Table VI
Crossover pH Values from N7 to N1 Coordination[a]

	adenosine	inosine	guanosine
CH_3Hg^{+} [b]		4.3	5.6
$dienPd^{2+}$	1.5	6.1	
Ni^{2+}	~2.1	7.1	7.8
Cu^{2+}	2.3	6.1	6.9
Zn^{2+}	2.7	6.7	7.5

[a] Reprinted with permission from: Kim, S. H.; Martin, R. B. *Inorg. Chim. Acta* **1984**, *91*, 19. Copyright 1984, Elsevier. [b] Calculated in ref 4 from results of: Simpson, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 2059.

>3. At pH >4.5 the [N1]/[N7] molar ratio for adenosine is given by the antilog of the values in Table V.

Conclusions

The strong log stability constant vs. pK_a correlations provide the vehicle for estimating metal ion stability constants at nucleic base sites of established pK_a. The results for the N1 to N7 binding ratio in purine nucleosides are summarized in Tables V and VI. For adenosine Table V shows that the N1 to N7 binding ratio is 320 for the proton, 3 for Ni^{2+}, 2.5 for Cu^{2+}, and 1.0 for Zn^{2+}. Thus Zn^{2+} is distributed equally between the adenosine N1 and N_7 sites in neutral solutions.

N7 coordination in purine nucleosides predominates at low pH and gives way to favored N1 coordination at higher pH. Table VI shows for the three aqueous metal ions that the crossover pH for N7 to N1 coordination occurs from pH 2.1 to 2.7 for adenosine, pH 6.1 to 7.1 for inosine, and pH 6.9 to 7.8 for guanosine. Thus for all three purine nucleosides aqueous metal ion binding at both the N7 and N1 sites is important in neutral solutions.

The conclusions should be applicable for metal ion interactions to nucleic bases in single-stranded polynucleotides. For double-stranded helices, N3 of pyrimidines and N1 of purines are blocked by specific base pairing, paving the way for relatively greater N7 interactions with metal ions.

Polymer Excluded Volume and the Renormalization Group

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Roughly half of the American chemical industry is involved with polymers, and the study of polymers is obviously relevant to the understanding of a variety of biological systems. Theories of polymer properties in solution and the melt pose complicated mathematical problems because polymers have long-range cooperative interactions of both intramolecular and intermolecular character. Whereas these problems were untractable for many years, new theoretical developments now enable the approximate description of wide variety of large-scale polymer properties in a manner which can be tested by experiment.

An important aspect of the practical utilization of polymers and the understanding of their properties centers upon the determination of their physical properties in the limit of infinite dilution. No complete description of more concentrated solutions is possible until this foundation is laid. Experimental methods of polymer characterization include light scattering, osmometry, sedimentation, viscometry, etc. When the polymer concentration c approaches zero, osmometry provides a determination[1] of the molecular weight M of the polymer, while small-angle light scattering yields the polymers' radius of gyration R_G. The limiting slope of light-scattering intensity vs. c in the zero-angle limit gives the polymer second virial coefficient[1] A_2 as a measure of the effective volume that a polymer excludes to others. The translational diffusion coefficient D is written for $c \to 0$ using Stokes' and Einstein's laws[2] in terms of a hydrodynamic radius[1] R_H as $D = kT/6\pi\eta_0 R_H$, where T is the absolute temperature, k is Boltzmann's constant, and η_0 is the solvent viscosity. If η is the viscosity of the polymer solution, the intrinsic viscosity $[\eta] = \lim_{c \to 0} (\eta - \eta_0)/c\eta_0$ gives another estimate of the volume occupied by a single polymer chain.[1]

All of these large-scale measurable properties of polymers provide different measures of the overall size and shape of the polymer. They are frequently observed to vary with polymer molecular weight with a power law form KM^b, where the proportionality factors K and the exponents b are dependent on polymer, solvent, and temperature. It is the goal of a comprehensive theory to explain this variation of K and b with system and temperature over the full experimentally accessible range.

