# From Riemann's metric to the graph metric, or Applying Occam's razor to entanglements

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In 1854 Riemann prophesied: 'Either the reality underlying space must form a discrete manifold, or the reason for measurability must be sought externally, through forces acting thereon to constrain it.' Matter is in a graph-like state if its particle coordinates have been or are being randomized in all dimensions but one, by Brownian motions induced by random forces which maintain equipartition of kinetic energy. The graph-like particle generates a graph metric, which is one-dimensional and discrete. Physical theories of amorphous polymers generally evolve intuitively by embedding the particles in a three-dimensional continuum regarded as physically real, or in a configuration space regarded as an auxiliary. After integration over random coordinates, it appears that the end results no longer depend on the embedding space at all. The historical theories of amorphous polymer systems by Hermans and Kramers, Debye, Zimm and Stockmayer, Rouse, Fixman and some others may have the added advantage of demonstrating how the Riemann metric degenerates to the non-trivial graph-metric. The analysis of random networks, embedded in a three dimensional space with all the complications arising from chain entanglements, generally seems to result in small semi-empirical corrections which graph-like-state theories could readily develop without such complications. A programme for establishing a new axiomatic basis is suggested along these lines. The benefits would include not only a clearer relation between strikingly different theories and between their geometric and physical ingredients, but substantially simpler calculations and algorithms. Simplifications, especially some inspired by the achievements of Chompff and of Forsman, are briefly sketched. An analogy is drawn with the early programme culminating in the proof that, by virtue of their metric structures, the continum and discrete (matrix) formulations of quantum theory are isomorphic. It is suggested that the operator calculus of Rota, especially as recently perfected in his work with Roman, should be helpful in making explicit the isomorphism sought for the graph-like state.

## INTRODUCTION

Riemann's probationary lecture[1] in 1854 secured him the chair at Goettingen and the admiration of posterity. In it he defines a metrical fundamental form for an $n$- dimensional manifold:

$$ds^2 = \sum_{i,j=1}^{n} g_{ij}\, dx_i\, dx_j \qquad (1)$$

Later Weyl[2] remarked that the metric tensor field $\mathbf{g}_{ij}$ enters explicitly into all formulae of geometry and physics. He correctly attributes its power to the principle that in Riemannian Geometry, and in a Physics which renounces action at a distance (*Nahwirkungsphysik*), all problems are linearized by a return to the limit of infinitesimal neighbourhoods. The crucial ingredient for the physics of Riemann's deed stemmed from Gauss's *theorema egregium*, which demonstrates that curvature of a surface 'depends only on the geometry of the surface, but not on the manner of its embedding in space[3]'. The effects of freeing theoretical physics from effects attributed to space-embedding can be traced from Gauss, through Riemann to Einstein's curvature tensor and beyond.

But Riemann also pointed out in his lecture that 'either the reality underlying space must form a discrete manifold, or the reason for measurability must be sought externally, through forces acting thereon to constrain it.' Now the random forces which are postulated to produce Brownian motions generally contribute average net effects which are so simple that we might as well model suitable physical systems according to Riemann's alternative assumption, viz. a discrete manifold without use of random forces. In modern terms this can be formalized by showing that the degenerate case of equation (1) for a one-dimensional space ($n$ = 1), i.e. one component tensors, can be further simplified by discretization to a *graph* with a non-trivial metric belonging to the class already defined in graph theory. (In polymer science, this essentially entails replacing the mean-square end-to-end distance by a constant × the contour length). The dreaded loss of linearization through the renunciation of continuity across infinitesimal neighbourhoods does not materialize, because the relevant problems are now linear in any case, even over finite distances! (Paradoxically, the loss of linearity has meanwhile been stoically accepted by quantum theorists moving in projective Hilbert space[4].)

Specifically this discrete and one-dimensional formulation is applicable to systems which are totally randomized like a gas, or are in a graph-like state. We can define this state in current terminology as matter whose particles carry coordi-

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nates randomized in all dimensions but one, by past or present Brownian motion. The manner in which the embedding may be dropped here, earlier summarized in the dictum 'randomness destroys dimensionality'[5], is usually traceable to averaging procedures, based on another discovery of Gauss's, viz. the normal (Gaussian) distribution. Examples range from the most elementary to the most advanced levels. The totally randomized particle-in-the box model is usually presented to beginners in the form of a one-dimensional box. He is immediately reassured by having the partition function cubed to fit a 'proper' box. The energy of the particle is the important result ($= 3kT/2$), where the coefficient $n = 3$ gives comforting solidity, until we realize that $nk/2$ is all we measure, but not $n$ and $k$ separately.

Einstein's derivation of the displacement of a Brownian particle analogously started with the one-dimensional case ($\lambda_x = [2D_1 t]^{1/2}$), and immediately ascended to three dimensions with ease, because, like the energy levels of the particle-in-the-box, the Brownian displacement follows Gaussian statistics. But again all we can really deduce is

$$D_n = nD_1$$

and experiment does not determine $n$ and $D_1$ separately.

