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(41) As pointed out to us by Dr. K. Kubota, the first exponential within the curly brackets of eq A1 was printed with an incorrect minus sign. Also, in the expression for a_0 a factor 13 is missing from the third term and is now correctly displayed in eq A3.

Universality of the Stockmayer Distribution[†]

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ABSTRACT: The molecular distribution function for random *f*-functional polycondensates was derived by Stockmayer in 1943 and has since found wide applications. He used a brilliant variational argument, in which the consideration of motion of model particles in space was not required. Recently, several groups have tried to refine the argument and then to generalize the model in terms of a spatial version of statistical mechanics. Although we are concerned with liquid systems, in which only vibrational modes are usually taken to generate the equation of state, successful generalizations of the Stockmayer distribution have been based on partition functions using explicitly only translational or only rotational motions of the particles! A fundamental explanation of such statistical equivalence of mechanical models generally requires an invariance principle, based on group symmetries. This is here applied, and the useful role of the rotational version (among equivalent spatial or nonspatial versions) is shown to lie in the ease with which it harmonizes with current visualizations of chemical kinetics and of configurational processes in polymer science. The mean-field treatment absorbs any detectable excluded-volume correction in its adjustable parameter (the free energy change in forming a bond). The modern approach to gelation via bond-percolation models on multidimensional lattices does not raise new philosophical issues but is shown to involve seriously faulty molecular (cluster) distributions for gelling systems, to which such models should not be applied.

1. Introduction

Stockmayer[1] published the formula for the equilibrium weight fraction distribution $w(x)$ of a random *f*-functional polycondensation (RFFP) system only 2 years after this new model had been presented to polymer science by Flory:[2]

$$w(x) = [(fx - x)!f/(x - 1)!(fx - 2x + 2)!]p^{x-1}(1 - p)^{fx-2x+2} \quad (1)$$

Here, $w(x)$ is the weight fraction of x-mer, f the functionality of the repeating unit, and p the equilibrium fractional conversion. This result and its implications have aroused tremendous interest and elicited applications in fields including not merely gelation but vapor/liquid equilibria,[3,4] the structure of water in solutions in hydrocarbons,[5] and, recently, immunology.[6,7]

Many authors have been stimulated to generalize the theory in various directions, especially toward dynamics. Whittle's[8] stochastic formulation accounts for compositional fluctuations, while Donoghue and Gibbs[9] succeeded in averaging over fluctuations in *finite* systems. Recently, Stockmayer himself, with Burchard and Schmidt,[10] used advanced techniques for harmonizing the characterization of the molecular architecture of randomly branched systems with their dynamic molecular behavior in terms of diffusion coefficients, first cumulants, hydrodynamic mean square radii, etc. The elimination of the preaveraging approximation for the Oseen tensor was a specially welcome feature.

Yet when Stockmayer originally derived eq 1, he did not define a mechanical model from which statistical properties could be calculated by analyzing particle motions in space. Instead, he employed brilliant intuitive shortcuts, avoiding the need to mention space or motions in his paper.[1] His analysis is amply confirmed by experiments, apart from minor amendments whose need was already indicated by Flory and to whose theoretical developments Stockmayer contributed, e.g., in his paper with Jacobson[11] on ring-chain competition for the case $f = 2$. Most confirmations,[12] but not all,[13] were concerned with kinetic (irreversible) gelation, to which eq 1 also applies.[1,7] Authors who have tried later to deepen the statistical-mechanical analysis by cutting out the intuitive shortcuts include Gordon and Judd,[14] C. Cohen et al.,[15] and R. J. Cohen and Benedek.[16] Of these, the last-cited paper does not introduce space or motion either; its analysis does not go beyond Stockmayer's in the direction of interest here. Gordon and Judd use the rotational partition functions of the molecules and remark that the "translational factor of the partition functions are not relevant to condensed polymer systems and are omitted". Cohen et al.,[15] on the other hand, assign to their particles translational motion and no others. Meanwhile textbooks of statistical mechanics typically asserted[17] that "translational and rotational terms disappear in the partition function and are replaced by vibrational terms" in the liquid state (in which RFFP is carried out). Accordingly, a fundamental explanation is required.

In conformity with the practice followed from nuclear physics to cosmology, I propose to define as *fundamental* an explanation which establishes an invariance principle on the basis of group symmetries, in order to demonstrate

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[†] To Stocky, with high regards, for his 70th birthday.

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the statistical equivalence of mechanical models. Here only discrete groups of finite order will be involved, and I will start by deriving eq 1 from the statistical mechanics of molecules moving in three-dimensional space, using only sophomore mathematics, specifically avoiding the calculus or analysis of limits. When I come to compare Stockmayer's theory of gelation with so-called modern theories based on scaling of continuous functions and renormalization based on continuous groups, an interesting result emerges: not only the critical exponents but the discrete Stockmayer distribution (1) as a whole are invariant to dimensionality of the space which the particles may be assumed to explore by their motions.

Key concepts and equations are collected from our previous papers[18-21] to specify a partition function (section 2) and to derive therefrom the Stockmayer distribution (section 3).

2. Specification of the Canonical Partition Function

Exactly two kinds of statistical weights are given to each treelike condensate species: (i) p for each of its interunit bonds (if any), i.e., for each link introduced by the condensation reaction, and $1 - p$ for each of its unreacted functionalities (equireactivity assumption); (ii) one factor r, being the number of its distinct rotational states, when one of its points is fixed in space.