Theoretical Models

For the description of large-scale polymer properties like R_G, A_2, D, and $[\eta]$, it suffices to employ apparently simple models,[1,3] which capture the essential large

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(1) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971 and references therein.
(2) Stokes, G. G. *Trans. Cambridge Philos. Soc.* **1851**, *9*, 8. Einstein, A. *Ann. Phys. (Leipzig)* **1906**, *19*, 289; **1911**, *34*, 591.
(3) Rouse, P. E., Jr. *J. Chem. Phys.* **1953**, *21*, 1272. Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.

length scale characteristics of long chainlike molecules, where many of the microscopic details of the polymers become irrelevant. For instance, one widely used polymer model treats the chain as having the configuration of a random walk with effective monomer units sequentially numbered 0, 1, ..., n at the spatial positions $r_0, r_1, ..., r_n$. Obviously no two monomers on the chain can occupy the same space, so even the simple random walk model must be amended to contain volume exclusion effects. This polymer excluded volume effect introduces the essential mathematical complexity into the description of polymer properties.

Theories of the effects of polymer excluded volume have utilized the simple "two-parameter" model[1] in which the bonds between effective units $r_j - r_{j-1}$ have a Gaussian length distribution with a rms value of l. In addition, there is a repulsive contribution to the free energy when a pair of segments occupies the same position in space.[4] Hence, the dimensionless (free) energy associated with a chain conformation $\{r_k\}$ is taken as

$$H = (d/2l^2)\sum_{j=1}^{n}|r_j - r_{j-1}|^2 + (\beta_0/2)\sum_{i \neq j=0}^{n}\delta(r_i - r_j) \qquad (1)$$

with β_0 the volume excluded by an effective segment due to the presence of another and d the dimensionality of space, three in ordinary space and two for polymers confined to a surface. The first term on the right-hand side in (1) represents the entropy of the polymer chain conformation associated with the many degrees of freedom of internal motion in the coarse grained effective units.[1,3-5] Equation (1) implicitly assumes the presence of a large number of these units. Retention of only this term yields the simple Gaussian chain model of polymers at the theta temperature θ, a model for which the large length scale polymer properties are readily calculated. The entropic or elastic energy accounts in the model for the connectivity of the polymer chain.

The second term on the right hand side of (1) converts the simple Gaussian chain model into a true many-body problem since this second term contains a pairwise sum over all effective monomer units. Describing polymer properties with the full energy (1) has been termed the polymer excluded volume problem. The analysis uses standard statistical mechanics[1,4,5] where the probability density for obtaining the chain conformation $\{r_k\}$ is proportional to Boltzmann weight e^{-H}. Note that (1) contains the temperature- and solvent-dependent parameters l and β_0. For nonzero concentrations there is a term like (1) for each polymer with excluded volume interactions between all pairs of monomers on different polymers.

We emphasize that (1) does not provide a true microscopic description of the polymer structure and interactions on a monomer length scale. Hence, when we derive universal large-scale laws for polymer properties, their explicit dependence on the separate model parameters l, n, and β_0 are combined together into phenomenological constants in order to describe *real polymers*. This combination is possible because the same form of the universal laws would emerge from

more realistic models with the resultant phenomenological constants of the universal laws being different functions of the parameters of this new model. Thus, the computed dependence of the parameters on l, n, and β_0 *is not to be taken literally* as if the model (1) is a complete representation of reality. Experience has shown that (1) *suffices* to determine the universal laws for uncharged polymers over a wide range of experimental conditions. A fuller understanding of the theoretical questions posed by these universal laws emerges from a brief summary of some of the previous theoretical analyses.

Given the simple Gaussian chain description of the long random walk polymer and the complexity introduced by the excluded volume, it is natural to take the Gaussian chain as a zeroth order approximation and to compute polymer properties by expansion in powers of β_0. This produces the excluded volume perturbation theory[1] which is predicated on the hope that β_0 is somehow small enough. Very near θ, this theory to order β_0 with β_0 treated *empirically* is quite successful in explaining experimental data,[1] but it quickly breaks down away from θ for the following reason: Excluded volume perturbation theory is readily shown[1] to be an expansion in the dimensionless quantity $\beta_0 l^{-d} n^{\epsilon/2}$ with $\epsilon = 4 - d$. Hence, for high-molecular-weight polymers, n is large, and the expansion is in a large parameter as long as $\beta_0 l^{-d} > n^{-\epsilon/2}$ and $d < 4$. Hence, the perturbation theory alone is of little use except for $T \simeq \theta$ where the empirical β_0 vanishes.