Turning from the gas-like to the graph-like state, Gaussian statistics bristle with incompletely systematized surprises. For instance, Graessley[6] noted as a 'fortunate simplification', the lack of dependence of his network theory on the eigenvalues of a principal-axis transformation in the relevant multivariate Gaussian. A more basic example concerns the surprising invariance law which asserts the constancy of ratios of overall statistical weights in the partition function for any pair of structural isomers in a space. Torkington[7] has generalized this law for spaces of $n$ dimensions. The condition remains the free rotation about the interunit bonds, which randomizes the coordinates in $n$-1 dimensions.

Finally, changes in the dimensions of physical quantities, attending changes in the dimensionality of a model, need not worry us. A one-dimensional gas exerts a *force* rather than a *pressure* on its walls. If an $n$-dimensional friction coefficient has to be re-scaled according to the volume ($1/n!$) of the unit simplex in $n$-dimensional space, as seems to emerge below, we provisionally accept it. We now show how Riemann's alternative recipe simplifies, in retrospect, some central parts of polymer science.

## VISCOSITY INCREMENT AND MEAN-SQUARE RADIUS OF FREE-DRAINING RANDOM-FLIGHT MOLECULES

### *Graph-like state formulation for non-cyclic (tree-like) molecules*

For the general notion of a discrete graph metric, which is simpler than that for higher dimensional continua, the reader may consult Jardine and Sibson[8]. We only need the simplest case, the direct analogue of the tensorial metric. The distance $d_{ij}$ between two points in a graph is then given by:

$$d_{ij}^2 = \left(\sum_{\mu} L_{\mu ij}^2\right) \tag{2}$$

Here $L_{\mu ij}$ is the length of the $\mu$th bond on the unique path from point $i$ to point $j$ available in a tree-like molecule. Instead of a bond length we may take the diameter of a bead, or the mean-square length of a statistical segment in variants of the model.

Light scattering yields a characteristic length, the root-mean square diameter. As in the tensor calculus generally[9], it is convenient to operate with the square length directly as the metric length. We *postulate* that what we measure for the graph-like molecule is the mean metric length of all the walks (connected non-self-intersecting sequences of bonds) in the graph. In norming this mean, the walks of length zero (from point $i$ to point $i$) must be counted, as is also appropriate in three-dimensional theory of scattering.

Thus for a molecule of $N$ atoms (beads, etc.) the postulate gives

$$\langle \overline{R^2} \rangle = \sum_{\mu,i,j} L_{\mu ij}^2 / 2N^2 \tag{3}$$

where, in a tree-like molecule the $N^2$ paths from $i$ to $j$ ($i = 1,2, \ldots N; j = 1,2, \ldots N$) are uniquely defined. This equation was first given by Dobson and Gordon[10] as a generalization (see ref 19) of the case (known in a form, which they showed to be graph-theoretically equivalent to Kramers's theorem) for equality of all the bond lengths.

The viscosity increment due to one molecule of $N$ beads per $cm^3$ of solution must depend on a friction coefficient $N\zeta^*$ and the mean metric distance of each bead from every other, including again the zero distance of a bead from itself, since even a single monomer bead produces a viscosity increment. Thus we cannot devise a simpler graph-like state *Ansatz* (postulate) than

$$\delta_\eta = \zeta^* \sum_{\mu,i,j} L_{\mu ij}^2 / 2N \tag{4}$$

Of course equations (3) and (4) agree with Debye's formula, with his three-dimensional friction coefficient $\zeta = 6\zeta^*$:

$$\delta_\eta = \zeta N \langle \overline{R^2} \rangle / 6 \tag{5}$$

A look at the history of three-dimensional theories in the next section will show that the space-embedded models yielded the same results, not as postulates, but from quite fundamental theories, which is greatly to their credit. But with hindsight we should now query if initial postulates about the embedded models, from which these results were derived with considerable labour, remain more useful than the direct graph-like postulates just applied to Riemann's alternative: a discrete manifold.

### *Brief history of the continuum formulation*

Two papers were published consecutively in 1946: (1) a translation by Kramers[11] of his Dutch paper with J. J. Hermans in *Physica* 1944, entitled 'The behaviour of macromolecules in homogeneous flow'; and (2) Debye's[12] 'The intrinsic viscosity of polymer solutions'. Kramers and Hermans start from the differential equation for the force components $X_i$, $Y_i$, $Z_i$ exerted by the liquid through a velocity potential $\psi(\mathbf{r}_i)$ on the $i$th bead, at point $x, y, z$:

$$X_i = -\frac{\partial U}{\partial x_i} - \zeta \dot{x}_i + X_i'$$

$$U = \sum_i \zeta_i \psi(x_i, y_i, z_i) \qquad (6)$$

'Here $x_i'$ is a random force of such a nature that for a free particle it would maintain the equipartition[11].' While in this postulate we recognize the recipe from which all simplifying cancellations flow, it will be interesting to show the simplifications emerge, or fail to emerge, in instalments. For a start, the factorizability just introduced allows the authors to ascend conveniently to the 6*N*-dimensional phase space with generalised coordinates and moments, with the kinetic energy given by:

$$T = a_{kl}\dot{q}^k\dot{q}^l \qquad (7)$$

where $a_{kl}$ is the Riemannian metric. The introduction of $N-1$ weightless rods (vectors $\underset{\sim}{\omega}_i$, $i = 1,2 \ldots$), each of length $|\omega_i| = L$, as constraints serves to connect the $N$ beads into a linear pearl-necklace. The 3$N$ laboratory coordinates $x_i$, $y_i$, $z_i$ are transformed into the $3N-3$ vector coordinates ($\underset{\sim}{\omega}_i = \alpha_i, \beta_i, \gamma_i$) without loss of information, since motion of the centre of gravity may be discounted. Geometry leads to