Weights of the first kind, under (i), are partly *energetic* and partly *entropic* in character. They are related to the bond free energy ΔF rather inelegantly; thus

$$p = (2\exp(-\Delta F/kT) + 1 - (4\exp(-\Delta F/kT) + 1)^{1/2})/(2\exp(-\Delta F/kT)) \quad (2)$$

because then the statistical weight of an interunit bond relative to the weight of two unreacted functionalities becomes

$$p/(1-p)^2 = \exp(-\Delta F/kT) \quad (3)$$

as it should (see section 4.2 for volume dependence). This amounts to a choice of the arbitrary reference level for the bond energy, which makes p the equilibrium fractional conversion of functionalities. The statistical weight r, under (ii), is purely *entropic*, because no allowance is made for energy differences between rotational isomers nor explicitly for an excluded-volume potential (see section 4.4). Instead, we are dealing with freely rotating *phantom* chains, which helps to justify ignoring summation over momentum space.

The proof that the specified partition function implies the Stockmayer distribution (eq 1) is conveniently visualized in terms of the formal self-condensation of methane,[22,23] with elimination of dihydrogen, to produce a mixture of alkanes (which is at equilibrium for the specified partition function). Then the monomer methane may be represented by a tetrahedron, and a typical octamer (octane) is shown in Figure 1. The same proof and diagram extend immediately to a case like the polyetherification of pentaerythritol $C(CH_2OH)_4$ by elimination of water, since all bonds (here of types C–O or C–C) which freely rotate in both monomer and polymer species can be contracted away, because they do not bias the polycondensation equilibrium.

3. Derivation of the Stockmayer Distribution from the Specified Partition Function

(a) Tetrahedral Units. Our choice of energy zero implies that the statistical weights for the $x - 1$ links and the $fx - 2x + 2$ free functionalities in any x-mer produce the total (for equireactive functionalities):

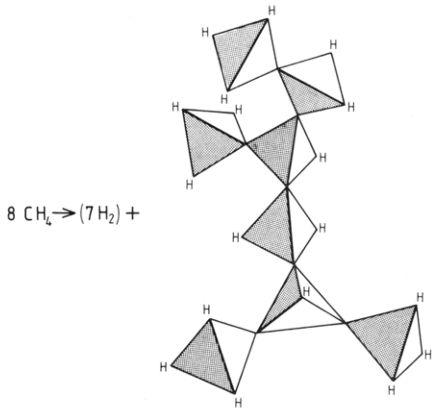


Figure 1. Formal polymerization model for methane and free-rotation model of a typical octane produced.

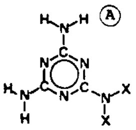
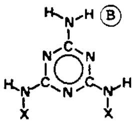
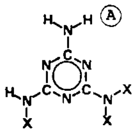
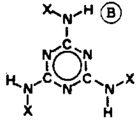
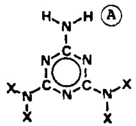
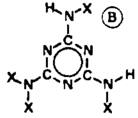
$$e(x) = p^{x-1}(1-p)^{fx-2x+2} \quad (4)$$

which occurs also as a factor in $w(x)$ (eq 1). Purely from the rotational partition function in its zeroth (equienergetic) approximation, the combinatorial degeneracy factor remains to be found (see (ii) above). This needs no calculus, provided we "quantize" the rotational states, as is familiar from the next higher approximation, the rotational isomeric state theory.

In the paradigmatic case of tetrahedral centers (Figure 1), we shall, therefore, count only those states in which one constituent tetrahedron (called the *starter*) of every x-mer species ($x = 1, 2, ...$) has its edges parallel to directions which remain fixed in space throughout (and similarly for cubic, octahedral, etc. centers, if used as starters). This starter tetrahedron rotates about its fixed center to generate the external rotational states of our particular x-mer molecule. The remaining tetrahedral centers will then generate the internal rotational states by rotating about all the interunit links they carry. First we imagine the corners of all the polyhedra in the molecule to bear distinct labels, so that all these links and all the free functionalities are treated as distinguishable. Then the number of rotational states is P^x/f^{x-1} for an x-mer consisting of x labeled polyhedra with f (=4 for tetrahedra) corners and symmetry number P (=12 for tetrahedra), because we may build up the molecule starting with any one of its labeled polyhedra as starter, which may be oriented in P ways, rendered distinct by the labels on its corners. We then add the remaining $x - 1$ polyhedra one by one so that each one is bonded either to the starter or to the requisite polyhedron added previously. (The corner to be bonded to a previously added polyhedron is predetermined by the distinct labeling of the corners which unite to form links.) Each of the latter $x - 1$ polyhedra can be oriented in P/f ways (=3 for a tetrahedron, just as in isomeric rotational state theory).

The second move is called delabeling. When all the labels are removed from a molecule of the ith isomer class of the x-mer, any two previously distinguishable orientations (rotational states) of our x-mer become indistinguishable, if they are related by one of its $R(i,x)$, say, symmetry operations. This symmetry number is best thought of as the number of ways in which the unlabeled molecule, here the ith isomer of the x-mer fraction, can be superposed upon itself after operating on it with any distinct combination of external and internal (bond) rotations which are available. (The identity operation, which does not use any rotation at all but merely replaces the

Table I
Proof of Symmetry Weights[45] Using Equilibrium Data[44]

compound X = CH_2OH	symmetry no. *R*	no. of data	mean measured concentration ratios: symmetry weighted $[A]R_A/[B]R_B = y$	unweighted [A]/[B]
	16	6	0.284 ± 0.057	0.071
	4			
	4	18	0.265 ± 0.031	0.398
	6			
	16	10	0.261 ± 0.042	0.066
	4			

molecule as it was must be counted and is always available even for totally unsymmetric molecules.) For instance, the rotational symmetry number $R(i,x) = 81$ for the octamer in Figure 1, i.e., one factor of 3 for each of its four (freely rotating) methyl groups. No external rotation operation is available to superpose this molecule on itself, none of the four methyl groups being equivalent by symmetry. For examples of molecules with internal and external symmetry and their symmetry numbers, see Table I.

