalization such that $\langle\langle 1\rangle\rangle = 1$. A helpful property of this definition is the inclusion of the summation over τ and c_0 but without any of the determinant-based weighting factors for the zeroth replica (i.e. the product above is over replicas $\alpha \geqslant 1$). By this point an approximate expression for $\mathcal{E}_{\mathrm{ent}}$ can be simplified significantly. The identity

$$\langle\langle\mathrm{e}^x\rangle\rangle \geqslant \mathrm{e}^{\langle\langle x\rangle\rangle} \tag{3.42}$$

provides a basis to separate the factors of the determinant as derived in appendix B. Furthermore, one can also use this identity, with the substitution $x = \ln y$ above, to write

$$\exp - \operatorname{Tr}\ln\langle\langle y\rangle\rangle \leqslant \exp - \operatorname{Tr}\langle\langle\ln y\rangle\rangle. \tag{3.43}$$

The use of the identities (3.42) and (3.43) together with the factorized expression (3.38) means that it is possible to separate the contributions of the entanglement to the partition function into three parts. Naming one of the traces,

$$K_1 = \operatorname{Tr}_{a,\boldsymbol{k}}\ln(\mathbf{1} + \varrho^2\Delta_S^2\tilde{\sigma}^T\mathbb{D}_5\tilde{\sigma}\mathbb{D}_5) \tag{3.44}$$

the product terms give

$$\mathcal{E}_{\rm ent} = \sum_{\tau=0,1} \frac{1}{4^{n+1}} \sum_{\{c_\alpha\}} (\mathrm{e}^{+\mathrm{i}\pi c_0\tau - \mathrm{Tr}\ln\det(\mathbf{1}+\varrho^2 c_0^2 \Delta_S^2 \tilde\sigma^T \mathbb{A}_1 \tilde\sigma \mathbb{A}_1)}) \prod_{\alpha=1}^{n} (\mathrm{e}^{+\mathrm{i}\pi c_\alpha\tau - \mathrm{Tr}\ln\det(\mathbf{1}+c_\alpha\varrho^2\Delta_S^2\tilde\sigma^T\mathbb{D}_5\tilde\sigma\mathbb{D}_5)})$$
$$\times \exp\left[-\mathrm{Tr}\ln\det\left(\mathbf{1}+\sum_{\beta=1}^{n}\mathbb{B}_\beta\right)\left(\mathbf{1}+\sum_{\beta=1}^{n}\tilde{\mathbb{B}}_\beta\right)\right] \tag{3.45}$$
$$= \mathcal{N}\langle\!\langle \mathrm{e}^{-\mathrm{Tr}\ln\det(\mathbf{1}+\varrho^2c_0^2\Delta_S^2\tilde\sigma^T\mathbb{A}_1\tilde\sigma\mathbb{A}_1) - \mathrm{Tr}\ln\det(\mathbf{1}+\sum_{\beta=1}^n\mathbb{B}_\beta)(\mathbf{1}+\sum_{\beta=1}^n\tilde{\mathbb{B}}_\beta)}\rangle\!\rangle \tag{3.46}$$

with the following definitions,

$$\mathbb{B}_\beta = \varrho\Delta_S c_\beta \tilde\sigma \mathbb{D}_4(\mathbf{1}+\varrho c_\beta\Delta_S\tilde\sigma\mathbb{D}_5)^{-1} \tag{3.47}$$
$$\tilde{\mathbb{B}}_\beta = \varrho\Delta_S c_\beta \tilde\sigma^T \tilde{\mathbb{D}}_4(\mathbf{1}+\varrho c_\beta\Delta_S\tilde\sigma^T\mathbb{D}_5)^{-1} \tag{3.48}$$
$$\tilde{\mathbb{D}}_4(c_0) = \mathbb{D}_4(-c_0). \tag{3.49}$$

The use of the inequalities now provides the estimate:

$$\mathcal{E}_{\rm ent} \geqslant \sum_{\tau=0,1} \tfrac{1}{2}\{\cos\pi\tau(\tfrac{1}{2}+\tfrac{1}{2}\cos\pi\tau\,\mathrm{e}^{-K_1})^n + (\tfrac{1}{2}+\tfrac{1}{2}\cos\pi\tau\,\mathrm{e}^{-K_1})^n\}$$
$$\times \exp(-\mathrm{Tr}\ln\langle\!\langle \mathbf{1}+\varrho^2c_0^2\Delta_S^2\tilde\sigma^T\mathbb{A}_1\tilde\sigma\mathbb{A}_1\rangle\!\rangle)$$
$$\times \exp\left(-\mathrm{Tr}\ln\left\langle\!\left\langle \mathbf{1}+\sum_\beta \mathbb{B}_\beta\right\rangle\!\right\rangle + \mathrm{Tr}\ln\left\langle\!\left\langle \mathbf{1}+\sum_\beta\tilde{\mathbb{B}}_\beta\right\rangle\!\right\rangle\right). \tag{3.50}$$

The first factor, i.e. the first line of the above equation, gives in the replica limit,

$$-\beta F_{\rm ent}^{(1)} = \frac{N}{2}(N-1)\ln\frac{1}{2}(1+\mathrm{e}^{-K_1})\frac{(2\pi)^3}{V}. \tag{3.51}$$

The second line containing solely c_0 when averaged inside the logarithm is proportional to $\sum_\tau \cos\pi\tau$ and gives a factor one in the partition function. In this approximation the term with a direct dependence on the formation replica does not play a role. However, it is noted that a role of this replica is still maintained as it appears in the definitions of $\mathbb{D}_3$ and $\mathbb{D}_4$.

The third remaining contribution occurs inside the natural logarithm, after averaging, as

$$-\beta F_{\rm ent}^{(2)} = -\frac{N}{2}(N-1)\,\mathrm{Tr}_{a,\boldsymbol{k}}\ln(1+n\mathcal{A}) \tag{3.52}$$

where $\mathcal{A}$ represents the averaged term and gives

$$-\beta F_{\rm ent}^{(2)} = -\frac{N}{2}(N-1)\,\mathrm{Tr}_{a,\boldsymbol{k}}\,\mathcal{N}\frac{2\varrho^2\tilde\sigma^T(\mathbb{D}_4^\star+\tilde{\mathbb{D}}_4^\star)\tilde\sigma\mathbb{D}_5}{|\mathbf{1}+\varrho\tilde\sigma\mathbb{D}_5|}\mathrm{e}^{-K_1} \tag{3.53}$$
$$= -\frac{N}{2}(N-1)K_2. \tag{3.54}$$