Flory has introduced a uniform expansion model[4] based upon the zeroth-order approximation $H_0 = (d/2l^2\alpha^2)\sum_{j=1}^{n}|r_j - r_{j-1}|^2$, containing the expansion factor α which is determined variationally by minimizing the approximate free energy of the polymer chain. The uniform expansion model is very successful in describing the qualitative swelling of the polymer's dimensions as the strength of excluded volume increases, but it is deficient in a number of respects arising presumably from an inadequate representation of fluctuations. Flory's approach and the self-consistent methods generalizing it[5-7] are variational treatments for the pairwise interacting monomers much in the same spirit as self-consistent field methods for molecular electronic structure.

Much information concerning polymer excluded volume has been gained from computer studies[8-11] of self-avoiding or interacting random walks on lattices using enumeration[9] and Monte Carlo methods.[10,11] These calculations suffice to show that the asymptotic variation of, say, R_G with n for $n \to \infty$ is of the form $R_G^2 \propto n^{2\nu}$ with 2ν very close to the Flory value[6,7] of $6/(d + 2)$ for $1 \leq d \leq 4$ and $2\nu = 1$ for $d \geq 4$ independent of lattice details. Lattice computations are useful because they must lead to the same universal large-scale laws as models like (1), so these computer studies yield important data on the polymer properties to aid in the

(4) Flory, P. J. "Principles of Polymer Chemistry"; Cornell Press: Ithaca, NY, 1953.
(5) Freed, K. F. *Adv. Chem. Phys.* 1972, 22, 1.

(6) Edwards, S. F. *Proc. Phys. Soc., London* 1965, 85, 613. Edwards, S. F.; Singh, P. *J. Chem. Soc., Faraday Trans. 2* 1979, 75, 1001. Muthukumar, M.; Edwards, S. F. *J. Chem. Phys.* 1982, 76, 2720.
(7) Kosmas, M. K.; Freed, K. F. *J. Chem. Phys.* 1978, 68, 4878.
(8) (a) Domb, C. *Adv. Chem. Phys.* 1969, 15, 229. (b) Barrett, A.; Domb, C. *Proc. R. Soc. London, Ser. A* 1981, 376, 361. (c) Domb, C.; Barrett, A. *Polymer* 1976, 17, 179.
(9) Tanaka, G. *Macromolecules* 1980, 13, 1513.
(10) Teramoto, E.; Kurata, M.; Chujo, R.; Sujuki, C.; Tani, K.; Kajikawa, T. *J. Phys. Soc. Jpn.* 1955, 10, 953.
(11) Wall, F. T.; Erpenbeck, J. *J. Chem. Phys.* 1959, 30, 634.

construction of full analytical theories. Lattice and computer-assisted analytical methods[12] can also generate higher order terms in the perturbation expansion which provide additional useful checks on analytical calculations.

Early renormalization group (RG) approaches,[13-18] designed originally for critical phenomena in magnets, fluids, etc., and heuristic scaling theories[13b,19] of polymer excluded volume have been adopted to describe polymer properties only in the asymptotic scaling limit where polymer properties have power law forms like $R_G \propto N^\nu$ with exponents like ν having universal, polymer, solvent, and temperature independent values. These first RG methods are couched in the obscure terminology of magnets and field theory and are deficient because they do not describe the properties of polymers in the experimentally important nonscaling limit where effective exponents vary with excluded volume.

There are a wide variety of renormalization group approaches[14-18,20,21] which appear on the surface to be quite different but which produce the same final results because identical physical considerations are effectively incorporated. Wilson style[22] RG explicitly introduces a coarse graining transformation[17,21] with subsequent scaling to define the RG transformation. A more powerful set of techniques for polymer excluded volume is provided by the direct RG methods[14-16,20,23,24] whose origins lie in the field theory renormalization methods originated by Gell-Mann and Low[25] for quantum electrodynamics.