The only variable in counting the rotational states of the whole class of (structural and/or stereo) isomers, e.g., for the 22 distinct octamers—one of which is shown in Figure 1—is precisely the delabeling factor $1/R(i,x)$. The number of rotational states for the whole x-mer set after delabeling is therefore

$$r(x) = (P^x/f^{x-1})\sum(1/R(i,x)) \qquad (5)$$

This is easily evaluated in terms of f and x, provided each molecule rotates as a whole and provided that (for dimensionality >2) all the polyhedric centers are connected at corners by freely rotating bonds, because then the *fundamental principle of dimensional invariance*[19] applies, here in the form

$$P^x\sum(1/R(i,x)) = (f!)^x\sum(1/G(j,x)) \qquad (6)$$

Here, the symmetry number P of the monomeric polyhedron on the left is replaced by $f!$, the symmetry number of the (one-dimensional) monomeric graph, on the right. Analogously, the summation on the left goes over the reciprocals of the rotational symmetry numbers $R(i,x)$ of the x-mers embedded in three-dimensional space, while on the right $G(j,x)$ is the symmetry number, i.e., the order of the automorphism group, of the (unembedded, one-dimensional) graph of the jth structural isomer. Equation 6 reveals surprising properties of space especially for copolymers of different centers,[19,24] here more weakly illustrated by the fact that the summations on the two sides generally go over different numbers of terms; e.g., for the octanes $i = 1, 2, ..., 22$, while $j = 1, 2, ..., 18$. This arises because 2,2,3-trimethylpentane and 2-ethylhexane each have one molecular graph but two enantiomorphs with identical symmetry numbers in three-dimensional space, and 3,4-dimethylhexane has one graph but three diastereoisomers in three-dimensional space with variable symmetry numbers. Equation 6 is valid[25] for $R(i,x)$ in any number of dimensions d and not merely[19,24] for $d = 1, 2$, and 3. The number of distinct octanes returns to 18 if $d \geq 4$.

(b) Copolymers of Different Centers. To evaluate $\sum(1/G(j,x))$ on the right of eq 6 requires only the most elementary aspects of Pólya's counting theory.[26] We use the opportunity to generalize eq 6 to embrace copolymers from x_i ($i = 1, 2,...$) units of any kind of symmetry and having symmetry number P_i and functionality f_i (=1, 2,...), as illustrated before for tetrahedra and cubes:[19,24]

$$P_1^{x_1}P_2^{x_2}\ldots\sum_k(1/R(k,x)) = (f_1!)^{x_1}(f_2!)^{x_2}\ldots\sum_j(1/G(j,x)) \qquad (7)$$

when all bonds connecting paris of units with functionality >2 rotate freely and where the total number of units is

$$\sum_i x_i = x \qquad (8)$$

(Stockmayer himself already generalized[1] eq 1 for binary copolymers of bifunctional and polyfunctional units). Combining eq 1 and 2 (the latter is proved elsewhere[21]) of Gordon and Leonis[20] and correcting the misprint in their eq 1 by removing the factorial sign from $(y - 1)!$, we obtain, in the present notation, for a total of y (including monofunctional) units

$$\sum_j(1/G(j,y)) = (y-2)!/\prod y_i![(f_i-1)!]^{y_i} \qquad (9)$$

For the straightforward case of RFFP, we have x centers of valency f and $fx - 2x + 2$ centers of valency unity (free functionalities), so that $y - 2 = fx - x$. Thus eq 9 completes our derivation with the result of Gordon:[18]

$$\sum_j(1/G(j,x)) = (fx-x)!/x!(fx-2x+2)!((f-1)!)^x \qquad (10)$$

Substituting this into eq 6 and the result into eq 5, we have obtained the entropic statistical weight $r(x)$ for an x-mer, which was required. By combining $r(x)$ with the energetic weight in eq 4 and multiplying the result by a further weight x to pass from number fractions to weight fractions, we discover that we obtain the Stockmayer distribution (1), which is already normalized to unity for all p. To prove this normalization requires higher level mathematics than we have needed in order to derive merely the relative weights. Stockmayer himself proved the normalization in his Appendix B, eq B1 and B10. He used generating function methods still far from familiar to chemists at the time, but since popularized through the rise of graph theory.

Surprisingly, eq 10 entails that asymptotically, for $x \to \infty$, $\sum(1/G(j,x)) \to 0$ if $f > 4$, but $\to \infty$ for $f = 3$ or 4. I omit the demonstration that p actually represents the fractional conversion of functional groups, which is easy with a little differential calculus. The existence and magnitude of the gel conversion and the failure of the normalization condition beyond that conversion can be shown without calculus.[27]

4. Discussion

Four facts emerge from the above derivation:

(i) By including individual isomeric species within the x-mer fraction in the partition function rather than giving the x-mer fraction its overall weighting, we have refined the treatment in an important direction. See section 4.1.