In writing the last expression a simplification with the view of the results in appendix A has been made, although there is no problem associated with a more general approach. The definition of K_2 is given implicitly and the star on the matrices $\mathbb{D}_4$ refers to their values with $c_0 = 1$. Use has been made of the fact that in the approximation used for $\mathbb{D}_5$ it is a diagonal matrix, and that $|\mathbf{1}+\varrho c\tilde\sigma\Delta_S\mathbb{D}_5| = |\mathbf{1}-\varrho c\tilde\sigma\Delta_S\mathbb{D}_5|$. Here the matrices are defined as in appendix B, and the tilde indicates $\mathbb{D}_4$ with the sign of c_0 in it changed. The reader is referred to compare with equation (3.40);

$$\tilde{\mathbb{D}}_4 = \mathbb{A}_4 + \mathbb{A}_2(\mathbf{1}-\varrho\Delta_S c_0\tilde\sigma\mathbb{A}_1)^{-1}\varrho\Delta_S c_0\tilde\sigma\mathbb{A}_2. \tag{3.55}$$

$\mathcal{N}$ is the normalization:

$$\mathcal{N} = 1+\mathrm{e}^{-K_1}. \tag{3.56}$$

The sum can be expressed in terms of the more familiar quantities,

$$\mathbb{D}_4^\star + \tilde{\mathbb{D}}_4^\star = 2\mathbb{A}_4 + \frac{2\varrho^2\Delta_S^2\mathbb{A}_2\tilde{\sigma}\mathbb{A}_1\tilde{\sigma}\mathbb{A}_2}{|\mathbf{1}+\varrho\tilde{\sigma}\Delta_S\mathbb{A}_1|}. \tag{3.57}$$

The results presented above are largely due to the symmetries in the summations over the c_α and τ.

A quick check of the results so far can be obtained by investigating the intuitively understandable limiting situation of the variational parameter. When $\tilde{q} \to \infty$, i.e. the affine case, $\mathbb{D}_5$ tends to zero and no entanglement contributions can occur in the free energy. This is in agreement with the argument that a system deformed affinely everywhere, cannot show the effect of entanglements. In the other extreme of vanishing $\tilde{q}$ the entanglements have their maximum effect in the sense that completely phantom fluctuations are permitted. The correlations $\mathbb{A}_2$ and $\mathbb{A}_4$ vanish to the fourth order in $\tilde{q}$ for small $\tilde{q}$. $\mathbb{A}_3$ has a contribution of zeroth order in $\tilde{q}$ and $\boldsymbol{k}$, which leads to divergence when taking the traces for K_1 and K_2 as were found in annealed case [7].

The variational free energy of the system with entanglement has now been established and forms the central result:

$$\begin{aligned}\beta\tilde{F}_{\rm var}(q) = N\sum_a \tilde{q}_a - N_c\frac{L^2N(N-1)}{V}\sum_a\left(\ln\tilde{q}_a - \frac{1}{2}\lambda_a^2\right)\\ -\frac{N}{2}(N-1)\ln\frac{1}{2}(1+\mathrm{e}^{-K_1}) + \frac{N}{2}(N-1)K_2.\end{aligned} \tag{3.58}$$

The values of the variational parameter can be determined by minimizing the total free energy with respect to $\tilde{q}_a$, done with the help of appendix A, yielding these as functions of ϱ and of N and N_c. Up to this point the variational ansatz, and the exponential inequality used, the pairs of rings have been decoupled, and the RPA used to compute the entanglement term. What remains is that the integrals over arc parameter for the rings and the traces over the Fourier variables be taken. This is not analytically straightforward in the least and necessitates numerous additional approximations. At hand are the parameters $\tilde{q}$ and ϱ, for which the integrands can be approximated in various limits.

3.3. Dependence on cut-off

Section 3.2 contains the derivation of the terms contributing to the free energy which are pertinent to entanglement. As was noted for the annealed case, and in comparison with the equations of appendix A, related to the stiffness or number of bonds in each of the (identical) ring molecules, $x_c \propto \sqrt{N_b}$, for the number of bonds in a ring, N_b, is introduced. For the purposes of investigating the dependence on this it is helpful to treat it separately. By redefining the average,

$$\langle\!\langle\mathcal{Q}\rangle\!\rangle = \mathcal{N}\sum_{\tau=0,1}\sum_{\{c^\alpha\}}\frac{1}{4^{n+1}}\mathcal{Q}\prod_{\alpha=1}^{n}\mathrm{e}^{-[\mathrm{Tr}\ln|\mathbf{1}+c_\alpha\varrho\tilde{\sigma}\Delta_S\mathbb{D}_5|-c_\alpha^2\varrho^2\zeta_k k^{-2}]+\mathrm{i}\pi c_\alpha\tau} \tag{3.59}$$

with ζ_k representing a function comprising the divergent contribution, the inequality follows as before but with another factor:

$$\begin{aligned}\mathcal{E}_{\rm ent} \geqslant \sum_{\tau=0,1}\tfrac{1}{2}\{\cos\pi\tau(\tfrac{1}{2}+\tfrac{1}{2}\cos\pi\tau\,\mathrm{e}^{-K_1^\star})^n + (\tfrac{1}{2}+\tfrac{1}{2}\cos\pi\tau\,\mathrm{e}^{-K_1^\star})^n\}\\ \times\mathrm{e}^{-\mathrm{Tr}\ln\langle\!\langle\mathbf{1}+\varrho^2c_0^2\Delta_S^2\tilde{\sigma}^T\mathbb{A}_1\tilde{\sigma}\mathbb{A}_1\rangle\!\rangle e^{-\mathrm{Tr}\sum_{\alpha=1}^n\langle\!\langle c_\alpha^2\varrho^2\zeta_k/k^2\rangle\!\rangle}}\\ \times\mathrm{e}^{-(\mathrm{Tr}\ln\langle\!\langle\mathbf{1}+\sum_\beta\mathbb{B}_\beta\rangle\!\rangle+\mathrm{Tr}\ln\langle\!\langle\mathbf{1}+\sum_\beta\tilde{\mathbb{B}}_\beta\rangle\!\rangle)}\end{aligned} \tag{3.60}$$

with

$$K_1^\star = \mathrm{Tr}_{a,k}\{\ln(\mathbf{1} + \varrho^2 \Delta_S^2 \tilde{\sigma}^T \mathbb{D}_5 \tilde{\sigma} \mathbb{D}_5) - \varrho^2 \zeta_k / k^2\}. \tag{3.61}$$

After taking the replica limits there are now three terms: $F_{\mathrm{ent}}^{(1)}$, $F_{\mathrm{ent}}^{(2)}$ with the replacement $K_1 \to K_1^\star$, and

$$-\beta F_{\mathrm{ent}}^{(3)} = -N(N-1)/2\varrho^2 \,\mathrm{Tr}\, \zeta_k / k^2 \mathrm{e}^{-K_1^\star}(1 + \mathrm{e}^{-K_1^\star})^{-1}. \tag{3.62}$$

The term denoted by $F_{\mathrm{ent}}^{(2)}$ above is rather tedious to compute. In order to make further analytical progress, it shall be assumed that only one variational parameter $\tilde{q}$ is used (independent of Cartesian coordinate) and that in the limit of extremely large $\tilde{q}$. In the variational context one can make the contribution $F_{\mathrm{ent}}^{(2)}$ zero by factorizing the last factor of equation (4.38) into terms only linear in in the c_β and by making use of inequality (4.43). All eigenvalues are positive.

