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Random Networks, Graphs, and Matrices

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Summary: The theory of elasticity based on the distribution function of the gyration tensor is reviewed. It is shown that the James-Guth potential for a network is a model potential of mean force, derivable in principle from the true many-body potential for the elastic body. The determination of the modulus of elasticity is resolved in the calculation of the statistical mechanical average of the smallest, non-zero, eigenvalue of the connectivity matrix that describes the network. The mathematical problem to determine the spectrum of eigenvalues of the random network can be couched in both the language of random graphs and of random matrices.

Keywords: elasticity; random graph; random matrix; random network; theory

Introduction

This review of the theory of high elasticity places the treatment of rubbery materials in the familiar context of the statistical mechanics of fluids. The reason for doing so is that the historical development of elasticity theory generally by-passed these traditions so as to get straight to the physical models – the price that we have paid for these shortcuts is that rubber elasticity has not entered into the general chemical or physical curriculum. Traditional polymer models are not obviously related to other systems of general interest. This is most unfortunate, as cross-linked polymers have many attributes that are seen in other types of disordered materials, such as glasses and neural networks. It hoped that by proceeding through a few formal steps in traditional statistical mechanical language it can be made clear that rubber elasticity fits comfortably in these traditions, yet offers some new insights and even new principles that need to be more generally appreciated in the larger context of random materials.

The other aspect of reviewing this topic is to alert the reader to pertinent developments in areas of mathematics that have a direct bearing on the solution to difficult problems in elasticity. As has long been known, the structure of randomly cross-linked polymers can be encoded in a graph.[1] It will be shown that there is a direct relation between the structure of graphs and elastic properties, but quantitative evaluation of this relation for large random systems is not trivial. It therefore behooves one to be aware of developments in Random Graph theory that are occurring in the mathematical community. Furthermore, since the structure of random graphs is encoded in a matrix, Random Matrix theory also has something to offer.

Statistical Mechanics of High Elasticity

The theory of elasticity presented here is intended to be of pedagogical value, and might follow the treatment of liquids in a graduate course on statistical mechanics. It is hoped that the presentation is both comprehensive and sufficiently simple that it can be integrated with traditional topics in the mainstream of statistical mechanics. The models that are generally used for high elasticity are *ad hoc*, and seem not to connect with other statistical mechanical problems, but this can be easily remedied.

High elasticity is comprehensible as a classical rather than a quantum phenomenon. Let us assume that we are presented with a sample of a not too densely

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cross-linked polymer, the elastomer. For our purposes, this means that the proportion of the material that is cross-links *per se* is a relatively small percentage of the total mass of the elastic body. The reason for restricting attention to lightly cross-linked systems is to facilitate approximations that we will encounter as the theory develops. The usual place to start a discussion of a classical statistical mechanical system is with the Hamiltonian. For any system this is denoted by $H(p,q)$, and is described in as much atomic detail as one likes. Here p and q are the set of $6N$ momenta and coordinates, respectively, where N is the number of "particles" (atoms, molecules, repeat units, etc.) in the system. The probability that the system will be found in a state with specified values of the momenta and coordinates is proportional to $\exp[-\beta H(p,q)]$, where $\beta = 1/kT$ as usual, with kT being the thermal energy. To be more precise, the probability that the system will be found in a state specified by (p,q) is

$$P(p,q)dpdq = Q^{-1}\exp[-\beta H(p,q)]dpdq. \tag{1a}$$

where

$$Q = \int_C \exp[-\beta H(p,q)]dpdq \tag{1b}$$

is the partition function. The subscript C on the sign of integration is to indicate that the integral is generally computed with constraints of one kind or another acting on the system. For example, if the system is a gas, the integration over all coordinates is constrained by the dimensions of the container. In our case, the internal connectivity of the network is the primary, but not the only, constraint of interest.

A very general, if formal, procedure for extracting information on probability distributions that are subspaces of the state space is now required. Suppose we wish to find the probability that the system at temperature T will be found in a state specified by a function $f(p,q)$ of the state variables. This might be a scalar, vector, or tensor valued function, but for simplicity of notation all these different objects will be denoted by the symbol f. Let the natural volume element associated to the function f be df, so that on multiplying and dividing Equation (1a) by this volume element we can write

$$dfP(p,q)dpdq/df = df\,Q^{-1}\exp[-\beta H(p,q)]dpdq/df. \tag{2}$$

This has not altered the value of the probability. The shorthand $dpdq/df$ means to factor the volume element df from $dpdq$. This can be literally accomplished by making the change of variables $(p,q) \rightarrow (p*,q*,f)$ with corresponding change of volume element so that df is explicit. But for now, we will formally integrate over the part of the state space that is the complement of f. What is obtained from this integration is a probability, but now it is the probability that the system is found in a state specified by f, regardless of any other detail of the system. That is

$$P(f)df = df\int_C P(p,q)dpdq/df = df\,Q^{-1}\int_C \exp[-\beta H(p,q)]dpdq/df. \tag{3}$$