(ii) The available *option* of assigning to the rotational partition function a controlling role over the chemical equilibrium is paramount for harmonizing the interpretation of equilibrium measurements with the great bulk of polymer science and especially with kinetic data. See sections 4.3 and 4.6.

(iii) Our treatment allows the *equivalence* of Stockmayer's and other formulations of RFFP to be demonstrated by the mathematical invariance principle (eq 6) and thus to clarify which explicit assumptions of different models are reflected in, and testable by, experimental data. See section 4.3.

(iv) The same invariance principle allows a fruitful comparison between Stockmayer's formulation and the nonequivalent lattice percolation model. See sections 4.5 to 4.7.

4.1. Refinement of the Stockmayer Distribution to Individual Polymer Species. Since the neglected free energy changes due to substituents introduced by the condensation reaction itself (section 4.6), as well as those due to cyclization (section 4.5), generally differ from isomer to isomer within any x-mer fraction, their exact treatment requires prior refinement from x-mers to their isomers.

For historical continuity, this refinement can simply be shown directly within the framework of Stockmayer's original derivation, i.e., finding the most probable distribution, rather than the mean distribution derived from a partition function. Stockmayer defined a quantity w_n, which I will rename $A(x)$, as the "number of ways in which x polyfunctional units, each bearing f distinguishable equivalent functional groups,...can be formed into a single polymer molecule" without introducing cycles. He showed that

$$A(x) = f^x(fx - x)!/(fx - 2x + 2)! \qquad (11)$$

To refine this quantity to the number $A(i,x)$, the number of ways of forming from the same set of x labeled polyfunctional units bearing labeled functional groups, merely the ith isomer in the x-mer fraction (instead of one replica of each of the isomers), requires the following simple argument: If the isomer has no symmetry elements, it can be formed in $A(i,x) = x!(f!)^x$ ways, where the factor $x!$ arises from permuting the x labeled units and each factor $f!$ from the permutation of the functional groups borne on one unit. All the $A(i,x)$ unsymmetric molecules thus put together differ only in their labeling schemes. If, however, the unlabeled isomer is not totally unsymmetric but features $G(i,x)$ distinct symmetry operations, $A(i,x)$ becomes reduced to

$$A(i,x) = x!(f!)^x/G(i,x) \qquad (12)$$

because the symmetry operations split the original $x!(f!)^x$ distinct replicas—formed in the absence of symmetry—into $G(i,x)$ equivalence classes, each containing $x!(f!)^x/G(i,x)$ members which have become indistinguishable by the removal of the labels. Now sum the last equation over i to obtain

$$A(x) = \sum A(i,x) = x!(f!)^x\sum(1/G(i,x)) = f^x(fx - x)!/(fx - 2x + 2)! \qquad (13)$$

by comparison with eq 11. By solving the last equality for $\sum(1/G(i,x))$, we recover eq 10, now proved directly from Stockmayer's scheme. The proof shows the relation to the term $\sum(1/G(i,x))$ in graphlike-state partition functions of Stockmayer's quantity $A(x)$ (which he denoted w_n). Its calculation was clearly the most difficult part in his derivation of his distribution. He acknowledged help from Maria Goeppert-Mayer, who, with her husband and Brunauer, had proved 10 years earlier[28] that rotational symmetry numbers are required by quantum statistics as factors in partition functions. The argument we have used for refining $A(x)$ to $A(i,x)$ is the simple basic ingredient underlying Pólya's powerful contribution to chemistry (as well as to mathematics) entitled "Combinatorial Counts of Groups, Graphs and Chemical Compounds", which had appeared in a mathematical journal[26] only 6 years before. Understandably, Dr. Goeppert-Mayer did not notice the implicit connection between her earlier work[28] and Stockmayer's combinatorial problem. Later, by a kind of feedback, theories familar to chemists (e.g., steady-state kinetics) allowed[20] a greatly simplified mathematical proof of Pólya's main chemical result to be given, viz., the asymptotic number of structural isomers of the alkanes C_xH_{2x+2} for large x. The price paid for the simplification was either in terms of wider error bounds than Pólya's own or else a loss of proven bounds for an error in a plausible estimate, which Pólya's method shows to be extremely close to the truth! The simplification involved eliminating all recourse ot the calculus, apart from invoking the first two terms of Stirling's approximation. Pólya's original and beautiful proof comprised 17 pages of calculations involving the properties of improper Riemann integrals and steepest descent methods, which in one place he called tricky ("heikel").

4.2. Role of Volume Dependence. So far we have neglected the well-known volume dependence of RFFP equilibria. Three points arise here: the illusory belief that a purely three-dimensional model is essential, the conventional association of volume dependence with the translational factor in the overall partition function, and the question of the generalization of RFFP to allow for an excluded volume.

Implicitly, we have contracted eq 3 by absorbing the volume ratio term required in the full form:

$$p/(1 - p)^2 = (V_0/V)\exp(-\Delta F/kT) \qquad (14)$$

into the free energy for forming a bond as the corresponding entropy contribution:

$$(V_0/V)\exp(-\Delta F/kT) = \exp[-\Delta F + kT\ln(V_0/V)]/kT \qquad (15)$$

(where V_0 is some reference volume). Even if ΔF could be measured or calculated independently of the volume-entropy term, no experiment could prove that this term corresponds to a space which is specifially three dimensional, because the accepted value of Boltzmann's constant already contains the assumed dimensionality[29] 3 of "physical space" as a factor which—despite appearances to the contrary—is not verifiable experimentally. In particular, if space is assumed to be one-dimensional, the constant takes the value $3k$, as follows by comparing measurements on an ideal gas with the model for a particle in a one-dimensional box. The factorization was mentioned already by Ehrenfest[30] in terms of the specific heats of a monatomic gas.