$$\sum_1^N x_i^2 = N\dot{x}^2 + (L^2/N)\sum_{\mu,\nu} g_{\mu\nu}[\dot{\omega}_\mu \dot{\omega}_\nu] \qquad (8)$$

with the components $\mathbf{g}_{\mu\nu}$ of the metric tensor in the new coordinates given surprisingly simply by:

$$g_{\mu\nu} = \begin{cases} \mu(N-\nu), & \nu \geqslant \mu \\ \nu(N-\mu), & \mu \geqslant \nu \end{cases} \qquad (9)$$

For a branched molecule the whole treatment carries through with the generalization for the diagonal elements of the metric tensor, the only ones that subsequently matter (see later):

$$\mathbf{g}_{\mu\mu} = N_1(\mu)N_2(\mu) \qquad (10)$$

where $N_1(\mu)$ and $N_2(\mu)$ are the number of beads in the two respective fragments formed by splitting the $\mu$th link of the molecule.

The solution of the flow problem is now simplest if the rods are freely hinged in analogy to Kuhn's model. The viscosity $\eta$ is found as the ratio of the appropriate component $P_{xy}$ of the stress tensor to the shear gradient $k$ along the $y$-axis for Poiseuille flow in the $x$-direction. The viscosity increment $\delta_\eta$ due to a single chain necklace (per cm$^3$) of $N$ beads is found using statistical averages over the beads thus:

$$\kappa\delta\eta = \sum_i \ln(\langle \dot{x}_i y_i\rangle + \langle \ddot{x}_i y_i\rangle) - \left\langle \frac{\partial U}{\partial x_i} y_i \right\rangle \qquad (11)$$

(Kramers points out that this expression also follows from Burger's considerations in connection with Einstein's theory of viscosity). Most of the statistical averages 'fortunately' vanish so that:

$$\delta\eta = (\zeta L^2/6N)\sum_{\mu,\nu} g_{\mu\nu}$$

$$= (\zeta L^2/6N)\sum_{\mu=1}^{N-1} N_1(\mu)N_2(\mu) \qquad (12)$$

However, this evaluation and elimination of statistical averages from the continuum treatment requires an elaborate examination of the determinant $|a_{ik}|$ of the 6$N$-dimensional Riemannian metric. Complete rigour was achieved only 30 years later by Fixman[13].

In section 7 of his paper, Kramers generalized the formalism to a branched macromolecule. The kinetic energy is again written as the appropriate bilinear form:

$$T = (mL^2/N)\sum g_{\mu\nu}[\omega_\mu \cdot \omega_\nu] \qquad (13)$$

but the branched structure of the molecular graph leads to new values for the components $g_{\mu,\nu}$ of the Riemannian metric. In a sequence of elegant moves, these components are again simplified miraculously. The form of the kinetic energy for the complex structure is shown to be equivalent to that of three particles connected by two freely hinged rods, and, 'since the $g$s are numerical coefficients, it will suffice to consider the case where the particles momentarily are lying on a straight line'. Mathematically this means that the embedding in space of high dimensionality 3$N$-3, or the initial embedding in the physical space of three dimensions, is a detour for the case in hand, since the information is fully contained in a one-dimensional subspace. Only the diagonal terms $g_{\mu\mu}$, moreover, turn out to be non-zero, and $g_{\mu\mu}$ is equal (ref 10) to the product (an integer!) $(N_1(\mu)N_2(\mu)$ of the number of mass points in the two pieces produced from the molecule by cutting its $\mu$th link ($N_1 + N_2 = N$). At this stage then, the continuous measure has become discrete. The integral trace of the metric tensor is what determines the viscosity increment:

$$\delta\eta = (\zeta L^2/6N)\sum_{\mu=1}^{N} g_{\mu\mu} = (\zeta L^2/6N)\sum_{\mu=1} N_1(\mu)N_2(\mu) \qquad (14)$$

Debye's[12] analysis of the same 3-D continuum pearl-necklace model for the intrinsic viscosity required less manipulation and detail, but led rigorously to the alternative expression:

$$\delta\eta = (\zeta/6)\sum \langle r^2\rangle_{A\nu} = (N\zeta/6)\langle\overline{R^2}\rangle \qquad (15)$$

where $\Sigma\langle r^2\rangle_{A\nu}$ is the mean square distance of the bead centres from their centre of gravity and $\langle\overline{R^2}\rangle$ that of the whole molecule. Debye's method skilfully exploits averaging procedures at an early stage of his proceedings, which are equivalent to reducing the metric to that of the graph.