Now one needs to relate this probability to thermodynamics. To do this, make the formal change of variables suggested above, so that

$$P(f)df = df\,Q^{-1}\int_C \exp[-\beta H(p*,q*,f)]dp * dq * \tag{4}$$

and now the ratio

$$\frac{P(f_2)df_2}{P(f_1)df_1} = \frac{df_2\int_C \exp[-\beta H(p*,q*,f_2)]dp * dq*}{df_1\int_C \exp[-\beta H(p*,q*,f_1)]dp * dq*} \tag{5}$$

is seen to be related to the Helmholtz free energy change, ΔA, for the process that takes the system through the transformation $\{N, C, \beta, f_1\} \rightarrow \{N, C, \beta, f_2\}$ according to

$$\Delta A = -kT \ln[P(f_2)df_2/P(f_1)df_1]. \quad (6)$$

[Note that the volume elements are not necessarily the same in the two states, but they differ only by a Jacobian determinant, so that differential parts cancel in the ratio. That is, $df_2 = |J(\partial f_2/\partial f_1)|df_1$]. Perhaps this focus on probabilities belabors the obvious, but if one is not used to thinking of configuration spaces in these terms it may be instructive.

These formal operations are perfectly consistent with the usual presentation of the theory of simple fluids where the pair correlation function is introduced. At the beginning, the only difference between the theory of fluids and elastomers is that the former generally consist of indistinguishable particles, while the ''particles'' of the latter are distinguishable.

For our classical system the momenta and coordinates separate, and on integrating over the momenta one is left to consider the configuration space only, with the potential energy, $V(q)$, being the object of interest. Rather than retaining general coordinates, let us suppose that the potential for our elastomer is determined by the Cartesian coordinates (X, x) of cross-links, X, and mid-chain segments, x. Now fix the locations of the cross-links and integrate over the coordinates of the mid-chain segments. The formal manipulation of the volume element for this integration is $\int dq \rightarrow \int dXdx \rightarrow dX \int dx$. The probability distribution of cross-links is given by the operation described by Equation (3) restricted to the configuration space, to give

$$\begin{aligned} P(X)dX &= \exp[-\beta \hat{A}(T, X)] \exp[-\beta \hat{V}(X)]dX \\ &= dX \int_C \exp[-\beta V(X, x)]dx. \end{aligned} \quad (7)$$

where $\hat{V}(X)$ must now be identified as a potential of mean force (PMF) acting among the cross-links and $\hat{A}(T, X)$ is the configurational part of the free energy of the underlying polymer – this term having been generated by the integration over the mid-chain coordinates. [That such a term exists is seen by considering the same polymer system without the cross-links. Computation of the configuration integral for it will give this free energy for the base polymer without the $\hat{V}$ part. How closely one approximates the free energy of the un-cross-linked polymer by the $\hat{A}(T, X)$ in Equation (7) is determined by the detail that is put into the molecular description of the system. This free energy is implicitly dependent on the number of polymer units in the elastic body.] It is now asserted that the constraint on the integral in Equation (7) is such that the connectivity of the network, as well as the entanglement (over and under) relations between the chains, is preserved without permutation throughout the integration. This integral is precisely analogous to an n-particle distribution function in a simple fluid, but for a missing combinatorial factor because the cross-links are distinguishable. We are also assuming for this presentation that the network consists of a single connected component.

Now is the time to introduce a model PMF. Before doing so, it is noted that everything to this point is compatible with the highest level of atomic detail, and therein lies its justification – we would have something exact if we only knew how to compute the integrals for the complicated potentials that command our polymeric system. Of course, these integrals cannot be computed (except possibly by molecular dynamics methods), so it is required that we make an approximation for the PMF. Now, Equation (4) is completely general and works just fine for a single chain, say, in a theta solvent. If X is the end-to-end vector of the chain, then $P(X)dX \rightarrow W(r)d\mathbf{r}$ is the probability distribution of the end-to-end vector, $\mathbf{r}$. In the usual way, this is approximated by a Gaussian function for long chains (which is one of the reasons that this

treatment of elasticity is restricted to lightly cross-linked systems). This is an appropriate time to remember that the PMF is a free energy, which endows the function with non-trivial temperature dependence. For the single chain, the PMF is largely entropic, so that $\hat{V}(\mathbf{r}) \propto T$ is a good approximation for the elasticity problem, and because of symmetry, $\hat{V}(\mathbf{r})$ depends only on the magnitude, r, of the **r**vector and not on its direction. Thus,

$$W(r)d\mathbf{r} = (\gamma/\pi)^{3/2} \exp(-\gamma r^2)d\mathbf{r}, \tag{8}$$

with $\gamma = 3/2\langle r^2 \rangle_0$, is invoked from single chain configuration statistics. One might now discuss the configuration statistics of simple branched molecules, such as a three-arm star, to assert that, as a first approximation, the arms are independent of one another in a theta solvent.[2] This in turn means that the PMF for the star is the pair-wise sum of terms, one for each chain.