The conventional inclusion of the volume as a factor in the translational partition function and its experimental verification do not exclude alternative nonspatial formulations (for the "existence" of space, see section 4.7). Textbooks show how this factor combines with the correction $1/N!$ for the translational symmetry number to reduce the volume dependence to a mere density dependence, equally applicable for one-dimensional particles. It is shown in section 4.3 that the experimental evidence actually excludes effects due to particle translation in polycondensation equilibria.

4.3. Equivalence of Seemingly Different Mean-Field Models. Our derivation of the Stockmayer distribution (1) assigns to each species a weight which includes as a factor the reciprocal rotational symmetry number (5). The Mayers and Brunauer proved the need for such a factor in 1933 from the quantum theory of particles moving in space.[28] The invariance principle (6) shows that the weighting arises equivalently (but more generally) from the structure of the molecular graph and independently of any assumption of a space of any number of dimensions. Implicitly, Stockmayer's combinatorial derivation exploited this simplification which rests on reduction in dimensionality. Cohen and Benedek[16] follow Stockmayer closely in this respect, as many other have done.

But our derivation showed that the particles were fixed in space, and no allowance for translation was included, such as is factored out of the overall partition function of a particle as the familiar term $\Lambda = (2\pi mkT/h^2)^{1.5}$. Any factor $m^{1.5}$ involving the mass m of a polycondensate molecule, if thrown into the partition function we have derived, would cause the number average to diverge at the gel point (see section 4.4), which is at variance with experiment. Particle translation is thus proved to be inapplicable. Yet such a factor is introduced by Cohen et al.,[15] who nevertheless demonstrate full agreement with Stockmayer's distribution (1)! This paradox is now resolved.

These authors' purpose was to clarify Stockmayer's analogy between gelation and vapor condensation. Underlying the analogy is the recognition that there is no sharp separation between the weak "bonds" formed in liquefaction and strong covalent bonds. But vapors obey models including translational motion, while liquid polycondensates evidently do not. The critical condensation point is clearly just at or near a border between model validities. Cohen et al.[15] employ the device due to Hill,[31] whose rationale is seen in a new light in our context. In the critical region where translational degrees of freedom yield to vibrational ones, we should not use the *approximation* of factoring the overall partition function into overall translational and overall vibrational motions. Hill and Cohen et al. assign the familiar translational factor to the monomer particles but integrate the partition functions of all remaining particles over all positions in space of their constituent monomer particles (under central pairwise potentials as usual).

This leaves the Stockmayer distribution unchanged. The monomer/x-mer equilibrium constants are weighted by a factor Λ^x or $x\Lambda^{x-1}$, which gets appropriately hidden in the bond free-energy weight. The same is true of the vibrational degrees of freedom of the bonds, whose effects are not, therefore, detectable by nondynamic experiments on equilibrium systems.

The treatment of Hill and Cohen et al. is equally illuminating in its approach to the connection between the kinetics of chemical reactions and the equilibria which they approach. Chemical reactions in polymer liquids require statistical factors (end of section 4.6) in respect of reaction sites within a molecule equivalent under rotational symmetry. Indeed these factors for the forward and backward reactions always combine to produce the rotational symmetry numbers in the equilibrium partition functions, as first proved by Gordon and Temple.[32] Thus in modeling chemical kinetics in liquids as processes in space, rotations matter, even when in smaller molecules, external rotations are too slow to contribute on the time scale of the equation of state. In macromolecules bond rotations dominate everything.

4.4. Excluded-Volume Effect: Mean-Field and "Modern" Theories. The proven invariance principle (eq 6) makes the mean-field theory universal in respect of dimensionality, but not in respect of anything else. Modern scaling and renormalization group methods, which claim to have superseded the Flory–Stockmayer mean-field model for gelation (for reviews, see de Gennes[33] and Stauffer et al.[34]), have led their supporters to the opposite conclusion: dimensionality is the important variable, while the constancy of all other results that seem important (especially critical exponents) is *assumed* by a hypothesis of universality. Stauffer et al.[34] have concluded that "At present, we do not know which theory is more suitable for which materials". The novice must be surprised that after so much effort, experimentalists have failed to settle the choice between two such opposing formulations! The answer lies in the difficulty of verifying critical exponents[12,35,36] and the formal impossibility,[37] for reasons of a mathematical nature, or falsifying theories relevant to them. The general malaise about "*asymptopia*" (a blending of *asymptotics* with *utopia*) is apparent when Stauffer et al., in their generally very fair review, discuss the famous question "how close [to the gel point] is close?". They also suggest, on the basis of model-dependent criteria, that coverage by data of one or a few decades in $p - p_c$ should be sufficient. Wherever these decades may be picked out by the experimentalist's data, one thing is mathematically certain: he is always an *infinity* of decades away from p_c itself in his log–log plot (which automatically projects the critical point to minus infinity). Stauffer et al. regard the model for random uniaxial ferromagnets described by Liebmann et al.,[35] which delivers crossover regions "extending over 100 to 1000 decades", as an extreme case. But the mathematical analysis of the general process of model refinement in the direction toward the critical point shows that a few minute adjustments in the model Hamiltonian,[37] rapidly decreasing below the limit of experimental significance, will extend any crossover region over arbitrarily many decades. This renders exponents unfit for discrimination between physical models by experiment; no two *physical* models differ "qualitatively" in measurable exponents.