4. The variational free energy and conclusions

In this section it will be assumed that $\tilde{q} \gg x_c^2$ and that $\tilde{q} \gg \varrho$ which are the easiest limits in which to compute the free energy for the entangled system. Consulting the appendices (A and C) one finds that there is the cut-off x_c:

$$K_1 = \frac{\varrho^2}{5}\left(\frac{\ell L}{6}\right)^{3/2} \frac{x_c^5}{\tilde{q}^2} d(\lambda) \frac{(2\pi)^3}{V} \tag{4.1}$$

with

$$d(\lambda) = \left(\lambda^2 + \frac{1}{\lambda} + 1\right)\left(\frac{1}{3}\lambda^2 + 1 + \frac{5}{3}\frac{1}{\lambda}\right) \tag{4.2}$$

such that one has

$$-\beta F_{\mathrm{ent}}^{(1)} \simeq -\frac{N}{4}(N-1)\frac{\varrho^2}{5}\left(\frac{\ell L}{6}\right)^{3/2} \frac{x_c^5}{\tilde{q}^2} d(\lambda) \frac{(2\pi)^3}{V}. \tag{4.3}$$

The variational free energy density is now,

$$\beta f_{\mathrm{var}}(\tilde{q}) = 3\frac{N}{V}\tilde{q} - \varrho_{\mathrm{crossl}}\left[3\ln\tilde{q} - \frac{1}{2}\left(\lambda^2 + 2\frac{1}{\lambda}\right)\right] + \frac{1}{2}\varrho_{\mathrm{ent}}\frac{1}{\tilde{q}^2} d(\lambda). \tag{4.4}$$

Here the definitions of the variables ϱ_{ent} and $\varrho_{\mathrm{crossl}}$ are implicit.

A minimization of this expression yields the equation,

$$0 = \frac{3N}{V} - 3\varrho_{\mathrm{crossl}}\frac{1}{\tilde{q}} - \varrho_{\mathrm{ent}}\frac{1}{\tilde{q}^3} d(\lambda) \tag{4.5}$$

for the variational parameter.

In the case of extremely strong crosslinking which from previous work is known to increase the degree of affinity of the system in such models as that of Deam and Edwards, one finds the usual (extremal solution),

$$\tilde{q} \simeq \varrho_{\mathrm{crossl}}\frac{V}{N}. \tag{4.6}$$

When the entanglement contribution is taken as considerably greater than the contribution in a lightly crosslinked system (there also $\tilde{q}$ appears at a lower order), one finds for the system that a large localization exists,

$$\tilde{q} \simeq \left[\frac{N(N-1)}{2V^2}\varrho^2\left(\frac{\ell L}{6}\right)^{3/2} x_c^5 d(\lambda)\right]^{1/3} 2\pi = \varrho_{\mathrm{ent}}^{1/3} d^{1/3}(\lambda). \tag{4.7}$$

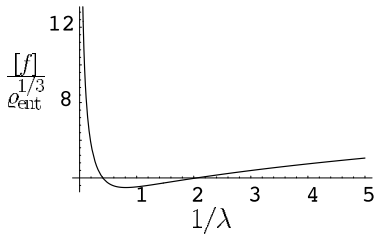

Figure 3. This plot of the contribution to the reduced stress shows the typical Mooney–Rivlin behaviour. The horizontal axis represents the deformation in the form $1/\lambda$ and the vertical axis is the reduced stress normalized by $\varrho_{\rm ent}^{1/3}$. At large deformations the modulus shows a rapid increase, and for smaller deformations the slope of the plot changes.

This agrees with the fact that the contribution of the entanglements to the elasticity, must start from zero before increasing. Consequently, for this case one has,

$$\beta f_{\rm min} = \left(\frac{3N}{V} + 1\right) \varrho_{\rm ent}^{1/3} d^{1/3}(\lambda) - \varrho_{\rm crossl} \ln(\varrho_{\rm ent} d(\lambda)) + \frac{1}{2}\varrho_{\rm crossl}\left(\lambda^2 + \frac{2}{\lambda}\right). \tag{4.8}$$

In order to make conclusions about the modulus of the network the reduced stress, defined as,

$$[f] = \left(\frac{{\rm d}\beta f_{\rm min}}{{\rm d}\lambda}\right)\left(\lambda - \frac{1}{\lambda^2}\right)^{-1} \tag{4.9}$$

is usually plotted. By definition then,

$$\frac{{\rm d}\beta f_{\rm min}}{{\rm d}\lambda} = \frac{\partial \beta f_{\rm min}}{\partial \tilde{q}}\frac{\partial \tilde{q}}{\partial \lambda} + \frac{\partial \beta f_{\rm min}}{\partial \lambda} = \frac{\partial \beta f_{\rm min}}{\partial \lambda}. \tag{4.10}$$

This gives

$$\begin{aligned}[f] &= \varrho_{\rm crossl} + \varrho_{\rm ent}\left(\frac{1}{\tilde{q}^2}\frac{\partial d(\lambda)}{\partial \lambda}\right)(\lambda - \lambda^{-2}) \\ &= \varrho_{\rm crossl} + \varrho_{\rm ent}^{1/3}\frac{\frac{4}{3}\lambda^3 + \frac{8}{3}\lambda + 2 - \frac{8}{3}\lambda^{-2} - \frac{10}{3}\lambda^{-3}}{(\lambda - \lambda^{-2})(\frac{1}{3}\lambda^4 + \frac{4}{3}\lambda^2 + 2\lambda + 1 + \frac{8}{3}\lambda^{-1} + \frac{5}{3}\lambda^{-2})^{1/3}}.\end{aligned} \tag{4.11}$$

The crosslinks in this approximation again give a term which does not depend on the deformation of the sample. However, the entanglements do give such a contribution dependent of λ. This is shown diagrammatically in figure 3. The figure shows the typical behaviour as seen in Mooney–Rivlin experimental plots. The modulus increases dramatically with large extension, but shows a decreasing tendency in the region $\lambda \lesssim 1$. This corresponds to the experimental situation and other theoretical work (e.g. [3]). The behaviour around $\lambda = 1$ is generally understood in terms of slipping links, the later increase of modulus due to the dominance of the restraining tube effect. The slipping links cause a softening because the stretched polymers gain more freedom before the links can slip up to the permanent crosslinks. A model using topological invariants should reproduce these two types of effects. Even after all the approximations made this behaviour is still seen.