Given these preliminaries, it should be apparent that on assuming pair-wise additivity one may write the PMF for the elastomer as

$$\beta\hat{V}(X) = \sum_{\langle i,j \rangle} \gamma_{ij}(X_i - X_j)^2 \tag{9}$$

where the X_i are the coordinate vectors of the cross-links relative to an arbitrary origin, $\gamma_{ij} = 3/2\langle r_{ij}^2 \rangle_0$, where $\langle r_{ij}^2 \rangle_0$ is the mean squared end-to-end distance of the unperturbed chain that connects cross-links i and j, and the sum is over all chains in the network. Some chains may be dangling ends, *i.e.*, are connected at only one end. [Whether one chooses to integrate over the end coordinate or not of the dangling chains in Equation (7) is a matter of taste. If they are integrated out, one must remember their implicit effect on the number of chains connected to the cross-link to which they are attached. There are good pedagogical reasons for leaving them explicit in Equation (9).] Other chains, called loops, may be connected to the same cross-link at both ends. Chains of the latter category do not appear in the sum in Equation (6), but their effect will be found in the $\hat{A}(X)$ in Equation (7). The structure of the network may be described by a graph, in which the cross-links are vertices and chains are edges. A small representative graph is shown in Figure 1.

All that has been accomplished to this point is a formal justification for the

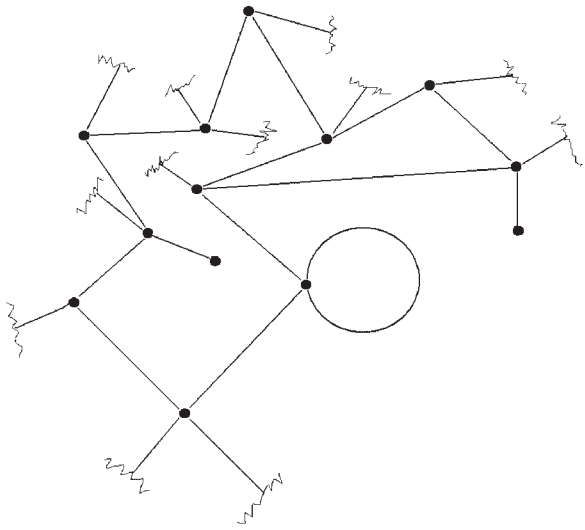

Figure 1.
A section of a representative network presented as a graph. The connections to the remainder of the network are indicated by the squiggles. Chains are represented as edges in the graph and the cross-links by vertices. This graph has one loop – the circle.

James-Guth[3–6] model of the elastomer; Equation (9) is just the James-Guth model potential. The advantage of this model over the Wall-Flory[7,8] treatment is that it explicitly acknowledges the many-body aspects, alias connectedness, of the elastomer network. The disadvantage is that it requires more sophisticated methods to extract an elastic equation of state than does the Wall-Flory independent chain model. Before turning to this topic, it will be beneficial to introduce more compact notation for Equation (9) to facilitate further development.

The quadratic form in Equation (9) can be written in matrix notation by introducing the $3 \times \mu$ matrix of coordinates, X, each column of which consists of the (x, y, z) coordinates of one of the cross-links. The number of cross-links in our elastomer is μ. The matrix of the quadratic form in Equation (9) is the Kirchhoff-Laplace (KL) matrix, K_γ, where

$$K_\gamma = \begin{bmatrix} \gamma_{12} + \gamma_{14} + \cdots & -\gamma_{12} & 0 & -\gamma_{14} & \cdots \\ -\gamma_{12} & \gamma_{12} + \gamma_{2k} + \cdots & 0 & \cdots & -\gamma_{2k} \\ 0 & 0 & \ddots & \cdots & \cdots \\ -\gamma_{14} & \vdots & & \ddots & \\ \vdots & -\gamma_{2k} & & & \ddots \end{bmatrix} \tag{10a}$$

has off-diagonal elements equal to $-\gamma_{ij}$ at location i, j if there is a chain connecting cross-links/junctions i and j, and is zero otherwise. The diagonal elements are the negatives of the sums of all off-diagonal elements in the corresponding row(column). The quadratic form is symmetric, as is K_γ. If all chains are the same length, this matrix becomes

$$K_\gamma = \gamma K = \gamma \begin{bmatrix} f_1 & -1 & 0 & -1 & \cdots \\ -1 & f_2 & 0 & \cdots & -1 \\ 0 & 0 & \ddots & \cdots & \cdots \\ -1 & \vdots & & \ddots & \\ \vdots & -1 & & & \ddots \end{bmatrix} \tag{10b}$$

where f_k is the number of chains attached to junction k (excluding loops), which is just the number of non-zero off-diagonal elements in a row(column). The matrix K is known as the Laplacian in graph theory – it is also associated with the name of Kirchhoff in its application to electrical circuits. The off-diagonal part of the KL matrix is the negative of the adjacency matrix, A; that is, $K = \Delta - A$, where Δ is the diagonal matrix of vertex degrees (cross-link functionalities), $(f_1, f_2, \cdots, f_\mu)$. With these conventions, Equation (9) may be written compactly as

$$\beta \hat{V} = \mathrm{tr}(X K_\gamma X') \tag{11}$$

where X' is the transpose of X, and $\mathrm{tr}(\bullet)$ denotes the trace of the argument. Another bit of notation is useful: $\exp[\mathrm{tr}(\bullet)] = \mathrm{etr}(\bullet)$.