A fundamental analysis of the excluded-volume problem is, however, important just because intuition is a source of theory. The formulation of the Stockmayer distribution in a nonspatial and therefore nondimensional form of statistical mechanics appears to do some violence to physical intuition, since it is equivalent to treating a three-dimensional (or n-dimensional) ensemble of *phantom* chains. However, the excluded-volume effect, which seems so important to intuition, is absorbed in the parameter ΔF, or p (eq 3). Thus if we imagine the presumed excluded-volume potential to be suddenly switched on, the exphantom system will substantially depolymerize, because large molecules will feel exponentially more uncomfortable than small ones. But the new distribution will not differ, in a currently detectable way (see next paragraph), from that obtained by heating the phantom chain system so as to produce the same degree of depolymerization. This is only one illustration of the motto "randomness destroys dimensionality".[38] An analogous effect has been emphasized over many years by Flory, in the face of its counterintuitive appearance, viz., the compensation of effects which give rise to "undisturbed" dimensions in bulk rubbers, gels, and even concentrated solutions, an effect which is contravened by the percolation model (section 4.5).

Unperturbed dimensions are reflected in the familiar random flight law ($\overline{R^2} = nL^2$), which, like the Stockmayer distribution, is universally valid in all dimensions.[38] If, as I have argued, any realistic excluded-volume potential is merely absorbed in ΔF, when added—according to taste—to a spatial interpretation of the mean-field model, the claim[33] that the classical theory works universally only in spaces of dimension $d > 5$ is wrong.

The (nonutopian) asymptotics $x \rightarrow \infty$ of eq 1 give, with Stirling's approximation and neglect of terms $\mathcal{O}(1/x)$

$$n(x) \simeq w(x)/x \simeq k_1 x^{-2.5} \exp(k_2 x) \qquad (f > 2) \quad (16)$$

for the number fraction $n(x)$ of x-mer, where

$$k_1 = f[(f-1)/(2\pi(f-2)^5)]^{0.5} \exp(+Q) \quad (17)$$

$$k_2 = (f-1)\ln(f-1) - (f-2)\ln(f-2) - Q + f \ln[((4\exp(-Q)+1)^{0.5} - 1)/(2\exp(-Q))] \quad (18)$$

with

$$Q = \Delta F/kT \quad (19)$$

(Equation 16, with different constants given by Pólya[26] for k_1 and k_2 allows $n(x)$ also to represent simply the asymptotic number of different isomers of the x-mer fraction. This reveals again the fundamental connection between the theories of Pólya and Stockmayer.) One easily checks that according to eq 18, 19, and 3, k_2 vanishes and changes sign from negative to positive as p increases through the *Flory gel point* ($p_c = 1/(f-1)$), which signals the *loss of normalizability* of $w(x)$, i.e., the appearance of the gel fraction.

On the basis of a variety of theories, e.g. Kesten's,[39] one may speculate that the leading factor in the appropriate mean-field correction for the excluded-volume term in the overall statistical weight of an x-mer is of form $\exp(-k_3 x)$. If so, the form of the Stockmayer distribution (1) is not changed. An essentially stronger convergence factor, say $\exp(-k_3 x^z)$, with $z > 1$, would prevent gelation.

Next consider a lower order weight of form x^q supposed to be contributed by an excluded-volume effect, which would leave the Flory gel point, as predicted by eq 1 and confirmed by ample data, unchanged. Although we expect the value of q to be negative, note the great sensitivity to a positive value of the number-average degree of polymerization at the gel point:

$$\mathrm{DP}_{\mathrm{nc}} = \sum n(x) x^{1+q} / \sum n(x) x^q \qquad (\text{with } k_2 = 0\text{; cf. eq 16}) \quad (20)$$

If $q \geq {}^1/_2$, $\mathrm{DP}_{\mathrm{nc}}$ would *diverge*, contrary to all evidence, which goes back to Carothers. A weight x^q, even as weak as $q = -{}^1/_2$, is incompatible with observation:[40] from the obvious preaveraging approximation, such a weight is estimated to reduce $\mathrm{DP}_{\mathrm{nc}}$ by a factor of about ${}^1/_2$ ($f = 4$) or about $3^{-1/2}$ ($f = 3$) relative to the results of eq 1.

4.5. Why Bond Percolation Is a Poor Model for Gelation. The claims of "modern" theories, typically based on scaling arguments applied to bond percolation, are motived as follows: (i) The distribution of polycondensate molecules are to be represented by a set of percolation clusters, because (ii) these can be embedded together in a regular lattice graph, which (iii) in turn can be embedded, in a topologically and metrically smooth manner, in $\mathbf{R}^3$ (Euclidian three-dimensional space), and—most importantly—(iv) such a space characterizes the real world (see section 4.7).

Burchard[41] has pointed out some weaknesses of the percolation model approach to gelation. These models do generate cyclic species directly (see c, Figure 2), but generally in the wrong proportions for gels.[12] Stockmayer[42] showed in 1945 how the usually rather small correction for cyclization can be made by extrapolation to zero reciprocal concentration. The spanning-tree approximation was later shown[12,13,41] to predict satisfactorily the slope and intercept of the extrapolation line by an argument based on configurational statistics of molecules such as are modeled in Figure 1.