Our recent progress[20,21,23,24,26-31] with describing polymer excluded volume involves applying the latter RG methods[32,33] *solely in polymer language* to the traditional polymer model (1) without analogies to magnets or field theory. This chain conformation space RG theory has been designed for polymers to address the important problem of treating the full excluded volume, temperature, and molecular weight dependence of large-scale polymer properties.

Here we provide a brief heuristic description of the chain conformation renormalization group treatment

of polymer excluded volume solely within the framework of the model (1). Our aim is to outline the basic physical concepts underlying the theory, its achievements and even its difficulties. An emphasis is placed on the so-called crossover regions where the effective exponents b in the molecular weight dependence M^b are functions of polymer, solvent, and T. The full theory[20,24,26] as well as extensive comparisons with experiment[31] are contained in a series of papers which describe the computational schemes.

Motivation for the Renormalization Group

A continuous polymer chain limit[5] is utilized in which the effective units in (1) may be viewed as the discrete representation of the continuous chain conformation $\mathbf{r}(\tau)$ with τ measuring the "distance" along the chain $0 \leq \tau \leq N_0 = n_0 l$ and $\mathbf{r}_j = \mathbf{r}(jl)$ being the discrete model. It is also convenient to use a set of variables $\mathbf{c}(\tau) = (d/l)^{1/2}\mathbf{r}(\tau)$ such that d and l do not explicitly appear in the configurational Hamiltonian $\mathcal{H}$ which now becomes[20]

$$\mathcal{H}[\mathbf{c}(\tau)] = \frac{1}{2}\int_0^{N_0} d\tau |d\mathbf{c}(\tau)/d\tau|^2 +$$
$$\frac{1}{2}\upsilon_0 \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \, \delta[\mathbf{c}(\tau) - \mathbf{c}(\tau')], \quad (2)$$
$$|\tau - \tau'| \geq a$$

where $\upsilon_0 = \beta_0 l^{-2}(l/d)^{d/2}$ is the bare coupling constant, and a is a cut-off to remove self-excluded volume interactions. Proceeding from (1) to the continuum limit (2) produces identical results as in older treatments[1] where sums over discrete bead indices are converted into integrals at the end of the calculation. The introduction of (2), however, from the outset results in the appearance of functional integrals whose use is becoming more widespread in various areas of theoretical chemistry.[5] The discussion below does not employ or assume any knowledge of methods of functional integration.

Perturbation expansions of polymer properties in powers of υ_0 are expansions in the dimensionless parameter $z = (d/2\pi l^2)^{d/2}\beta_0 n_0^{\epsilon/2}$ as noted above.[1,20] Hence, these expansions would appear to be of little use for $\epsilon > 0$ (i.e., $d < 4$) when β_0 or $\upsilon_0 \neq 0$ and $n_0 \rightarrow \infty$. However, this perturbation approach can be made controllable[22] by letting d become a continuous variable and by using a *double* expansion in powers of υ_0 and ϵ. This ϵ-expansion method yields, for instance,

$$n_0^{\epsilon/2} = 1 + (\epsilon/2) \ln n_0 + (\epsilon^2/8)(\ln n_0)^2 + ..., \quad (3)$$

so that when n_0 is large, we choose ϵ small in order that $\epsilon \ln n_0$ is a small expansion parameter. Hence, the ϵ-expansion makes perturbation theory an acceptable method of computation, but it remains to show how perturbation expansions in 3.99 dimensions can usefully be applied to three-dimensional real-world polymers.

The RG method accomplishes the analytic continuation from 3.99 to 3 dimensions by focusing on the analytic structure of the dependence of large-scale polymer properties on the chain length and excluded volume. For instance, if the renormalization group theory predicts a power law dependence $\propto n_0^x$ under certain circumstances, and if the ϵ-expansion method yields $A + \epsilon B \ln n_0 + O(\epsilon^2)$, then the *only* consistent analytic continuation is $An_0^{\epsilon B/A} + O(\epsilon^2)$. The RG me-

(12) Muthukumar, M.; Nickel, B. G. *J. Chem. Phys.* **1984**, *80*, 5839.

(13) (a) de Gennes, P. G. *Phys. Lett. A* **1972**, *36*, 339. (b) "Scaling Concepts in Polymer Physics"; Cornell Press: Ithaca, NY, 1979.