The matrix K_γ is diagonalized by an orthogonal transformation with a matrix T, such that $TT' = T'T = 1$, giving $T' K_\gamma T = \boldsymbol{\kappa}_\gamma$, where $\boldsymbol{\kappa}_\gamma$ is a diagonal matrix of eigenvalues of K_γ. It will later prove convenient to arrange the eigenvalues in non-decreasing order, such that $0 = \kappa_0 \leq \kappa_1 \leq \kappa_2 \leq \cdots \leq \kappa_{\mu-1}$. The matrix has a zero eigenvalue since every row and column sums to zero. The elements of the corresponding eigenvector are constants, which corresponds to a uniform translational motion of the elastomer. The operations that accomplish this transformation to normal coordinates are simple:

$$\begin{aligned} \mathrm{tr}(X K_\gamma X') &= \mathrm{tr}(XTT' K_\gamma TT' X') \\ &= \mathrm{tr}(XT \boldsymbol{\kappa}_\gamma T' X') = \mathrm{tr}(Q \boldsymbol{\kappa}_\gamma Q'), \end{aligned} \tag{12}$$

where $Q = XT$ is the matrix of normal coordinates. Since the left eigenvector corresponding to the zero eigenvalue is

$\mu^{-1/2}(1\,1\,1\cdots1)$, it is easy to see that the corresponding component of Q is given as the simple sum of all the coordinates in X, which is proportional to a ''center of mass'' coordinate (all cross-links have the same mass for convenience of this discussion). This degree of freedom is suppressed by the constraint C on the integral; the coordinate frame is fixed in the elastic body at the center of mass. Note, however, that no other volumetric constraint need be applied. The boundary of the elastomer is free and is ultimately determined by the topology of the network!

Given a free boundary, the size and shape of the elastomer has to be defined wholly by the internal constraints. In practical situations there are external constraints, of course, such as clamps or wheel rims. One does not want to make a theory that requires specification of these constraints for every different problem. Instead, one should think of the practical constraints as deforming the elastomer in a particular way, with an attendant free energy change as determined by the probability distribution $P(X)$. But this requires a relation between the atomic coordinates and the macroscopic dimensions. This can be done by identifying the tensor $S = \mu^{-1}XX' = \mu^{-1}QQ'$ with the macroscopic shape through

$$S_{ij} = \mu^{-1}(XX')_{ij} = V^{-1}\int x_i x_j d\mathbf{r}, \qquad (13)$$

where the integral on the right is taken over the volume of the elastomer *as constrained* by the appliances. This measure of strain will suffice for our purposes, since the macroscopic deformation gradient tensor $\boldsymbol{\lambda}$ acts on both sides of this equation by

$$(\lambda S\lambda')_{ij} = \mu^{-1}(\lambda XX'\lambda')_{ij} = (\tilde{V})^{-1}\int y_i y_j d\tilde{\mathbf{r}} \qquad (14)$$

where the

$$y_i = (\partial y_i/\partial x_k)x_k = \lambda_{ik}x_k \qquad (15)$$

are the coordinates in the deformed state, and the integration is taken over the deformed volume, $\tilde{V}$, for which the volume element is $d\tilde{\mathbf{r}}$. Strictly speaking, the deformation gradient tensor in Equation (15) is defined locally, whereas that on the left of Equation (14) is global. There is a distinct advantage in a global definition of strain, for if the elastic body is heterogeneous, say with added filler or reinforcement, the evaluation of microscopic strain is extremely difficult. On the contrary, determining the macroscopic strain matrix, λ, either by experiment on a real material or through the coordinates X. is very straightforward. [It is noted one might want to consider higher moments of the shape distribution, as given by higher (preferably even) order tensors of the type $S^{ij\cdots t} = \mu^{-1}\sum_{\sigma=1}^{\mu} x_\sigma^i x_\sigma^j \cdots x_\sigma^t$, giving a more exact description of the elastomer's shape.]