When we consider the variational localization parameter $\tilde{q}$ to be independent of the deformation (as with string crosslinking, for example), we see from equation (4.4) that the contribution to entanglements at large deformations scales as λ^4. This agrees with the considerations by Otto and Vilgis [18] and Frisch and Wasserman [19] for the scaling of the free energy for two interlinked polymer loops being pulled apart.

If we assume a dependence of $\tilde{q}$ as in equation (4.7) the large deformation-dependence scales as $\lambda^{4/3}$. This is weaker than for a purely crosslinked phantom network since the chains are far less constrained by entanglements than by crosslinks. Other authors [20] found that olympic gels shows two regimes with the large deformation, the highly linked regime having

a dependence $\lambda^{5/2}$. Our present approach considers only two-state linking and must, as a consequence, underestimate these effects. We have also represented results valid for large $\tilde{q}$.

We also observe that the contribution of the entanglements increases with the density of polymeric material per unit volume. Because the calculations have been presented in the regime of high localization and with the present implementation of the linking invariance it is not possible to conclude about the low localization regime where the modulus due to the entanglement of *uncrosslinked* chains decreases as the chain length is increased at constant number density of loops which is only reached after a suitable crossover.

In this paper a method of dealing with quenched topological constraints within the context of the simplest two-topological-state considerations has been discussed and its application in a network has been computed. The complexity of the system necessitated a strongly approximative approach. Nevertheless, we have been able to compute the contribution to the network elasticity due to including the effects of entanglements already at this level. We have shown the Mooney–Rivlin behaviour for entanglement-dominated networks and argued that olympic gels will be softer than their crosslinked counterparts in some regimes. Future work should address improving the approximations made. The system behaves according to intuition in the extrema of $\tilde{q}$. In the limiting case of extremely large $\tilde{q}$ investigated above, it is seen that the qualitative behaviour of the reduced stress, as observed experimentally, is produced. From the analytical complexity it can also be seen that a disadvantage of the present variational formalism is the use of the $\tilde{q}$ which adds another scale to all integrands, making already tedious and difficult analysis more complex. It should be helpful to investigate further regimes of $\tilde{q}$.

Acknowledgments

The funding of KKMN by the Emanuel Bradlow Foundation and the Committee of University Principals and Vice-Chancellors in the UK and St John's College, Cambridge, who have also provided financial assistance, is most gratefully acknowledged. SFE acknowledges an emeritus fellowship from the Leverhulme Foundation.

Appendix A. Gaussian approximation

A.1. Gaussian approximation

The aim of this appendix is to compute the RPA replicated collective variable probability distribution for the two-ring collective bond-vector density variables as defined in the main text:

$$P_{\vec{\Psi}}[\{\vec{\Psi}_1^{\alpha}, \vec{\Psi}_2^{\alpha}\}] = \exp\left(-\frac{1}{2}\,\mathrm{Tr}\ln\frac{\mathbb{A}_{ij}^{\alpha\beta}}{2\pi}\right)\exp\left(-\frac{1}{2}\sum_{i,j}\sum_{\alpha,\beta}\sum_{\boldsymbol{k}}\vec{\Psi}_i^{\alpha}(\boldsymbol{k})\cdot(\mathbb{A}^{-1})_{ij}^{\alpha\beta}\cdot\vec{\Psi}_j^{\beta}(\boldsymbol{k})\right). \tag{A1}$$

Here again, as in the arguments presented in [7] and the main text, the ring-conditions upon the functions $\vec{\Psi}$ apply. This means that in the final calculation the transverse matrices will be used.

The following definitions, which serve as extensions to those in [7] are made:

$$\mathbb{A}_{ij}^{\alpha\beta} = \begin{pmatrix} \mathbb{A}^{\alpha\beta;(1)} & 0 \\ 0 & \mathbb{A}^{\alpha\beta;(2)} \end{pmatrix} \tag{A2}$$

$$\mathbb{A}^{\alpha\beta;(1)} = MV^{-1}\mathbb{A}^{\alpha\beta} \tag{A3}$$

$$\mathbb{A}^{\alpha\beta;(2)} = (N-M)V^{-1}\mathbb{A}^{\alpha\beta} \tag{A4}$$

$$\mathbb{A}^{\alpha\beta} = \begin{pmatrix} \mathbb{A}_1 & \mathbb{A}_2 & \dots & \mathbb{A}_2 \\ \mathbb{A}_2 & \mathbb{A}_3 & \mathbb{A}_4 & \dots \\ \vdots & \mathbb{A}_4 & \mathbb{A}_3 & \dots \\ \vdots & \vdots & \dots & \dots \end{pmatrix}. \tag{A5}$$

The calculations are performed in the context of the variational Hamiltonian dependent on a possibly component-dependent harmonic localization parameter, $\boldsymbol{q}$ or q_a, and the coordinates related to it which are written here as,

$$r_a^{(0)}(s) = \sigma_a X_a^0(s) + \sigma_a\lambda_a\sqrt{n}X_a^1(s) \tag{A6}$$

$$r_a^{(\alpha)}(s) = \sigma_a\lambda_a X_a^0(s) - \sigma_a\frac{1}{\sqrt{n}}X_a^1(s) + \frac{1}{\sqrt{n}}\sum_{m=2}^{n} Y_a^m(s)\mathrm{e}^{-2\pi\mathrm{i}\alpha m/n} \tag{A7}$$

with

$$\sigma_a = \frac{1}{\sqrt{1+\lambda_a^2 n}}. \tag{A8}$$

The λ_a represent the components along the diagonal of the diagonal deformation tensor. Subscripts a and b indicate Cartesian components. The replica localization term of the Hamiltonian is then given by,

$$Q = \sum_a \frac{q_a^2\ell}{6}\int_0^L \mathrm{d}s\left(|X_a^{(1)}(s)|^2 + \sum_{m=2}^{n}|Y_a^m(s)|^2\right). \tag{A9}$$