The comparison of equations (15) and (16) gives a formula, called Kramer's theorem by Zimm and Stockmayer[14]:

$$\langle\overline{R^2}\rangle = L^2\sum_{\mu=1}^{N-1} N_1(\mu)N_2(\mu)/N^2 \qquad (16)$$

Zimm and Stockmayer derived this directly, again from the dynamics of a one-dimensional object, a dumb-bell, in a three dimensional embedding space. Their ingenious derivation is transcribed in Appendix A. Dobson and Gordon[10] gave a simpler derivation in which the Brownian dynamics of the random flight molecule (arbitrarily branched) are directly averaged by the familiar postulate that all subchains linking two points (segments) in the molecule have the mean-square dimensions dictated by random-flight statistics. Through the following simple step equation (17), they pass from the definition of $\langle\overline{R^2}\rangle$ [second equality in equation (15)] to equation (18):

$$\langle\overline{R^2}\rangle = \sum_{i,j} \langle\overline{r_{ij}^2}\rangle/N^2 \tag{17}$$

where $\langle\overline{r_{ij}^2}\rangle$ is the mean-square distance of point $i$ from point $j$. It then follows from random flight statistics that:

$$\langle\overline{R^2}\rangle = \sum_{\mu,i,j} L_{\mu ij}^2/2N^2 \tag{18}$$

$L_{\mu ij}$ is the length of the $\mu$th bond on the unique path from the $i$th to the $j$th point. Accordingly, Kramers's theorem became generalized to the case where the bonds may all be of different lengths, thus:

$$\langle\overline{R^2}\rangle = \sum_{\mu=1}^{N-1} N_1(\mu)N_2(\mu)L_\mu^2/N^2 \tag{19}$$

where $L_\mu$ is the length of the $\mu$th bond in the molecule. The step from equation (18) to (19) follows ('graph-theoretically') by noting that the $\mu$th bond ($\mu = 1,2 \ldots, N$) in the molecule contributes its square length $L_\mu^2$ to the triple summation in equation (18) exactly once for each of the $N_1(\mu)N_2(\mu)$ paths which pass through it. By comparing equation (5) with equations (19) and (18), we see that Kramers's metric $g_{\mu\mu}$ is nothing but the contribution made by the square length $L_\mu^2$ of the $\mu$th bond in the molecule to the total sum of the square bond lengths along all distinct linear paths in the molecule, as in equation (18).

The rationalization thus achieved in retrospect on the basis of graph theory – here very elementary – of the strikingly different-looking results of Kramers and Hermans and of Debye for $\delta\eta$ foreshadows the parallel historical sequence in the next round of developments. It is clear that if we want to proceed from tree-like molecules to cyclic and network structures, there can be walks of different lengths between a pair of points in the molecular graph. For exactly $r$ *independent* paths between points $i$ and $j$, (2) becomes generalized to:

$$d_{ij}^2 = \left[\sum_{k=1}^{r}\left(\sum_{\mu(k)}^{r} L_{\mu(k),i,j}^2\right)^{-1}\right]^{-1} \tag{2a}$$

where $k$ labels the paths. We need not pursue this here. The resulting contracton and viscosity behaviour of molecules induced by cyclization or crosslinking became rationalized in terms of relaxation spectra in the powerful theory of Rouse[15], applied in the work of many theorists listed by Chompff[16]. His own work is most pertinent to our purpose. However, Forsman[17] discovered the very direct relation between graph theory and the theories of Rouse and Zimm[18] In the next section, we build upon those foundations.

*Linear viscoelastic parameters and mean-square radii of free-draining graph-like random flight molecules*

Over two decades following the two papers by Hermans and Kramers, and by Debye, Bueche[19], Nakada[20], Tschoegl[21], Fixman[22], Harris and Hearst[23], Reinhold and Peterlin[24], Blatz[25], Chompff[16,26] and others exploited a third formula besides equations (14) and (15) for the viscosity increment, for one polymer molecule in unit volume, which is valid for non-free-draining chains as well as free draining ones:

$$\delta\eta = \mathrm{kT}\sum_{1}^{N} \tau_i \tag{20}$$

where $\tau_i$ is the relaxation time of the $i$th normal mode of the chain, in the spectrum from which all linear viscoelastic properties are derived:

$$\tau_i = \langle\overline{r_S^2}\rangle\,\zeta/6kT\lambda_i \tag{21}$$

Here $\langle r_S^2\rangle$ is the mean-square end distance of a segment (corresponding to a bond-length $L^2$ above) and $\lambda_i$ an eigenvalue of the generalized Rouse matrix (see below). Chompff[16], in reviewing these developments remarks that Debye obtained his expression (our equation 15), 'by an entirely different method', and Chompff derives, comparing equations (15), (20) and (21) the equation:

$$\langle\overline{R^2}\rangle = \langle\overline{r_S^2}\rangle \sum_{1}^{N} \lambda_i^{-1}/N \tag{22}$$

He continues by observing that this equation was confirmed by Zimm and Kilb[27]. Their derivation was a rigorous procedure of averaging over generalized coordinates using integrals in $3N$-dimensional configuration space.

Thus it was left for Forsman[17] to bring into the open the unity and simple graph-theoretical connections between the three formulae for the dynamic and scattering behaviour of arbitrarily branched random-flight polymers. It had taken 20 years after Zimm had used what in graph theory is called graph-matrix before Forsman showed its relation to the Rouse matrix, (duly generalized to deal with branching), and how the eigenvalues of the latter determine both statistical properties [as in equation (22)] and dynamic ones [as in equations (21) and (20)].