(14) des Cloizeaux, J. *J. Phys. (Orsay, Fr.)* **1975**, *36*, 281; **1981**, *42*, 635.

(15) Schäfer, L.; Witten, T. A., Jr. *J. Chem. Phys.* **1977**, *66*, 2121; **1981**, *74*, 2582.

(16) Burch, D. J.; Moore, M. A. *J. Phys. A: Math. Gen.* **1976**, *9*, 435. Lawrie, I. D. *J. Phys. A: Math Gen.* **1976**, *9*, 961. Elderfield, D. J. *J. Phys. A* **1978**, *11*, 2483.

(17) de Gennes, P. G. *Riv. Nuovo Cimento Soc. Ital. Fis.* **1977**, *7*, 363. Gabay, M.; Garel, T. *J. Phys. (Orsay, Fr.)* **1978**, *39*, L123. Al-Noaimi, G. F.; Martinez-Mekler, G. C.; Velasco, R. M. *J. Chem. Phys.* **1983**, *78*, 3316.

(18) Family, F.; Gould, H. *J. Chem. Phys.* **1984**, *80*, 3892.

(19) See Appendix A: Kosmas, M. K.; Freed, K. F. *J. Chem. Phys.* **1978**, *68*, 4878.

(20) Oono, Y.; Ohta, T.; Freed, K. F. *J. Chem. Phys.* **1981**, *74*, 6458.

(21) Oono, Y.; Freed, K. F. *J. Chem. Phys.* **1981**, *75*, 993.

(22) Wilson, K. G.; Kogut, J. *Phys. Rep. C* **1974**, *12*, 75.

(23) Kholodenko, A. L.; Freed, K. F. *J. Chem. Phys.* **1984**, *80*, 900.

(24) Kholodenko, A. L.; Freed, K. F. *J. Chem. Phys.* **1983**, *78*, 7390.

(25) Gell-Mann, M.; Low, F. E. *Phys. Rev.* **1954**, *95*, 1300.

(26) Amit, D. J. "Field Theory, The Renormalization Group and Critical Phenomena"; McGraw-Hill: New York, 1978.

(27) Ohta, T.; Oono, Y. *Phys. Lett. A* **1982**, *89*, 460. Freed, K. F. *J. Chem. Phys.* **1983**, *79*, 6357.

(28) Oono, Y.; Freed, K. F. *J. Chem. Phys.* **1981**, *75*, 1009.

(29) Kholodenko, A. L.; Freed, K. F. *J. Phys. A.* **1984**, *17*, L55.

(30) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 1854.

(31) Douglas, J. F.; Freed, K. F. *Macromolecules* **1983**, *15*, 1800; **1984**, *17*, 2344.

(32) 'tHooft, G.; Veltman, M. *Nucl. Phys. B* **1972**, *44*, 189.

(33) Ramond, P. "Field Theory. A Modern Primer"; Benjamin/Cummings: Reading, MA, 1981.

thod which we employ describes the important and theoretically more difficult polymer properties between the Gaussian chain and $n \to \infty$ scaling limits. The ϵ-expansion methods for polymer excluded volume, actually an expansion in $\epsilon/8$, yield only asymptotic expansions for the asymptotic $n \to \infty$ power law exponents. Truncation of the expansions at second order $[O(\epsilon^2)]$ yields very accurate values, and we take the pragmatic approach of evaluating the exponents through second order[24,30,31] (even in the crossover domain) as providing good agreement with experiment. Summations have been made of the dominant terms for ν through infinite order in ϵ, and the results[34] agree well with truncation to ϵ^2. This infinite order treatment is not available in the crossover region where the fortunately accurate second-order theory is applied by us instead.