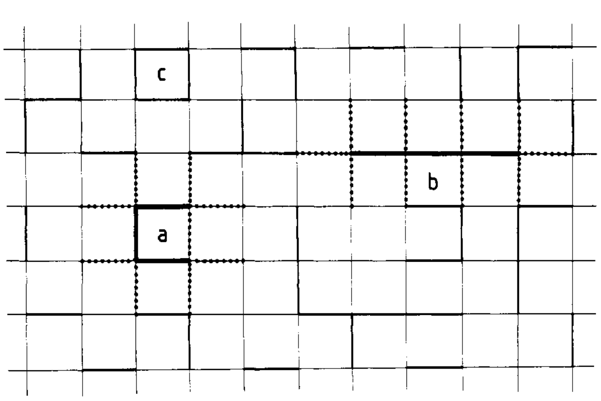


Figure 2. Percolation model: (a) compact "rotamer" of trimer cluster; (b) extended "rotamer"; (c) a cyclic species.

Next consider the most important claim of modern theories, namely, that they avoid a mean-field approximation by providing exact summations over all states, a refinement held to be required by the physical behavior of systems near their gel points. Unfortunately, the exact summations would be an advantage only if the statistical-mechanical model represented at least approximately the distribution of chemical species occurring in gelling systems. However, the requirement of embedding the clusters together in a regular lattice graph amounts to imposing entropic "potentials" which distort the cluster distribution out of the range of usefulness for gelling systems. The distortion can appropriately be illustrated by the two-dimensional square lattice, although that model does not give the "universality" class claimed to be applicable for gelation in chemistry. The use of a diamond lattice for the same illustration would bring out the same trends but would require much larger clusters than those shown in Figure 2.

It emerges immediately that the clusters of a lattice model in two or more dimensions do not behave like molecules in polymer science. The ratio of the concentration of two rotamers is seen generally to vary with conversion, so as to cause only the most compact forms to survive in the limit of full conversion (the bond probability, which takes the place of p, going to unity). This collapse, far below undisturbed dimensions, is not, however, observed. Even more unrealistic are the parallel shifts of concentration ratios of structural isomers, of which again only the most compact forms survive in the same limit. These consequences of the packing requirement imposed by embedding the molecules as clusters in lattice graphs follow easily from inspection of Figure 2. The two rotameric trimers shown have statistical weights proportional to

$$p^3(1-p)^9$$

and

$$p^3(1-p)^{10}$$

respectively, so that their concentration ratio indeed goes as $1/(1-p)$, varying with conversion and finally eliminating b in favor of its compact rotamer (a). Compared to the molecules with familiar structures illustrated in Figure 1, compatible with Stockmayer's mean-field theory, those in Figure 2, belonging to the lattice percolation model, do not generate a chemically or physically acceptable behavior. The number of free functionalities of the clusters, which are available to x-mers for intermolecular reaction, varies from rotamer to rotamer, from isomer to isomer, and with conversion.

Bond percolation is a model of great mathematical beauty and of very wide interest in physics. To cancel from the list of its physical applications the gelation of polyfunctional systems is therefore a relatively minor matter. Within the restricted framework of polymer science, it is, however, in my view a rather urgent item for action in order to unblock further progress in modeling the physical chemistry of gels. To this end, the imagined weaknesses of the classical mean-field treatment must first be recognized to constitute, on the most fundamental plane (as defined in the Introduction), its real strength. In the next section, the opportunities arising for this future progress within the classical theoretical framework are sketched by way of a positive example of the fine tuning of the thermodynamic analysis of data, made possible through modern spectroscopic techniques. The final section 4.7 briefly recalls the historical tradition by which the renewed progress could once again be sustained.

4.6. Literature Data by Tomita[44] Verify Symmetry Theory, Constancy of Isomer Ratios, and Substitution Effect. This section tries to show how (a generalization of) eq 1 can and should be verified and how the correction of even energetically minute deviations can be approached in terms of standard (indeed canonical[22,23]) model refinement procedures. Such procedures start at low conversions, far from the gel point of a system.

NMR measurements by Tomita have earned the 10-member family of melamine and its methylol derivatives nomination[45] for the thermodynamically most accurately characterized family of compounds throughout chemistry. This system generalizes the RFFP model to a copolymerization of a hexafunctional (melamine) with a monofunctional one (formaldehyde), as long as the reactivity of the second functionality of formaldehyde remains suppressed.

Recently, Tomita's data covering a 30 °C range of temperature and a tenfold range of the parameter that corresponds to p in RFFP, viz., the fractional conversion of melamine hydrogens to methylols, were analyzed by Gebregeorgis.[45,46] He showed that deviations from equireactivity could be reconciled with a single parameter y, whose optimized value makes tertiary amino hydrogens less reactive than secondary ones by 480 J/mol at infinite dilution in water. Tables showing the fit, almost always within experimental error, of the measured concentrations of all ten members of the family are too long to reproduce here. How accurately these measurements reflect the dependence of concentrations on symmetry numbers is shown in Table I. This verifies the theory of partition functions given by the Mayers,[28] a theory polymer scientists have sadly neglected.[45] The test in the table is based on the principle[47] of constancy of ratios $[\mathrm{A}]R_{\mathrm{A}}/[\mathrm{B}]R_{\mathrm{B}}$, where [A] and [B] are concentrations of two isomers and R_{A} and R_{B} their respective symmetry numbers. The successful test also illustrates how the refinement of the Stockmayer theory to isomeric x-mers (section 4.1) opens the way to correcting simply and accurately, but by equally neglected procedures, the energetically minute deviations from equireactivity (viz., from $[\mathrm{A}]R_{\mathrm{A}}/[\mathrm{B}]R_{\mathrm{B}} = 1$), which would not be accessible otherwise.