The introduction of the ''gyration tensor'' S into the potential of mean force requires a polar decomposition of the configuration space. This is equivalent to the singular value decomposition that is used extensively in analytical chemistry for partial least squares data analysis. It is not difficult to show that the polar decomposition is

$$Q = \mu^{1/2}RS_d^{1/2}\hat{U}, \qquad (16)$$

where R is a 3×3 orthogonal matrix, S_d is a diagonal matrix of eigenvalues of $S = \mu^{-1}QQ'$, and $\hat{U}$ is a $3\times(\mu-1)$ matrix such that $\hat{U}\hat{U}' = 1$, but $\hat{U}'\hat{U} \neq 1$. The R matrix is a rigid body rotation, as will be seen from its action on XX' (or QQ'). The space $\hat{U}$ is called a Stiefel manifold (see any text on differential geometry, for example, p. 6 of Kobayashi and Nomizu[9]). Insertion of Equation (16) in the equation for the PMF, Equation (11), gives

$$\beta\hat{V} = \mathrm{tr}(XK_\gamma X') = \mu\,\mathrm{tr}(S_d\hat{U}K_\gamma\hat{U}') = \mu\,\mathrm{tr}(S_dU\kappa_\gamma U'). \qquad (17)$$

The omitted steps to get the successive versions of the PMF utilize the invariance of the trace to cyclic permutations, $R'R = 1$, conversion to ''normal'' coordinates, $\hat{U}$, on the Stiefel manifold by $\hat{U} = UT$, and suppression of the center of mass coordinate.

The calculation of the corresponding change in volume element is more involved,

and for completeness is contained in the Appendix. Putting the pieces together, the probability distribution to be calculated is

$$P(S)dS = G(S)\int_C \mathrm{etr}(-\mu S U \kappa_\gamma U')dU \qquad (18a)$$

where

$$G(S) = const \times \exp[-\beta \hat{A}(T,S,U)] \times |S|^{(\mu-5)/2}|S_1 - S_2| \times |S_2 - S_3| \times |S_1 - S_3| dS_1 dS_2 dS_2. \qquad (18b)$$

The factor dU is the volume element on the Stiefel manifold, and is constrained by $UU' = 1$. This space is of dimension $3(\mu-1) - 3*4/2 = 3(\mu-3)$. The switch to polar coordinates has been indicated in the free energy for the base polymer, $\hat{A}(T,S,U)$. This free energy is certainly independent of rigid body rotations, R. The Flory-Rehner[7] assumption of independence of elastic and mixing free energies would have $A(T,S,U)$ also be independent of U, leaving just the S dependence. Since the components of S are proportional to the squares of the dimensions of the elastic body, the volume, V is proportional to $|S|^{1/2}$. Therefore, in the simplest case, $\hat{A}(T,S,U) = \hat{A}(T,\mathrm{V}) = \hat{A}\left(T,|S|^{1/2}\right)$.

The integration required in Equation (18a) is difficult because of the constraint $UU' = 1$ on U. However, a good approximation to the integral is easy to come by if we make use of the structure of the KL matrix. First note that, owing to the explicit factor of μ in the exponent, only those terms with the very smallest values of $\mathrm{tr}(S\hat{U}\kappa_\gamma\hat{U}')$ will contribute. Since $S$is fixed, this in turn means that $\hat{U}\boldsymbol{\kappa}_\gamma\hat{U}'$ must be as small as possible. Since the eigenvalues are arranged on non-decreasing order, the smallest value of $\hat{U}\kappa_\gamma\hat{U}'$is obtained on the subspace where $\hat{U} = (u \quad 0)$, with $uu' = 1$. If the random network is isotropic, it is expected that the small, non-zero, eigenvalues of the KL matrix will be three-fold degenerate. [This can be verified for a simple cubic lattice. The eigenvalues are $4\gamma[\sin^2(\pi i/2n_1) + \sin^2(\pi j/2n_2) + \sin^2(\pi k/2n_3)]$ if all edges have the same weight γ. Here the n_ℓ are the number of vertices in the coordinate directions specified by the subscripts. The total number of lattice sites is $n_1 n_2 n_3 = \mu$. If $n_1 = n_2 = n_3$, it follows that the smallest, non-zero, eigenvalue is triply degenerate and has the value $\kappa_1 = \gamma\pi^2/\mu^{2/3}$.] Assume that the smallest, non-zero, eigenvalue for an isotropic random network is triply degenerate, and let its value be $\kappa_{\gamma,1} = \overline{\gamma}\kappa_1$, where $\overline{\gamma}$ is just the $\gamma = 3/2\langle r^2\rangle_0$ for the chains in the network when they are all the same length, and is an average value for this quantity if they are not.

The difficult integral is not so bad after all if we accept this approximation (which should be a very good one). By a poor-man's steepest descents it just becomes

$$\int_C \mathrm{etr}(-\mu S U \kappa_\gamma U')dU \approx \exp[-\mu\overline{\gamma}\kappa_1(S_1 + S_2 + S_3)]. \qquad (19)$$

The extension ratios are $\lambda_i = L_i/L_{i,0}$, and from the definition of the macroscopic gyration tensor, Equation (13) and (14), it follows that the right hand side of Equation (19) is just $\exp[-\mu\overline{\gamma}\kappa_1 S_0(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)]$, where, by the assumed symmetry, S_0 is the undeformed S_i, all of which are equal. Putting Equation (19) together with Equation (6) and Equation (18), gives the free energy of the elastomer (as characterized by the constraint C), as

$$A_{el}(\mu,T,S) = kT\mu\overline{\gamma}\kappa_1 S_0(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) + const + \hat{A}(T,S) - kT(\mu-5)\ln(V) - kT\ln\left[|S_1 - S_2||S_2 - S_3||S_1 - S_3|\right] \qquad (20)$$

The first term is consistent with the traditional theory of elasticity, but the remaining terms, with the exception of $\hat{A}(T,S)$, are unique to this approach. After

one more comment, all that remains of the formal theory is to average over the constraints.