In the annealed case it was seen that the dominant value was exact. Here this is not the case. This is because the formation and non-formation replicas couple, in Fourier space, by a vector proportional to $\boldsymbol{k}\cdot\Lambda$. Using the dominant value approximation circumvents this problem at the order of that approximation. Further comments on the approximation used and the definitions of the functions $B(s,s')$, below, will follow:

$$\mathbb{A}_{ab;1} \simeq \int_0^L\int_0^L \mathrm{d}s\mathrm{d}s'\,\langle\sigma_a\sigma_b\dot{X}_a^0(s)\dot{X}_b^0(s') + \sigma_a\sigma_b\lambda_a\lambda_b n\dot{X}_a^1(s)\dot{X}_b^1(s')\rangle B_1(s,s') \tag{A10}$$

$$\mathbb{A}_{ab;2} \simeq \int_0^L\int_0^L \mathrm{d}s\mathrm{d}s'\,\langle\sigma_a\sigma_b\lambda_b\dot{X}_a^0(s)\dot{X}_b^0(s') - \sigma_a\sigma_b\lambda_a\dot{X}_a^1(s)\dot{X}_b^1(s')\rangle \times B_2(s,s') \tag{A11}$$

$$\mathbb{A}_{ab;3} \simeq \int_0^L\int_0^L \mathrm{d}s\mathrm{d}s'\left\langle\sigma_a\sigma_b\lambda_a\lambda_b\dot{X}_a^0(s)\dot{X}_b^0(s') + \sigma_a\sigma_b n^{-1}\dot{X}_a^1(s)\dot{X}_b^1(s') + n^{-1}\sum_m \dot{Y}_a^m(s)\dot{Y}_b^m(s')\right\rangle B_3(s,s') \tag{A12}$$

$$\mathbb{A}_{ab;4} \simeq \int_0^L\int_0^L \mathrm{d}s\mathrm{d}s'\left\langle\sigma_a\sigma_b\lambda_a\lambda_b\dot{X}_a^0(s)\dot{X}_b^0(s') + \sigma_a\sigma_b n^{-1}\dot{X}_a^1(s)\dot{X}_b^1(s') + n^{-1}\sum_m \dot{Y}_a^m(s)\dot{Y}_b^m(s')e^{-2\pi\mathrm{i}(\alpha-\beta)m/n}\right\rangle B_4(s,s'). \tag{A13}$$

The results not in the exponent are derived using the following properties:

$$\langle\dot{X}_a^0(s)\dot{X}_b^0(s')\rangle = \delta_{ab}\left(\frac{\ell}{3L}\right)[L\delta(s-s') - 1] \tag{A14}$$

$$\langle\dot{X}_a^1(s)\dot{X}_b^1(s')\rangle = \delta_{ab}\left(\frac{\ell}{3L}\right)\left\{L\delta(s-s') - \tilde{q}_a\frac{\cosh\tilde{q}_a(1-2\frac{|s-s'|}{L})}{\sinh\tilde{q}_a}\right\}$$

$$= \delta_{ab}\left(\frac{\ell}{3L}\right)(L\delta(s-s') - C_{\tilde{q}_a}(s-s')). \tag{A15}$$

Above, the new function of contour length and $\tilde{q}_a$ has been defined implicitly:

$$C_{\tilde{q}_a}(s-s') = \tilde{q}_a \frac{\cosh\tilde{q}_a(1-2\frac{|s-s'|}{L})}{\sinh\tilde{q}_a}. \tag{A16}$$

The limit $\tilde{q} \to 0$, i.e. the case of no inter-replica localization, reproduces the results of [7] as expected. Here the transformed variable is given by,

$$\tilde{q}_a = \frac{q_a \ell L}{12}. \tag{A17}$$

In the limit $\tilde{q}_a \to \infty$, $\forall a$ the affine result is recovered.

The averages are derived by expanding the functions in terms of ring modes and by using the identity,

$$\sum_{m>0}\frac{\cos mx}{m^2+z^2} = \frac{\pi}{2z}\frac{\cosh z(\pi-x)}{\sinh z\pi} - \frac{1}{2z^2} \tag{A18}$$

to sum the resultant contributions in a standard procedure which is similar to the one by means of which Green functions for chains are computed (as in the book by Freed [17]):

$$G_\alpha(X, X', s, s') = \prod_a \left(\frac{q_a}{2\pi\sinh\ell q_a(s-s')/3}\right)^{\frac{1}{2}} \times \exp\left\{-\frac{q_a}{2}\frac{(X_a^2+(X_a')^2)\cosh\frac{\ell q_a(s-s')}{3} - 2X_aX_a'}{\sinh\frac{\ell q_a(s-s')}{3}}\right\}. \tag{A19}$$

The exponential contributions to the various elements and factors in the matrix come in two categories, and can be obtained from the following identities:

$$\langle e^{-ik_a(X_a^0(s)-X_a^0(s'))}\rangle = \exp\left[-\frac{\ell Lk_a^2}{6}\left(\frac{|s-s'|}{L} - \frac{(s-s')^2}{L^2}\right)\right] \tag{A20}$$

$$\langle e^{i(\kappa_a X_a^m(s)+\kappa_a' X_a^m(s'))}\rangle = \exp\left\{-\frac{\ell L}{12}\left((\kappa_a^2+(\kappa')_a^2)\left[\frac{\coth\tilde{q}_a}{2\tilde{q}_a} - \frac{1}{2\tilde{q}_a^2}\right] + 2\kappa_a\kappa_a'\left[\frac{\cosh\tilde{q}_a(1-2|s-s'|/L)}{2\tilde{q}\sinh\tilde{q}_a} - \frac{1}{2\tilde{q}_a^2}\right]\right)\right\}. \tag{A21}$$

Combining all the results above, the complete functions in the exponent are given by the following:

$$B_1(s,s') = \exp\left[-\frac{\ell Lk^2}{6}\left(\frac{|s-s'|}{L} - \frac{(s-s')^2}{L^2}\right)\right] \tag{A22}$$

$$B_2(s,s') = \exp\left\{-\sum_a \frac{\ell Lk_a^2}{6}\left[\lambda_a^2\left(\frac{|s-s'|}{L} - \frac{(s-s')^2}{L^2}\right) + \frac{1}{2}(1-\lambda_a^2)\left(\frac{\coth\tilde{q}_a}{2\tilde{q}_a} - \frac{1}{2\tilde{q}_a^2}\right) + \lambda_a^2\left(\frac{\cosh\tilde{q}_a(1-\frac{2|s-s'|}{L})}{2\tilde{q}_a\sinh\tilde{q}_a} - \frac{1}{2\tilde{q}_a^2}\right)\right]\right\} \tag{A23}$$

$$B_3(s,s') = \exp\left\{-\sum_a \frac{\ell Lk_a^2}{6}\left[\lambda_a^2\left(\frac{|s-s'|}{L} - \frac{(s-s')^2}{L^2}\right) + (1-\lambda_a^2)\left(\frac{\coth\tilde{q}_a}{2\tilde{q}_a} - \frac{\cosh\tilde{q}_a(1-\frac{2|s-s'|}{L})}{2\tilde{q}_a\sinh\tilde{q}_a}\right)\right]\right\} \tag{A24}$$

$$B_4(s,s') = \exp\left\{ -\sum_a \frac{\ell L k_a^2}{6}\left[\lambda_a^2\left(\frac{|s-s'|}{L} - \frac{(s-s')^2}{L^2}\right) + (1-\lambda_a^2)\left(\frac{\coth\tilde{q}_a}{2\tilde{q}_a} - \frac{1}{2\tilde{q}_a^2}\right)\right.\right.$$
$$\left.\left. +\lambda_a^2\left(\frac{\cosh\tilde{q}_a(1-\frac{2|s-s'|}{L})}{2\tilde{q}_a\sinh\tilde{q}_a} - \frac{1}{2\tilde{q}_a^2}\right)\right]\right\}. \tag{A25}$$