Another ingredient in RG theory involves an additional type of averaging (coarse graining) beyond that implicit in the model (1) or (2) by virtue of the use of effective units containing several monomers. The model (2) of a continuous random walk with δ function excluded volume departs considerably from the properties of real polymers, so model predictions must contain certain microscopic details which are irrelevant to the long-wavelength behavior. Coarse graining involves averaging over a certain length scale and, therefore, eliminating some information, albeit irrelevant for our purposes, from the original model. The combination of scaling (through dimensional analysis) and coarse graining provides a transformation, the RG transformation, between the original polymer and physically identical scaled coarse grained ones having different chain lengths and interaction strengths. Nevertheless, because of the lack of a characteristic length scale in the polymer excluded volume problem, when all these polymers are rescaled, they provide *identical* long-wavelength polymer properties as the original polymer. Because information is lost in the coarse graining, the RG is a semigroup as the transformation proceeds only in one direction, namely, in the direction of increased coarse graining.[21] However, the desired long-wavelength properties are unaffected by this transformation provided the coarse graining scale is small compared to polymer sizes.

The next section shows how the RG provides generalized and simple scaling laws and explains the physical motivation for the RG. Less mathematically inclined readers might skip to a discussion of the results and comparison with experiment.

Chain Conformation Space Renormalization Group

The probability density for the chain conformation $c(\tau)$ is given by e^{-H}. Long-wavelength observables are obtained as averages with this weight over all possible chain conformations $c(\tau)$. Dimensional analysis of (2) shows that if the dimensions of τ are defined as C, then those of N_0 and a are the same. This is written as $[\tau] = [N_0] = [a] = C$. Likewise, it follows that $[c] = C^{1/2}$ and $[v_0] = C^{-\epsilon/2}$ in the units defined by the use of $c(\tau)$ as the conformation variable. It is convenient therefore to utilize the dimensionless variable $u_0 = v_0 L^{\epsilon/2}$, where L is the phenomenological coarse graining length scale.

(34) LeGuillou, J.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977**, *39*, 95.

Consider a wide variety of polymer models of differing microscopic details which lead to the same universal long-wavelength laws. The models differ in their chain lengths N_i. All N_i must be proportional to the molecular weight of the real polymer, so the N_i must be proportional to each other. Hence, N_0 of our model (2) is proportional to the real polymer chain length $N = Z_N N_0$, where Z_N is dimensionless and independent of N. Within the model (2) Z_N may depend only on u_0 and a/L.

Interactions on a coarse grained length scale L may involve a number of correlated binary interactions between effective units, so these coarse grained interactions are represented by the parameter u which is a function of u_0 and which is summarized through the relation $u = Z_u^{-1}(u, a/L)u_0$ with the dimensionless Z_u independent of N. This relation enables us to also write $Z_N = Z_N(u, a/L)$. The parameters u and L become part of our final phenomenological variables and are dependent on polymer, solvent, and temperature.

Let $G_B(\mathbf{R}, N_0, v_0, a)$ represent the fixed end-to-end-vector partition function obtained by integrating e^{-H} over all chain conformations subject to the constraint that the ends are separated by $\mathbf{R}$. The subscript B designates "bare" quantities evaluated from H of (2). Varying polymer models from that of (2) in the same universality class would yield differing G_B, but when normalized they all must produce the same long-wavelength end-vector probability distribution. Consequently, $G_B(\mathbf{R}, N_0, v_0, a)$ can differ in the large scale limit from the real polymer quantity, the "renormalized" $G(\mathbf{R}, N, u, L)$, by an overall constant, and this is expressed through[20,24,26]

$$G(\mathbf{R}, N, u, L) = Z_G^{-1}(u, a/L) G_B(\mathbf{R}, N_0, v_0, a) \qquad (4)$$

A similar relation must apply for other long-wavelength properties P, involving P, P_B, and the renormalization constant Z_P. Calculated properties are general functions of N, u, and L which yield power law scaling limits only for certain ranges of these parameters. Outside these ranges, in the crossover domain, we term the full dependence, e.g., for $G(\mathbf{R}, N, u, L)$, on molecular weight and excluded volume as generalized scaling laws.