The $kT\ln[|S_1-S_2||S_2-S_3||S_1-S_3|]$ term might be seen as problematical, as it can blow up for a spherical body. In fact, this term in the probability distribution prevents the elastic body from becoming *precisely* spherical. A perfect sphere (or ellipsoid of revolution) is a configuration that is found on a subspace of lower dimension, and it has zero probability in the larger space of all ellipsoids. This factor arises naturally in the transformation to polar coordinates, and it therefore applies to any object. This is, of course, related to the entropy of a system. Any nominally spherical body gains entropy if it distorts, even a little bit, from perfect symmetry. However, this distortion is scarcely discernable, since $kT\ln[|S_1-S_2||S_2-S_3||S_1-S_3|]$ is only important, say relative to a surface tension term, if at least one of the $|S_i-S_j|$ is of order $\exp(-a\mu^{2/3})$, with $a\sim O(1)$. In other words, the term is thermodynamically significant only if the fluctuation from perfect symmetry is extremely small! That is the reason we do not see its action in the macroscopic world. Conversely, it is extremely important at the microscopic level in controlling fluctuations away from symmetrical configurations. Now we can discuss the average over constraints.

Brout-Edwards Averaging

A disordered system in which the disorder is frozen on the time scale of an experiment requires a special kind of averaging that was not envisioned by the founders of statistical mechanics. Apparently this average over constraints was first recognized by Brout[10] – Edwards[11,12] explained fully how it is used for networks. The constraints that have been alluded to in the above development consist in the connectivity of the network, and entanglements may be included for the truly ambitious. During the course of an experiment the cross-linkages are fixed in the structure; if they were not, any stress would relax by Le Chatelier's principle. That happens if one averages the cross-link positions before computing the free energy.

The proper averaging is done as follows: The *a priori* probability that a system being prepared in a state specified by the gyration tensor S^* develops the set of internal constraints C_η is proportional to $\exp[-\beta^* A^*(C_\eta, T^*, S^*)]$ where $A^*(C_\eta, T^*, S^*)$ is the free energy of the system at the time of its formation ($\beta^* = 1/kT^*$). It is a function of geometrical constraints that act on the system (which we take to be specified by S^* alone, but which might be require higher geometrical moments for complete specification as discussed above), such as might be provided by a container, and during formation the cross-linkages are locked into a particular pattern, as specified by the KL matrix, for example. The different instantiations of the system are indexed by η. The system might have been, and usually is, prepared at a temperature, T^*, different from the temperature T at which experiments are performed. In any event, the probability that the system has developed the internal constraints C_η is denoted by $\mathrm{P}(C_\eta)$.

The free energy of the elastomer with the constraints C_η will now be denoted as $A_{el}(C_\eta, \mu, T, S)$. This is just the free energy that was computed above – the dependence on the constraints was not made explicit in the notation for the free energy in Equation (20), but it is implicit throughout the discussion and is implied in the presence of the eigenvalue κ_1 of the KL matrix. What we need for the Brout-Edwards average is

$$\langle A_{el}(\mu, T, S)\rangle = \sum_\eta \mathrm{P}(C_\eta) A_{el}(C_\eta, \mu, T, S). \qquad (21)$$

Now comes the magic – by formulating the statistical mechanical average correctly, we have actually made things easier for ourselves. The average demanded by Equation (21) translates into Equation (20) as

an average of the $\overline{\gamma}\kappa_1$ term, which is simply stated as

$$\begin{aligned}\langle A_{el}(\mu,T,S)\rangle = {} & kT\mu\langle\overline{\gamma}\kappa_1\rangle S_0(\lambda_1^2+\lambda_2^2+\lambda_3^2)\\ & + const + \hat{A}(T,S)\\ & - kT(\mu-5)\ln(V)\\ & - kT\ln\left[|S_1-S_2||S_2-S_3|\right.\\ & \left.|S_1-S_3|\right].\end{aligned} \tag{22}$$

What remains is the very challenging problem of evaluating a respectable average smallest, non-zero, eigenvalue of the KL matrix for an ensemble of networks that are prepared in some prescribed geometry!

Random Graphs

The problem of computing the eigenvalues of one or another of the matrices that are used to describe the connectivity of a random graph has received considerable attention from the mathematical community. There is a problem however: What a mathematician calls a random graph is not a very good model for a physical random network. The reason that the math model is not a good one is that it has no constraints on edge lengths, nor is there any condition on the spatial density of the vertices. A physical network has these constraints – edge lengths are constrained by the lengths of the polymer chains (or other objects for other kinds of networks, *e.g.*, the size of nerve cells in the case of the central nervous system), and the cross-linkages are distributed more or less uniformly in space.