The replica limit has already been taken. One finds, as in the RPA for the excluded volume problem, that the off-diagonal replica-coupling terms have exponential contributions which remain finite when $s - s' \to 0$. The contributions standing before the exponential factors are listed below:

$$F_1 = \delta_{ab}\frac{\ell}{3L}\{\delta(s-s')L - 1\} \tag{A26}$$

$$F_2 = \delta_{ab}\frac{\lambda_a\ell}{3L}\{C_{\tilde{q}_a}(s-s') - 1\} \tag{A27}$$

$$F_3 = \delta_{ab}\frac{\ell}{3L}\{\lambda_a^2(\delta(s-s')L - 1) + (1-\lambda_a^2)(L\delta(s-s') - C_{\tilde{q}_a}(s-s'))\}$$
$$= \delta_{ab}\frac{\ell}{3L}\{L\delta(s-s') - \lambda_a^2 - (1-\lambda_a^2)C_{\tilde{q}_a}(s-s')\} \tag{A28}$$

$$F_4 = \delta_{ab}\frac{\ell}{3L}\{\lambda_a^2(\delta(s-s')L - 1) - \lambda_a^2(L\delta(s-s') - C_{\tilde{q}_a}(s-s'))\}$$
$$= \delta_{ab}\frac{\lambda_a^2\ell}{3L}\{C_{\tilde{q}_a}(s-s') - 1\}. \tag{A29}$$

In addition to the arguments presented above are the usual delta functions of the arguments of the wavevector as they are found in section 2 or appendix A, in that, for example, $\mathbb{A}_1(\boldsymbol{k},\boldsymbol{k}') = \delta(\boldsymbol{k}+\boldsymbol{k}')\mathbb{A}_1(\boldsymbol{k})$, etc.

A.2. The dominant contribution

It has already been mentioned that the dominant contribution approximation, i.e. the one of writing the average as a product of averages, cannot be dismissed as easily as in the quenched polymer case. The annealed calculation showed that the strongest contributions to the resulting average for entanglement constraint come from the highest powers in k as this becomes extremely large. The exponential contributions, of course will usually cause a zero except in the narrow regions of some width k^{-2} around where the argument in the exponent is very small and linear. Consequently, one has that

$$\int \mathrm{e}^{-k^2 s} \sim \frac{1}{k^2} \tag{A30}$$

$$\int s\mathrm{e}^{-k^2 s} \sim \frac{1}{2k^4} \tag{A31}$$

$$\int \delta(s)\mathrm{e}^{-k^2 s} \sim 1. \tag{A32}$$

The contributions proportional to $\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}$, $\hat{\boldsymbol{k}}\cdot\Lambda\hat{\boldsymbol{k}}$, etc, from a full expansion would have the structure as the second expression above and for large k^2 result in terms which do not contribute significantly in the sense that they produce no divergent term to the final result of the integration.

A.3. Limiting expressions

For extremely small $\tilde{q}_a$ the correction to $\mathbb{A}_3$ would be one plus order $\tilde{q}_a^2$, whilst other terms would appear at fourth order in the small parameter. Therefore, one has a large divergence in

the trace and it helpful to use the expressions developed for a divergent part. When $\tilde{q}_a \gg x_c^2$, where x_c is the cut-off due to the bond-number in the trace over $\boldsymbol{k}$, one finds only very small corrections of order $\tilde{q}^{-1}$.

However, here it is easiest to deal with the case where the value of the localizing parameters is still far less than the cut-off, which can be chosen arbitrarily large, but still much larger than one, i.e. the localization strength is more than the ring length.

Noting, that for large $\tilde{q}$,

$$\frac{\cosh \tilde{q}_a(1-2y)}{\sinh \tilde{q}_a} \simeq \exp -2\tilde{q}_a y \tag{A33}$$

one will find, for example, for large values of $\kappa^2 = k^2 \ell L/6$ that,

$$\mathbb{D}_5 \propto \frac{2\tilde{q}_a(\lambda_a^2-1)}{\kappa^2} - 2\lambda_a^2/\kappa^2 + 1. \tag{A34}$$

For small $\kappa^2/\tilde{q}$ one can expand the integrands and evaluate the lowest-order terms using the full expression for $C_{\tilde{q}_a}$, and determine that,

$$\mathbb{D}_5 = \frac{\ell L}{3}\delta_{ab} \sum_c \frac{\kappa_c^2}{2\tilde{q}_c}\left[\frac{\lambda_c^2\tilde{q}_c}{\tilde{q}_a+\tilde{q}_c} + \frac{\lambda_a^2\tilde{q}_a}{\tilde{q}_a+\tilde{q}_c} + \frac{\tilde{q}_a}{\tilde{q}_a+\tilde{q}_c}\right]. \tag{A35}$$

A.4. Transverse contribution

These matrices, for uniaxial, isovolumetric deformations

$$\Lambda = \begin{pmatrix} \lambda^{-1/2} & 0 & 0 \\ 0 & \lambda^{-1/2} & 0 \\ 0 & 0 & \lambda \end{pmatrix} \tag{A36}$$

are then easily reduced, such that

$$R\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{pmatrix} R^T \to \begin{pmatrix} a & 0 \\ 0 & c + (a-c)\cos^2\theta \end{pmatrix}. \tag{A37}$$

The direction of elongation has been denoted as $\hat{z}$ and θ describes the angle between $\boldsymbol{k}$ and this direction.