It suffices to state one graph-like-state axiom in terms of $\delta\eta$, since the extension to all linear viscoelastic parameters then follows from equation (21), which has no reference to the embedding space apart from the trivial factor 1/6. We again set $\zeta^* = \zeta/6$, and state the postulate for molecules in which all metric lengths of bonds (or mean metric lengths of segments) are $L^2$:

$$\delta\eta = L^2\zeta^*\sum\lambda_i^{-1} \tag{23}$$

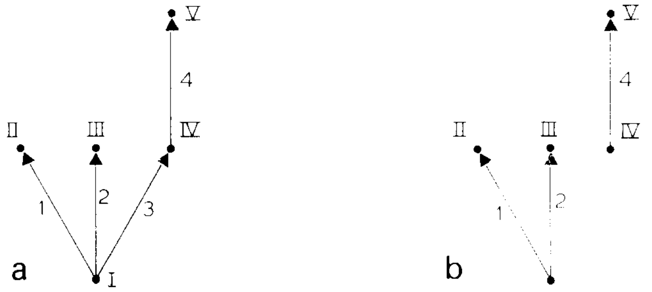


*Figure 1* (a) Random flight 2-Me-butane (carbon skeleton) as conventional rooted tree; (b) Same, disconnected by deleting arc 3

where $\lambda_i$ are the non-zero eigenvalues of the Rouse matrix.

Since a demonstration does not seem to have been given that equation (23) is compatible with the postulate, equation (4), for the special case of tree-like molecules, we now present it. As usual, a branched molecule is represented by a directed graph, rooted on an arbitrarily chosen point, and its edges oriented upwards as indicated by the arrows in *Figure 1*. Points are labelled 1,2 . . ., $N$ and arcs 1,2, . . .,$N$-1 is arbitrary fashion. Consider the incidence matrix $S$ in which the element:

$s_{ij}$ = 1, if arrow $j$ starts at point $i$

= −1, if arrow $j$ ends at point $i$

= 0, otherwise

Forsman's associated matrix is −$S$, but gives identical results since $(-S)^T(-S) = S^TS$, and, as he shows:

$$R = S^TS \tag{24}$$

is the Rouse matrix, suitably generalized to embrace branched molecules, and of order $(N-1) \times (N-1)$.

Incidentally, Forsman also points out that Zimm's[18] $(N \times N)$ matrix is:

$$Z = SS^T \tag{25}$$

Therefore all non-zero eigenvalues of $R$ and $Z$ are common to both. $Z$ is called the graph matrix in graph theory, and the product of eigenvalues of any of its principal minors counts the number of spanning tress of a graph. This theorem, with which Kirchhoff[29] initiated electrical engineering science in the first half of the 19th century, is relevent elsewhere to polymer science, e.g. in a recent treatment of the excluded volume problem[30].

The Rouse matrix $R$ for the molecule in *Figure 1* ('random-flight 2-methylbutane') is formed according to equation (24):

$$S^TS = \begin{bmatrix} +1 & -1 & 0 & 0 & 0 \\ +1 & 0 & -1 & 0 & 0 \\ +1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & +1 & -1 \end{bmatrix} \begin{bmatrix} +1 & +1 & +1 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & +1 \\ 0 & 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} 2 & 1 & 1 & 0 \\ 1 & 2 & 1 & 0 \\ 1 & 1 & 2 & 1 \\ 0 & 0 & 1 & 2 \end{bmatrix} = R \tag{26}$$

The number of points (junction points, atoms) being $N$, the number of arcs (or arrows) is $N-1$ for a tree-like graph, which is also the order of the matrix $R$ and its determinant $|R|$. Two propositions follow.

*Proposition 1.* |R| = N *for tree-like graphs.*

*Proof.* The proof is by induction. The proposition is true for the tree containing $N$ = 2 points and one arc O → O (since |2| = 2), and for O → O → O also. Any other tree can be constructed from O → O stepwise. In each step one point and one arc are added. Before each step, the points are renumbered if necessary, so that the arc to be added has its origin at the highest-numbered point (Point V was added in this way in *Figure 1a* using an arrow starting at point IV.) This ensures that the last row and last column of $R$ have zero entries, except for an element −1 in their penultimate, and +2 in their last, positions (cf ref 26). The renumbering leaves the determinant invariant because it merely induces the same permutation in both the row-set and the column-set of the determinant. Expanding the determinant $|R_N|$ of order $N$-1 reached after $N$-2 steps by its last column:

$$|R_N| = 2|R_{N-1}| - |R_{N-2}| \tag{27}$$

Thus using the induction hypothesis:

$$|R_N| = 2(N-1) - (N-2) = N \tag{28}$$

*Remark*: The element $(i,j)$ of $R$ is zero, if and only if arcs $i$ and $j$ are not incident on the same point.

*Proposition 2. The cofactor* $C_{ii}$ *of element* (i,i) *of* |R| *equals* $N_{i1}N_{i2}$, *where* $N_{i1}$ *and* $N_{i2}$ *are the number of points, respectively, in the two trees produced by deleting arc* i.