A random graph consisting of μ vertices and ν edges can be connected together in any way whatsoever, but each edge must be incident on two different vertices. (One way to generate a random graph is to start with a dust of vertices and connect random pairs of them together with edges.) A random regular graph is a random graph in which every vertex has the same degree or valence δ. McKay[13] computed the eigenvalue spectrum of the adjacency matrix of a large random regular graph in 1981 following some of our initial work on this topic.[14] Graphs of this class have circuits, but almost all of them are very large. That is, the local structure of a random regular graph with degree $\delta > 2$ looks like a tree, and this is what makes the eigenvalue spectrum solvable.

The recent monograph *Random Graphs*[15] has excellent coverage of this subject. The mathematical work was initiated by Erdős and Renyi, who formulated the general theory of random graphs in 1959 (see ref. 15 for citations to their work as well as that of others), but their publications, mainly in Hungarian mathematical journals, seem not to have been widely read in the scientific community. In 1960 Erdős and Renyi found conditions for the emergence of a ''giant component'' in a growing random graph, which is just the gel transition, using techniques that were similar to the branching theory notions that were used by Flory[16] in 1941. It will come as no surprise that the mathematicians have not credited Flory with the discovery of the conditions for a gel point in what might be called *almost* regular random graphs (almost regular, because in the chemical problem the maximum degree is δ, but the average degree can be less, and will be less at the gel point).

Computer modeling of network formation[17,18] with evaluation of the eigenvalue spectrum of the KL matrix[19] has thus far offered the best insights into this problem. The particularly delicate problem of evaluating κ_1 for large networks is critical, since on the face of it there is a problem with the modulus in Equation (22). The free energy must be a thermodynamic extensive variable, and hence must be proportional to μ. However, the explicit S_0 in Equation (22) is proportional to $\mu^{2/3}$ for an approximately isotropic elastic body. The only escape from the dilemma is for the smallest eigenvalue to vary as $\mu^{-2/3}$, thereby canceling the μ dependence of S_0. This behavior is seen in computer work on the spectrum of very large networks, containing $O(10^6)$ junctions. It would be most gratifying to have a good theory for this eigenvalue – that would give the small strain modulus in all detail.

Unfortunately, this *spectrum edge* problem is in a class of problems known to be notoriously difficult in solid state physics.

Graph theory provides a useful language for describing the basic structural features of random networks, and the matrices that arise in the theory are precisely those used in some aspects of graph theory. Nonetheless, it seems that graph theory *per se* is of limited use for physical networks at the present time because there is no obvious way to incorporate metric information directly into the structure of the abstract graph, which in essence in just an incidence relation amongst points. The author knows of only one example in the mathematical literature[20] where edge length constraints have been incorporated into a graph, but the approach does not appear to be useful for our graph spectrum problem. It is likely that computer simulations will remain the best way to tackle this problem from the graph theoretical standpoint. Other mathematical approaches may offer more hope.

Random Matrices

A random matrix, for our purposes, is a square matrix with elements that are drawn at random from a specified probability distribution. This type of matrix was invented by Wigner[21] as a way to describe the density matrix for a heavy nucleus having energy levels so numerous that they can only be described statistically. For the Wigner matrix, the underlying probability distribution is a Gaussian with zero mean, *i.e.,* the off-diagonal elements k_{ij} of the matrix are random variables with zero mean and a specified variance. A tremendous amount of very high level mathematics has gone into the theory of this particular type of random matrix because of a remarkable coincidence between the statistical properties of both the eigenvalues and the zeros of the Riemann zeta function. A proof of the conjecture that the zeros of the Riemann zeta function lie on the line $1/2 + iy$ is one of the outstanding problems in mathematics, which has motivated efforts to understand the relation between the two problems. The book by Mehta[22] is the standard reference and a more recent paper by Katz and Sarnac[23] has an extensive bibliography.

The work of Tracy and Widom[24] on random matrices has been used by Soshnikov[25] to show that at the edge of the spectrum the eigenvalues go as $O(\mu^{-2/3})$. This is an exciting result, but it is uncertain that it has anything to do with the network problem. Let it simply be stated that the result is suggestive – and if conjectures about the universality of random matrices that are found in Mehta[22] are correct, this might apply to the network problem.

The formulation of a random matrix representation for the network problem clearly will involve the Gaussian, but with a twist that makes it a bit different from the Wigner conditions. The probability picture can be built up as follows: Imagine the space that the network occupies to be subdivided as a simple cubic lattice. The probability that a cell, indexed by multi-index $J = (i, j, k)$, is occupied by a cross-link is easily computed from the grid size, total number of cells, and the concentration of cross-links. One wants to choose the cell size so that there is negligible probability for multiple occupancy of a cell by cross-links. Because the cross-linking density is relatively low, it is a satisfactory approximation to take the spatial distribution of cross-links to be random (the pair correlation function is unity). The probability that an edge (chain) joins two cells selected at random is proportional to $p^2 \exp[-c(J_1 - J_2)^2]$, where p is the probability that a cell is occupied by a crosslink. The parameter c is readily computable from chain and cell dimensions (here for simplicity all chains are assumed to have the same molecular weight). In one dimension, this describes a random Toeplitz matrix. That is the reason for introducing a grid; it is a way to relate the location of matrix elements to distances. To complete the description, there is a constraint on the row and column sums – they must normalize to the average

junction functionality less the correction for loops.[26]