For the sake of further simplicity it will be assumed that only a single variational parameter is used which is isotropic, in the sense that $\tilde{q}_a = \tilde{q}$, $\forall a$. From the above one has for the case of small $\kappa^2/\tilde{q}$ and for uniaxial, isovolumetric deformation for a,

$$a = \frac{\ell L}{3}\frac{\kappa^2}{2\tilde{q}}\left[\frac{2}{\lambda} + \left(\lambda^2 - \frac{1}{\lambda}\right)\cos^2\theta + 1\right] \tag{A38}$$

and for c,

$$c = \frac{\ell L}{3}\frac{\kappa^2}{2\tilde{q}}\left[\lambda^2 + \frac{1}{\lambda} + \left(\lambda^2 - \frac{1}{\lambda}\right)\cos^2\theta + 1\right] \tag{A39}$$

and the determinant in the main text then gets a contribution of the form

$$4\pi\left(\frac{\ell L}{3}\right)^2 \frac{\kappa^4}{(2\tilde{q})^2} d(\lambda,\theta) = a(c(1-\cos^2\theta)+a) \tag{A40}$$

with

$$d(\lambda) = \int \mathrm{d}(\cos\theta)\, d(\lambda,\theta) = \left(\lambda^2 + \frac{1}{\lambda} + 1\right)\left(\frac{1}{3}\lambda^2 + 1 + \frac{5}{3}\frac{1}{\lambda}\right). \tag{A41}$$

Appendix B. The determinant

This appendix gives a brief outline of the derivation of the determinant which results from the implementation of the random phase approximation and the constraint upon entangled states. At first, a general form is given with an identification of the relevant parts of the entanglement and the second part contains an expression for the determinant in the space of replicas. It is given that all the matrices are already in the transverse space.

B.1. General deduction

The integral under investigation is

$$I = \int \prod_{\alpha} \mathfrak{D}\psi_1^{\alpha}\mathfrak{D}\psi_2^{\alpha}\mathcal{N} \exp\left\{ -\tfrac{1}{2}\sum_{k}[\psi_i^{\alpha} A^{-1}_{\alpha\beta i}\psi_i^{\beta} - 2\pi \mathrm{i} c^{\alpha}\psi_1^{\alpha}\mathbb{E}\psi_2^{\alpha}]\right\} \tag{B1}$$

where $c^{\alpha} = 0, 1$ and $\alpha = 0, 1, \ldots, n$ are the replica indices (which are discarded for the annealed case). The functions ψ_i represents the vector collective fields for the categories of rings in the system $i = 1, 2$. Indeed, ψ, A and $\mathbb{E}$ all depend on Cartesian labels in the transverse space. $\mathcal{N}$ represent the usual Gaussian normalization. Since the ψ-fields describe the Fourier transformations of functions in $\mathbb{R}^3$, i.e. they are bond-vector densities, they are not unrelated at different values of $\boldsymbol{k}$ in that their complex conjugates can be related to the value at negative $\boldsymbol{k}$:

$$\psi^{\star}(\boldsymbol{k}) = \psi(-\boldsymbol{k}). \tag{B2}$$

This is dealt with here by rewriting the sums over $\boldsymbol{k}$ in the exponent of I over a half-space denoted by $\boldsymbol{k} > 0$ and also by expressing the complex functions in terms of two real functions, ϕ and $\bar{\phi}$:

$$\psi = \phi + \mathrm{i}\bar{\phi}. \tag{B3}$$

This gives the integral

$$I = \mathcal{N}\int \exp\left\{ -\tfrac{1}{2}\sum_{\boldsymbol{k}>0}[\phi_i^{\alpha} 2A^{-1}_{\alpha\beta i}\phi_i^{\beta} + \bar{\phi}_i^{\alpha} 2A^{-1}_{\alpha\beta i}\bar{\phi}_i^{\beta} - 2\pi \mathrm{i} c^{\alpha}(\phi_1^{\alpha}(\mathbb{E}+\mathbb{E}^{\star})\phi_2^{\alpha} + \bar{\phi}_1^{\alpha}(\mathbb{E}+\mathbb{E}^{\star})\bar{\phi}_2^{\alpha}) \right.$$
$$\left. +2\pi \mathrm{i} c^{\alpha}(\bar{\phi}_1^{\alpha}\Delta\phi_2^{\alpha} - \phi_1^{\alpha}\Delta\bar{\phi}_2^{\alpha})]\right\}. \tag{B4}$$

It follows from the fact that $-\mathbb{E}(-\boldsymbol{k}) = \mathbb{E}^{\star}(\boldsymbol{k})$ (as can be ascertained from the definition of $\mathbb{E}$) and by rewriting the $\boldsymbol{k}$-sum that the following holds:

$$\sum_{\boldsymbol{k}\neq 0}\psi_1\mathbb{E}\psi_2 = \sum_{\boldsymbol{k}>0}\psi_1\mathbb{E}\psi_2^{\star} + \sum_{\boldsymbol{k}>0}\psi_1^{\star}\mathbb{E}^{\star}\psi_2. \tag{B5}$$

The normalization is given in the usual way by,

$$\mathcal{N} = \exp\left[+\sum_{\boldsymbol{k}>0}\ln\det(2A^{-1}_{\alpha\beta 1}2A^{-1}_{\alpha\beta 2})\right]. \tag{B6}$$

The following definitions have been introduced too:

$$\mathrm{i}\Delta = \bar{\mathbb{E}} - \bar{\mathbb{E}}^{\star} \tag{B7}$$

$$\Delta = -\frac{2}{\boldsymbol{k}\cdot\hat{\boldsymbol{p}}}\begin{pmatrix} 0 & \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{p}} \\ -\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{p}} & 0 \end{pmatrix}$$
$$= \Delta_s \begin{pmatrix} 0 & \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{p}} \\ -\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{p}} & 0 \end{pmatrix}. \tag{B8}$$

These follow from the fact that

$$\mathrm{i}\Delta_s = E(\boldsymbol{k}) - E^{\star}(\boldsymbol{k}) = \int_{-\infty}^{\infty} \mathrm{d}\tau\, \mathrm{sign}(\tau) \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\hat{\boldsymbol{p}}\tau}. \tag{B9}$$

Equation (B8) can be deduced by making use of the expression for the Fourier transformation of the sign-function,

$$\mathrm{sign}(\tau) = \int_{-\infty}^{+\infty} \mathrm{d}\omega\, \frac{2}{\mathrm{i}\omega} \mathrm{e}^{+\mathrm{i}\omega\tau} \tag{B10}$$

which can be seen from the equations

$$\frac{\partial}{\partial\tau}\mathrm{sign}(\tau) = 2\delta_{\mathrm{Dirac}}(\tau). \tag{B11}$$

and

$$\mathrm{i}\Delta_s = \int_{-\infty}^{+\infty} \mathrm{d}\omega\, \frac{2}{\mathrm{i}\omega} \delta(\omega + \boldsymbol{k}\cdot\hat{\boldsymbol{p}}). \tag{B12}$$

The proportionality

$$(\mathbb{E} + \mathbb{E}^{\star}) \propto \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{p}}\delta(\boldsymbol{k}\cdot\hat{\boldsymbol{p}}) \tag{B13}$$

is noted and hence such terms have no contribution to I.