*Proof.* $C_{ii}$ is the determinant of a matrix notionally partitioned into four square blocks, by replacing row $i$ and column $i$ of $|R|$ by partitioning lines. By submitting, if necessary, the row-set and the column-set of $R$ to the same permutation (which leaves $|R|$ invariant), it is possible to reduce both off-diagonal blocks of the partitioned $|R|$ to zero, as follows from the *Remark*. The permutation is dictated by the requirement that the implicit renumbering of the points ensures that their new index numbers are such that all points in $T_1$ bear lower numbers than those in $T_2$, where $T_1$ and $T_2$ are the two trees resulting from deleting arc $i$ from the molecular graph (*Figure 1b*). The diagonal blocks of $C_{ii}$ are then the Rouse matrices of $T_1$ and $T_2$, and proposition 2 follows from proposition 1. The consistency of postulates (4) and (23) now readily ensues. By matrix algebra, the sum of reciprocal eigenvalues in (23) equals $\Sigma C_{ii}/|R|$ or, by proposition 1: $\Sigma C_{ii}/N$. By proposition 2 this equals $\Sigma N_{i1}N_{i2}/N$. By the argument of Dobson and Gordon[10], used in passing from equation (18) to (19), this in turn equals $\Sigma L^2/2N$. Equation (23) is thus transformed into equation (4) for the case $L_\mu = L$ (for all $\mu$) under consideration, if and only if the molecular graph has no cycles.

*From branched molecules to entangled networks*

It would be wrong merely to conclude that graph theory is a new technique which occasionally *solves* physical problems with economy of effort. Rather our physical *problems* themselves are mostly graph-theoretical (a rather old and elementary division of mathematics), and graph-theoretical problems can be solved by many different tools, including continuum methods and even Hamiltonian mechanics, though at a cost in effort. Chompff[16] did not succeed in disentangling the variety of methods used in our field, but he did inject the very diagrammatic techniques found most useful in pure graph theory, especially in his elegant decoupling procedure for treating networks[26]. The extension of our story to networks and entanglement theories can be done briefly. The conclusion may be summarized in advance: generally rather small correction terms have been deduced from complicated theoretical treatments, so as to correct simply graph-like state theory for steric effects supposed to arise from space-embedding. Significantly, these small terms represent pale shadows of the complicated three-dimensional topology of embedded networks, shadows which the simple unaided graph-like-state theory can readily pencil in on its own. Three examples follow from specially attractive theories in the recent literature.

(i) Forsman and Grand[31] analysed the effect of incorporating entanglement interactions between pairs of chains. The final result of the continuum (Fourier component) analysis resides in merely subtracting from the Rouse matrix $R$ a second matrix $M$. From symmetry arguments alone, they deduce that even-numbered relaxation times are unaffected altogether. Only the first few odd ones are changed, and then only a little. Later Forsman[17] himself gave the graph-theoretical interpretation of $R$ (equation 24) which will now help in looking at the second example.

(ii) Chompff and Duiser[32] showed how entanglement interactions can be modelled by a small slip parameter $\delta$ which represents a bond, between two chain units, much weaker than a covalency. If, following Forsman, we attempt to factorize $R$ into $S^TS$, what role emerges for $\delta$? We look at this factorization for n-pentane:

$$S^T = \begin{bmatrix} 1 & -1 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 1 & -1 \end{bmatrix} \qquad S^TS \equiv R = \begin{bmatrix} 2 & -1 & 0 & 0 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ 0 & 0 & -1 & 2 \end{bmatrix} \tag{29}$$

With neglect of terms in $\delta^2$, $R$ will be unchanged if we replace $S^T$ by:

$$(S')^T = \begin{bmatrix} 1+\frac{1}{2}\delta & \frac{1}{2}\delta-1 & 0 & 0 & 0 \\ 0 & 1+\frac{1}{2}\delta & \frac{1}{2}\delta-1 & 0 & 0 \\ 0 & 0 & 1+\frac{1}{2}\delta & \frac{1}{2}\delta-1 & 0 \\ 0 & 0 & 0 & 1+\frac{1}{2}\delta & \frac{1}{2}\delta-1 \end{bmatrix}$$

$$(S')^TS' \equiv R' \approx R \tag{30}$$

Now change the value $-1$ in $R$, or $\frac{1}{2}\delta - 1$ in $R'$, reserved for an element $s_{ij}$ of $S$ which represents the end of a covalency, to $-\delta$ (with $0 < \delta \ll 1$) to signify a weak interaction. Carrying this out in elements $s_{23}$ in n-pentane gives (neglecting $\delta^2$):

$$(S'')^T = \begin{bmatrix} 1+\frac{1}{2}\delta & \frac{1}{2}\delta-1 & 0 & 0 & 0 \\ 0 & 1+\frac{1}{2}\delta & -\delta & 0 & 0 \\ 0 & 0 & 1+\frac{1}{2}\delta & \frac{1}{2}\delta-1 & 0 \\ 0 & 0 & 0 & 1+\frac{1}{2}\delta & \frac{1}{2}\delta-1 \end{bmatrix}$$

$$(S'')^TS'' \equiv R'' = \begin{bmatrix} 2 & -1 & 0 & 0 \\ -1 & 1+\delta & -\delta & 0 \\ 0 & -\delta & 2 & -1 \\ 0 & 0 & -1 & 2 \end{bmatrix} \tag{31}$$

This modified Rouse matrix $R''$ is the general form obtained by Chompff and Duiser from their extensive analysis of space-embedded networks. This form is seen[32] as a submatrix in the bottom right hand corner of their equation (24). (For the stated reasons, they prefer the value of the bottom corner element to be 3 rather than 2, but this involves only a trivial change here). Along this line of argument, graph-like state theory would arrive simply at the same fitting of experimental data. The notion that non-bonded units can have weak interactions in a graph-like particle is simpler than that of a random force maintaining equipartition among particles constrained by entanglements in an embedding space.