This construction builds a random adjacency matrix with edge constraints, and is an attractive model to begin a theory for the eigenvalue spectrum. By introducing a grid an edge length constraint is built in via the structure of the matrix. It should not be difficult to construct an algorithm to build matrices according to these rules for comparison with the discrete graphical models that have been investigated previously.[19] After all, this is a percolation model, but one in which neighbors other than the nearest can be connected. It is hoped this the model will make its way into the mathematical community where appropriate attention can be given to it.

Conclusion

It is a pleasure and honor to dedicate this work to Prof. Robert Stepto, who has inspired us all through his insightful theoretical and experimental work in polymer chemistry and physics.

Appendix

The change of volume element that accompanies the polar decomposition of the configuration space is most easily gotten from differential geometry together with some non-commutative algebra. A different method, utilizing a direct calculation of the Jacobian, can be found in Mehta,[22] pp. 56–58. The metric in a differentiable manifold is defined by the line element $ds^2 = g_{ij}dx^i dx^j$, where the summation convention is used. The matrix g is symmetric, and has determinant $|g|$. The volume element for the space defined by this metric is $|g|^{1/2}\prod dx_i$. It turns out that these relations are easier to use than a brute-force calculation of the Jacobian of the polar decomposition. Given the fact that our volume element is $d\mathbf{X} = \prod_{i,\sigma} dx^i_\sigma = d\mathbf{Q} = \prod_{i,\sigma} dq^i_\sigma$, (the Jacobian of the transformation $X \to Q$ is unity because it is orthogonal and the coordinate frame is body fixed), it follows that the associated metric is conveniently written as

$$ds^2 = \mathrm{tr}(dQdQ'). \tag{A.1}$$

Dropping the subscript d on S_d for convenience, but insisting that S is a diagonal matrix for what follows, one gets

$$dQ = \mu^{1/2}\left[(dR)S^{1/2}U + \frac{1}{2}R(dS)S^{-1/2}U + RS^{1/2}(dU)\right] \tag{A.2}$$

and

$$ds^2 = \mu\,\mathrm{tr}\left[\frac{1}{4}S^{-1}dSdS + SdU(1 - U'U)dU' + d\theta d\theta'\right] \tag{A.3}$$

where

$$d\theta = S^{1/2}\delta u + \delta r S^{1/2} \tag{A.4}$$

with $\delta u = (dU)U' = -UdU' = -\delta u'$ on account of $d(UU') = 0$, and $\delta r = R'dR = -\delta r'$ for similar reasons. To get Equation (A.3) one makes repeated use of the invariance of the trace to cyclic permutations as well as the orthonormality (one sided in the case of U) of the matrices. The term $SdU(1 - U'U)dU'$ is not easy to handle as it stands, so a shortcut is called for. Let's do this for the most general case, considering Q to be an $m \times n$ $m \leq n$, matrix having mn degrees of freedom. Then $\dim(dS) = m$ and $\dim(\delta r) = \dim(\delta u) = m(m-1)/2$, leaving $m(n-m)$ dimensions to the space with metric $dU(1 - U'U)dU'$ (this space is a Grassmann manifold – see any book on differential geometry[9]).

The shortcut is to now compute the volume element, using the symmetry of the

Grassmann manifold to infer the structure of the components of S that comes from the troublesome term. Uninteresting constants will be dropped, since they will cancel on taking ratios of probabilities to get free energy changes. Now, the $S^{-1}dSdS$ term contributes $\det(S^{-1/2})\prod_{k=1}^{m} dS_k = |S|^{-1/2}\prod_{k=1}^{m} dS_k$ to the volume element. A brute force calculation of the $d\theta$ term yields

$$\prod_{j<k} |S_j - S_k| \delta u \delta r \qquad \text{(A.5)}$$

where the $\delta u \delta r$ is left in a cryptic state for the moment. Finally, we can use the symmetry of the Grassmann term to infer that it contributes $|S|^{(n-m)1/2}dZ$, where dZ is the volume element on the space with metric $\mathrm{tr}[dU(1 - U'U)dU']$. But this can be combined with the δu term to give the complete volume element on the Stiefel manifold. Finally, the δr term is just the volume element on the space of rigid rotations [consult your favorite differential geometry book[9] for details on the Lie group $SO(m)$]. Since the rigid body rotation does not appear in the potential of mean force [see Equation (17)], this integrates to an uninteresting constant. Thus, we are left with the significant terms

$$dQ \rightarrow |S|^{(n-m-1)1/2} \prod_{i<j} |S_i - S_j| \prod_j dS_j dU, \qquad \text{(A.6)}$$

for the volume element in polar coordinates, where dU signifies the volume element on the Stiefel manifold.

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