The result for I is:

$$I = \exp\left(-\sum_{\boldsymbol{k}>0} \ln\det(\mathbf{1}\delta_{\alpha\beta} + \pi^2 c^{\alpha}\Delta^T A_{\alpha\gamma 1} c^{\gamma}\Delta A_{\gamma\beta 2}) \right) \tag{B14}$$

where a summation convention is applied.

B.2. The replica space determinants

The result I, above, has certain disadvantages when a summation over the differing values of the c^{α} and a determinant is finally required. This can only be remedied by factorizing the resultant determinant and computing the averages with the help of a well known approximation. This is the procedure employed in the section where the entanglement contribution, $\mathcal{E}_{\mathrm{ent}}$ is computed.

It is necessary to compute the determinant and by making use of the definitions of all quantities:

$$D(\{c_\alpha\}) = \begin{vmatrix} \mathbf{1} + \varrho c_0 \Delta_S \tilde{\sigma}\mathbb{A}_1 & \varrho c_0 \Delta_S \tilde{\sigma}\mathbb{A}_2 & \dots & \varrho c_0 \Delta_S \tilde{\sigma}\mathbb{A}_2 \\ \varrho c_1 \Delta_S \tilde{\sigma}\mathbb{A}_2 & \mathbf{1} + \varrho c_1 \Delta_S \tilde{\sigma}\mathbb{A}_3 & \dots & \varrho c_1 \Delta_S \tilde{\sigma}\mathbb{A}_4 \\ \vdots & & & \\ \varrho c_1 \Delta_S \sigma_n \mathbb{A}_2 & \varrho c_n \Delta_S \tilde{\sigma}\mathbb{A}_4 & \dots & \mathbf{1} + \varrho c_n \Delta_S \sigma_1 \mathbb{A}_3 \end{vmatrix}. \tag{B15}$$

Elementary determinant manipulations can now be applied to the matrix above. Subtracting appropriate multiples of the first column from the remaining columns such that all elements but the first element of the first row are zero causes the first simplification. Now by subtracting the second column from all columns to its left, and thereafter by adding appropriate multiples of all rows to the second row, the determinant is reduced to:

$$D(\{c_\alpha\}) = |\mathbf{1} + \varrho c_0 \Delta_S \tilde{\sigma}\mathbb{A}_1| \left\{ \prod_{\alpha=1}^{n} |\mathbf{1} + \varrho c_\alpha \Delta_S \tilde{\sigma}\mathbb{D}_5| \right\} |\mathbf{1} + \varrho c_\alpha \Delta_S \tilde{\sigma}\mathbb{D}_4 (\mathbf{1} + \varrho c_\alpha \Delta_S \tilde{\sigma}\mathbb{D}_5)^{-1}|. \tag{B16}$$

The appropriate matrices are given by:

$$\mathbb{D}_5 = \mathbb{A}_3 - \mathbb{A}_4 \tag{B17}$$

$$\mathbb{D}_3 = \mathbb{A}_3 - \mathbb{A}_2[\mathbf{1} + \varrho c_0 \Delta_S \tilde{\sigma}\mathbb{A}_1]^{-1} \varrho c_0 \Delta_S \tilde{\sigma}\mathbb{A}_2 \tag{B18}$$

$$\mathbb{D}_4 = \mathbb{D}_3 - \mathbb{A}_3 + \mathbb{A}_4. \tag{B19}$$

Appendix C. Integral for quenched case

Here the simplest case for an isotropic variational parameter is assumed, and this $\tilde{q}$ is taken to be very large such that one can approximate the integrand to lowest order. For $\tilde{q} \gg \varrho$ and $\tilde{q} \gg x_c^2$, where x_c is again the cut-off due to the stiffness of the polymer molecules, one finds that,

$$\begin{aligned} K_1 &= \int \mathrm{d}k\, k^2\, \mathrm{d}\hat{k}\ \ln[1 + \varrho^2 \Delta_S^2 \tilde{\sigma} \mathbb{D}_5 \tilde{\sigma}^T \mathbb{D}_5] \\ &\simeq \int \mathrm{d}k\, k^2\, \mathrm{d}\hat{k}\, \varrho^2 \left(\frac{\ell L}{6}\right)^3 \frac{1}{\kappa^2} \frac{\kappa^4}{\tilde{q}^2} d(\lambda, \theta) \\ &= \frac{\varrho^2}{5} \left(\frac{\ell L}{6}\right)^{3/2} \frac{x_c^5}{\tilde{q}^2} d(\lambda). \end{aligned} \tag{C1}$$

The definition of the explicitly deformation-dependent part is:

$$d(\lambda) = \left(\lambda^2 + \frac{1}{\lambda} + 1\right)\left(\frac{1}{3}\lambda^2 + 1 + \frac{5}{3}\frac{1}{\lambda}\right). \tag{C2}$$

References

[1] Kholodenko A L 1991 *Phys. Lett.* A **159** 437
[2] Ball R C, Doi M, Edwards S F and Warner M 1981 *Polymer* **22** 1010
[3] See Vilgis T A 1992 *Elastomeric Polymer Networks* ed J E Mark and B Erman (Englewood Cliffs, NJ: Prentice-Hall)
[4] Iwata K 1985 *J. Chem. Phys.* **83** 1969
[5] Iwata K 1982 *J. Chem. Phys.* **76** 6363
[6] Iwata K 1982 *J. Chem. Phys.* **76** 6375
[7] Müller-Nedebock K K and Edwards S F 1999 *J. Phys. A: Math. Gen.* **32**
[8] Deam R T and Edwards S F 1976 *Proc. R. Soc.* A **280** 317
[9] Everaers R and Kremer K 1996 *Phys. Rev.* E **53** R37
[10] Everaers R, Kremer K and Grest G S 1995 *Macromol. Symp.* **93** 53
[11] Pearson D S and Graessley W W 1978 *Macromol.* **11** 528
[12] Goldbart P M and Zippelius A 1994 *Europhys. Lett.* **27** 599
[13] Goldbart P M and Zippelius A 1994 *J. Phys. A: Math. Gen.* **27** 6375
[14] Castillo H E, Goldbart P M and Zippelius A 1994 *Europhys. Lett.* **28** 519
[15] Edwards S F and Anderson P W 1975 *J. Phys. F: Met. Phys.* **5** 965
[16] Mezard M, Parisi G and Virasoro M A 1987 *Spin Glass Theory and Beyond* (Singapore: World Scientific)
[17] Freed K F 1987 *Renormalization Group Theory of Macromolecules* (New York: Wiley)
[18] Otto M and Vilgis T A 1998 *Phys. Rev. Lett.* **80** 881
[19] Frisch H L and Wasserman E 1961 *J. Am. Chem. Soc.* **83** 3789
[20] Vilgis T A and Otto M 1997 *Phys. Rev.* E **56** R1314