(iii) The third example concerns the equilibrium modulus $G'$ of rubber elasticity, related to viscoelasticity as the limit $\omega \to 0$ of the storage modulus $G'(\omega)$. I no longer share the widely-held view that numerous experimental studies reliably indicate that deviations from the classical theory based on graph-like (i.e. unembedded or 'phantom') networks occur. The main reasons for scepticism have been summarized in the report with Roberts[33]. Two independent recent experimental studies, which we regarded as the most accurate, were analysed and neither, in our view, gave deviations from the simplest form of the classical theory much beyond the small experimental error. As shown by Valles and Macosko[34], their data can be fitted also to a theory embodying the best available theory for an entanglement correction, that due to Langley[35]. This fitting equally applied to the data of Roberts[33]. However, to this end the simplest graph-like state theory had to be replaced by one amended by Staverman and Duiser, who argued that the front factor in the equation of state should be changed from unity (or possibly 1/2) to $(f-2)/f$ for a junction carrying $f$ active network chains. This correction was supported and rederived by Graessley[6]. Unfortunately, we found ourselves in disagreement with the theory for changing the front factor, and stated our objection, as far as possible in terms of an argument in algebra. It is most desirable to reach general agreement on this issue.

While the magnitude of the entanglement effect, which involves a semi-empirical parameter, is thus in dispute, the form of Langley's correction term is acceptable.

The classical theory leads to the dependence $G'(\gamma) \propto (\gamma - \gamma_c)^3$ of the modulus near the gel point, where the degree of crosslinking of the graph is $\gamma_c$. Langley's theory adds a further term $\propto (\gamma - \gamma_c)^4$ from arguments which, though inspired by considering entanglements in an embedding space, visibly reduce to graph-like terms. The added term is the one following the classical term in the Taylor expansion of $G'(\gamma)$. If it is accepted as representing measurable effects, it will hardly require the complications of the embedding space for its rationalization.

## DISCUSSION

### *Comparison with quantum theory*

A lesson can be drawn by comparison with the early history of quantum theory. We may develop a choice now, between a discrete and a continuum formalism, analogous to the choice that was then consciously exercised, between the discrete matrix formalism of Heisenberg and the continuum wave mechanics of Schrödinger. Their well-known mathematical equivalence will be found explained by von Neumann[36]. He emphasizes that the properties of the discrete index-space $\Omega$ of Heisenberg and the Hilbert space $Z$ of the rival continuum theory have been found to harbour essential differences, despite laborious attempts to unify them by abstract correspondences However, if the properties of these spaces are restricted to those actually used in quantum theory, a strict isomorphism (due to Fischer and Riess[37]) does exist. von Neumann's words are: '$Z$ and $\Omega$ are very different, to fabricate a relation between them must lead to insoluble mathematical difficulties. However, $F_Z$ and $F_\Omega$ are isomorphous, i.e. they are identical according to their inner structure (they realize the same properties within different mathematical structures) and because they (and not $Z$ and $\Omega$ themselves!) are the proper analytical substrate of the matrix and wave theory respectively, this isomorphism signifies that both theories must always give the same numerical results'. Now $F_Z$ and $F_\Omega$ are sets of functions which arise precisely from the postulated metricization of the discrete and continuum spaces, respectively, i.e. sums of integrals over inner products.

The exposition of all aspects of the equivalence of the discrete matrix and continuum wave-mechanical formulations occupies just the first 100 pages of von Neumann's book. On page 101 he begins the application of quantum theory to the statistical relationships between measurable quantities, by exercising his *choice*: 'On this occasion we adopt the wave-mechanical description as our basis – the equivalence of the two theories having now been secured already.' The choice of the continuum, conditioned by history, is not always the simplest.

Compared to the proof of equivalence in quantum theory, the above demonstration of the manner in which the Riemann metric degenerates to the graph metric in the work of Kramers and Debye is sketchy. The reader is likely to prefer the axiomatic basis underlying the differential equation (6) of of Kramers to the direct postulation of equation (6) of Kramers to the direct postulation of equation (23), even though it is based on a simpler metric and has eigenvalue-form, familiar from the axiomatics of quantum theory. It is sensible to prefer generality of axioms to any spurious simplicity. It may be thought that to simplify equations by integrating over random motions is one thing, to sever the axiomatics for the physics of amorphous materials from the Hamiltonian laws of motion is quite another. But my purpose is to stimulate interest in reformulating the axioms with ever greater generality by providing at least a sketch. Besides, the 'disappearance' of motion during the recasting of the axioms has a distinguished precedent in the general theory of relativity where, in Einstein's[38] phrase, 'physics turns from a *process* in three dimensional space into a *state* in the four-dimensional 'world' '. How to achieve generality in a new axiomatics based on the graph metric, for one graph-like state of matter, with the abandonment of the embedding function of a space (which Einstein quite generally regarded as an empty concept[39]) is the important problem. (For instance: how do Maxwell's electromagnetic equations behave in the discrete metric used here for rationalizing determination – by light-scattering – of $R^2$?). In the final section, I describe the modern mathematical machinery which seems to me most likely to be effective in this whole problem.