Bare (unrenormalized) quantities calculated from H of (2) are obviously independent of the subsequent coarse graining length scale L since L does not appear in (2) as a parameter. Hence, we have the trivial statement that

$$L \frac{\partial}{\partial L} G_B(\mathbf{R}, N_0, v_0, a)|_{N_0, v_0, a} = 0 \qquad (5)$$

etc., for P_B. This apparently vacuous equation becomes important upon substitution of the relations $N = Z_N N_0$ and $u_0 = Z_u u$ into (4) and use of the chain rule to provide the renormalization group equation

$$\left[L \frac{\partial}{\partial L} + \gamma_G + \beta \frac{\partial}{\partial u} + \gamma_N N \frac{\partial}{\partial N} \right] G(\mathbf{R}, N, u; L) = 0 \qquad (6)$$

an equation summarizing part of the analytic structure of the coarse grained G. In eq (6) we have the quantities $\gamma_G = \partial \ln Z_G / \partial \ln L)_{N_0, v_0, a}$ and $\gamma_N = \partial \ln Z_N / \partial \ln L)_{N_0, v_0, a}$, and $\beta(u) = \partial u / \partial \ln L)_{N_0, v_0, a}$ is the Gell-Mann–Low function.

The most general solution of (6) is verified by insertion to be

$$G(\mathbf{R},N,u,L) =$$

$$\exp\left[-\int^u \frac{\gamma_G(x)}{\beta(x)}\,dx\right] F\left(L\,\exp\left[-\int^u \frac{dx}{\beta(x)}\right],\right.$$

$$\left. N\,\exp\left[-\int^u \frac{\gamma_N(x)}{\beta(x)}\,dx\right],\mathbf{R}\right) \quad (7)$$

where F is not determined by (6) but must be computed from H as discussed below. Note that the left-hand side of (7) contains four independent variables, while the right side has only three, a great simplification. Furthermore, the choice of L larger than microscopic length scales can be shown to eliminate the necessity for inclusion of additional parameters in more realistic models than (1) or (2).

Dimensional analysis described at the beginning of this section shows that if all lengths along the chain are scaled by the distance s, then G behaves as

$$G(\mathbf{R},N,u,L) = s^{-d/2}G(\mathbf{R}s^{-1/2},Ns^{-1},u,Ls^{-1}), \quad s > 0 \quad (8)$$

A combination of (7) and (8) and some algebra leads to the generalized scaling law for the normalized G as[26]

$$P(\mathbf{R},N,u,L) = f(\zeta,\mathbf{R}/\langle\mathbf{R}^2\rangle_\zeta^{1/2}) \quad (9)$$

with f related to F of (7), and ζ a crossover scaling variable given by[23]

$$\zeta = (2\pi N/L)^{\epsilon/2}\exp\left\{-(\epsilon/2)\int^u [\gamma_N(x) - 1]\beta^{-1}(x)\,dx\right\} \quad (10)$$

It is found that ζ ranges between zero for the Gaussian chain and infinity in the good solvent limit of fully developed excluded volume. $\langle R^2\rangle_\zeta$ is the mean square value obtained from $\int d\mathbf{R}|\mathbf{R}|^2 P(\mathbf{R},N,u;L)$, so (9) specializes to the form postulated by scaling theories in the scaling limits $\zeta \to 0$ or ∞. In the important crossover domain $\zeta \nrightarrow 0$ or ∞, eq (9) has a general dependence on ζ, a variation which is absent in simple scaling theories. Note that now the right-hand side of (9) only contains two independent variables, so the RG equation, scaling, and coarse graining with $L/a \gg 1$ considerably reduce the number of independent variables in the problem.

The limit $\zeta \to \infty$ can be attained by (10) for $N \to \infty$ and $\beta(u) \to 0$. In general, simple scaling limits occur for the model (2) for the "fixed point" u^* such that $\beta(u^*)$ vanishes. Then the term $\beta\partial/\partial u$ in (6) can be dropped, simplifying the final solutions like (7) and (9) and providing expressions for the exponents like ν in terms of $\gamma_N(u^*)$. For instance, we find for $\beta(u^*) = 0$ that $\langle\mathbf{R}^2\rangle$ which is proportional to R_G^2 is given by[25]

$$\langle\mathbf{R}^2\rangle_{u^*} = (\text{constant})lN^{2\nu}L^{-(2\nu-1)} \quad (11)$$

where $2\nu = [1 - \gamma_N(u^*)]^{-1}$. Comparison of (11) with the observed behavior[35] of R_G^2 in good solvents shows that $L^{-1/2}$ is proportional to $[1 - (\theta/T)]$ in good solvents[30,31] with θ the theta temperature and the proportionality factor dependent on both polymer and solvent. Thus, L in good solvents is proportional to the size of a blob in the thermal blob model,[36] thereby justifying the in-

terpreting the meaning of L as a coarse graining length scale.