The resolution of symmetry numbers into statistical factors of forward and backward rate constants (see end of section 4.3) underlying[32] chemical equilibria, introduced[47] in the 1960s, has also recently[45] been illustrated and summarized for melamine and urea resins.

4.7. How Modern Is "Modern"? de Gennes insisted that, despite the correct prediction of the gel point by classical theory, "the behavior near the threshold ($p \rightarrow p_c$) *must* differ widely from the predictions of the classical theory" (my italics).[33] Scaling laws derived from the percolation model are, as a result, so different that "we might be tempted to skip a description of the classical theory"[33] which "is so poor in practice".[33] (The analysis of the meager experimental evidence for these judgments has been critized.[12]) The "source of the difference between the *real* exponents and their mean field values"[33] (my italics) is seen as the "fact that our world has a value of ... $d = 3$" for its dimensionality.[33] This fact also underlies the $4 - \epsilon$ expansion of renormalization group theory, which forces the "small" perturbation parameter ϵ heuristically to tend to unity.

However, was this fact about our world not known to Hermann Weyl[48] when he wrote in 1919: "But only the liberation from the restriction to a specific dimension number, [i.e.] the formulation of the laws of nature in such a form that in relation to them the dimension number appears as something *fortuitous* [his italics], becomes our guarantee that we have completely succeeded in their mathematical penetration."? The invariance principle of eq 7 extends this relativization of space to an essential part of statistical mechanics. Ehrenfest, who took the development of statistical mechanics over from Boltzmann, wrote the paper already cited[30] a year before Weyl. It was entitled "What part does the 3-dimensionality of space play in the basic laws of physics?" He gives examples like that of a moving electron which would, in dimensions 5, 7,... generate strong singularities. This followed from the model for the electron available to him, but he failed to realize how sensitively model-dependent this, and his other examples, were. They did not deflect Weyl from his program. In any case, Ehrenfest had the required insight to find questions like "Does space exist?" or even "Why does our space have exactly three dimensions?" as shocking (anstössig) in form and regarded his remarks as elementary and widely known. Such unanimity among physicists was somewhat precarious, because, 2 years later, Poincarê was to observe "everyone knows that space is relative, or rather everyone says so, but how many people still think as if they believe it to be absolute".[49]

Essentially the same battle had been fought and apparently unanimously settled on the mathematical level by pure mathematicans a 100 years earlier. Bolzano[50] put it very clearly, and in a form which directly applies to the proven mathematical equivalence of spatial and nonspatial formulations of the statistical mechanics of gelation: "for it is self-evident that a truly scientific proof, or the objective reason for a truth, which is valid for all quantities, whether they are [embedded] in space or not, cannot possibly lie in a truth valid only for quantities [embedded] in space". He mentions that there had already been deliberate elimination by mathematicians of analogous faults in hundreds of proofs.

Accordingly, I now summarize my argument. The combinatorial factor in eq 1 has previously been shown[24] to be equal to that number of distinct node-rooted planar x-mer trees of the relevant structure.[18] Alternatively, in this paper, it is proved to be also identical with the number of distinct rotational states of the same trees when embedded in three-dimensional space, or indeed in spaces of any number of dimensions. Of the two alternative representations, the former is simply the degenerate two-dimensional case of the latter. Bolzano's principle explains why, from the point of view of fundamental science, the degenerate case is to be preferred. It makes fewer assumptions. Elsewhere,[29] I have illustrated how the Riemann metric of spatial versions of polymer theories reduces to the degenerate (and discrete) graph metric and indicated the need and opportunities for further theoretical work.

By understanding the mathematical relationship between the two descriptions in terms of the invariance principle (eq 6 and 7), we are enabled to exploit more effectively our guiding spatial intuitions. The exclusion of the calculus (and hence all convergence problems) from the proof of that principle is to be contrasted with renormalization group theory and, more specifically, the $4 - \epsilon$ expansion. Such continuum theories do not lay claim to mathematical rigor and are now often reduced to seeking their validation by tests against physical measurements. The dangers of this procedure have been pointed out.[12,37] It seems likely that some of the impressive heuristic shortcuts taken by renormalization group theorists in physics will in time be validated by mathematical rigor also. The residuum, if any, of differences between mean-field and "modern" predictions concerning gels, which are actually susceptible to testing by physical measurements, will then become clear.

In particular, if the claim is granted that the graph-like-state description not only is equivalent to the model of phantom chains but also theoretically allows for the excluded-volume effect (section 4.4), at least as far as can be ascertained by the current precision of measurements, it should contribute to rehabilitating the mean-field modeling of gelation. Much exciting work is found in the recent literature on the physics of critical phenomena, but I have seen no discovery of facts which were not known to Weyl, Ehrenfest, Pôlya, and their contemporaries and which prove in a statistically acceptable manner that the three-dimensional nature of the universe has become a mandatory ingredient of scientific models for gelation. Instead, I suggest that Pôlya's "modern" theory and Bolzano's "classical" principle combine to demonstrate the true universality of the work of Walter Stockmayer.

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