*Towards a unification of physical theory by an operator calculus*

Although examples of the reformulation in terms of graph-like-state models could be multiplied, the general implications for the foundation of physical theory remain an enormous and challenging problem for the future. The often surprising identity of solutions obtained from models based on multidimensional continua with those of their discrete graph analogues, suggests isomorphisms of the two underlying operator algebras (as in quantum theory, see above). After all, the solution of the mathematical problems depends, as always, on the inversion of some operator as a formal working tool. To render explicit the algebraic structure of our tool kit is a worthwhile task for young theoreticians who are searching for improvement in rigour as well as economy of effort.

The task is rendered specially topical by quite recent work of Rota[40]. This has culminated[41] in a complete characterization of the isomorphisms linking the linear functionals (as used in continuum formulations) with former power series (e.g. generating functions arising in discrete formulations). The results cannot adequately be summarized here: they have implications in mathematics generally, e.g. by rendering the umbral calculus of the 19th century rigorous for the first time, or by recasting diverse classical theories of the calculus of finite differences into a systematic whole. From our viewpoint, the following brief catalogue may whet some healthy appetites: the relations between a functional and its associated and conjugate sequences of polynomials of binomial type are specially suggestive. As Rota points out, this concept of binomial-type sequences can serve *inter alia* to generalize compound Poisson processes; such processes are intimately connected with models of amorphous matter. Hermite polynomials form one example of binomial-type sequences, and they are frequently encountered in Brownian motion and in polymer theories. Abel polynomials[43] are intriguingly connected with Treloar's[43] formula for the end-to-end distance of a random-flight chain. Laguerre polynomials are a third instance, which Roman and Rota[41] connect with Feynman diagrams. Among a number of concrete combinatorial results derived by Roman and Rota at the end of their exposition, Cayley's tree-counting formula emerges from five lines of the simplest algebra. This formula was needed recently for the combinatorial analysis underlying the excluded-volume of polymer chains[44].

Philosophical implications of this paper can safely be postponed to a future occasion. Suffice it to say, that since Kant's Critique of Pure Reason, many leading physicists have considered a three-dimensional space with a continuous metric to be an ineluctable ingredient of the physical world itself. It has not proved to be a necessary ingredient of numerous physical models of the world. Einstein wrote[45]: 'If you wish to learn from the theoretical physicist anything about the methods which he uses, I would give you the following piece of advice: 'Don't listen to his words, examine his achievements. For to the discoverer in that field, the constructions of his imagination appear so necessary and so natural that he is apt to treat them not as the creation of his thoughts but as given realities'.'

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I am grateful to Professor Ziabicki for pointing out his arguments for doubting the general applicability to all kinds of networks of the 'Chompff and Duiser[32] theory. However the case of equation (31)(above) was merely intended to be illustrative of the power of graph-like models to simplify derivations, and this kind of matrix does simulate important features of observed spectra. I also thank Professor Slonimsky for drawing my attention to his 1948 paper on viscoelasticity with Kargin[46]. This paper not only gives the 'Rouse' matrix implicitly, and its spectrum explicitly, but, in equation (8), anticipates an important special case of the 1955 WLF transform. Reference to the Kargin–Slonimsky paper, which I understand was based on Slonimsky's PhD thesis, is missing from the generous review of the work of these two authors in the Encyclopedia of Polymer Science and Technology[47]. This review is notable for formulating the theory of viscoelasticity in terms of the calculus of continuum operators.

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## APPENDIX A

The following derivation of Kramers' theorem (see section 2 above) is copied from reference 14. It represents a solution to a graph theoretical problem by mechanics:

'Then the mean square radius of the molecule is given by

$$R^2/b^2 = \langle N_1 N_2 \rangle_{Av}/N \tag{35}$$

where the average in the second member is taken over all possibilities of cutting. The derivation of this theorem is briefly as follows: for any molecule, $\Sigma r_i^2$ may be expressed as a quadratic form $b^2 \Sigma_d \Sigma_k \lambda_{jk} (\sigma_j \cdot \sigma_k)$ where $\sigma_j$ is a unit vector along the $j$th bond and the $\lambda_{jk}$ are numerical coefficients. Closely related is the relative kinetic energy with respect to the centre of mass, given by

$$m \Sigma \dot{r}_i^2/2 = mb^2 \Sigma_j \Sigma_k \lambda_{jk} (\dot{\sigma}_j \cdot \dot{\sigma}_k)/2$$

where $m$ is the mass per chain atom. Consider now a special instantaneous phase of the molecular motion such that the relative kinetic energy happens to be simply $(mb^2/2)\lambda_{jj}(\dot{\sigma}_j)^2$; this would be the case if only the $j$th link were rotating, all others performing translations only. But then the relative kinetic energy is equal to that of a rotating diatomic molecule with masses $mN_1$ and $mN_2$ connected by a rod of fixed length $b$, and this equality gives $\lambda_{jj} = N_1 N_2/N$. Now if the molecule contains no rings, $\langle \sigma_j \cdot \sigma_k \rangle_{Av} = \delta_{jk}$ for flexible chains, and hence $R^2/b^2 = \Sigma_j \lambda_{jj}/N = \langle N_1 N_2 \rangle_{Av}/N$.'