This discussion of the RG so far is quite general and does not utilize ϵ-expansions or perturbation theory. It is also readily extended to consider concentration-dependent polymer[27] quantitites through the semidilute region until the concentration is sufficiently high that the model (2) no longer adequately describes effects due to polymer packing, occupied volume not represented by the model (2) of just entropy and excluded volume. When we desire calculations of the scaling functions like (9), the exponents like ν, and the prefactors like the constant in (11), then it is necessary to introduce a recipe for evaluating the renormalization constants Z_N, Z_u, ... and the scaling functions and to use approximations like ϵ-expansions.[20,24]

Methods for evaluating the renormalization constants are dictated also by considerations of universality which imply that large-scale polymer properties should be insensitive to the precise value of the cut-off parameter a in (2) in the long-wavelength limit $a/L \to 0^+$. Singularities develop in the ϵ-expansions of bare quantities when the formal limit $a/L \to 0^+$ is taken, and the renormalization constants may uniquely be defined such that the perturbation expansion of renormalized quantities in u and ϵ be free of these singularities.[20,24] The details of the calculations are tedious as is the demonstration that all singularities can be consistently removed by this choice of renormalization constants.[23] The important point is to note that the RG uses the analytic continuation in d to expose the singularities in bare quantities. This feature along with a description of the dependence of large length scale properties on N, u, c, and d enables the analytic continuation from $d = 3.99$ to $d = 3$.

Comparison with Experiment

Our chain conformation space RG calculations contain the phenomenological parameters L and ζ which, however, are not the natural phenomenological quantities employed by experimentalists. Most experimental data[1] (in $d = 3$) is represented in terms of a single phenomenological variable z, whereas the renormalization group theory contains two parameters L and ζ (or their equivalent). It turns out that the full second order in ϵ renormalization group calculations may approximately[30,31] be represented for large and small excluded volume in terms of a z-like variable $\bar{z} = AM^{1/2}[1 - (\theta/T)]$, with A polymer and solvent dependent.

For instance, consider properties Q for linear, ring, or regular star and comb polymers that scale naively as the pth power of the polymer radius. The Gaussian chain value for this property is written as $Q_0 = G_Q\langle S^2\rangle_0^{p/2}$ with $\langle S^2\rangle_0 = Nl/6$ the Gaussian chain squared radius of gyration R_G^2. Q_0 is assumed known as it is readily evaluated.[1] The perturbed Q scales naively as $G_Q\langle S^2\rangle_0^{p/2}f_Q(z)$ with $f_Q(0) = 1$. An approximation to the second-order renormalization group calculation yields $(d = 3)$[31]

$$Q = \begin{cases} Q_0(1 + 32\bar{z}/3)^{p/8}[1 + a_Q(32\bar{z}/3)/(1 + 32\bar{z}/3)], \\ \qquad\qquad\qquad\qquad\qquad\qquad \bar{z} \leqslant 0.15 \quad (12a) \\ Q_0(6.441\bar{z})^{p(2\nu-1)}(1 + a_Q), \quad \bar{z} \geqslant 0.75 \quad (12b) \end{cases}$$

where $\nu = 0.592$ to order ϵ^2 and a_Q is a pure number that depends on Q and that emerges *solely from a first order (in ϵ) calculation*. Hence, eq (12) represents a rather

(35) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550.

(36) Farnoux, B.; Boué, F.; Cotton, J.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P. G. *J. Phys. (Orsay, Fr.)* **1978**, *39*, 77. Stockmayer, W. H.; Albrecht, A. C. *J. Polym. Sci.* **1958**, *32*, 215. Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.

sophisticated resummation of the perturbation expansion in powers of $\bar{z}$. RG methods may be viewed as a mathematical approach to effect this resummation. Values of a_Q may be obtained from RG calculations, but good approximations emerge from available $d = 3$ first-order (in z) perturbation calculations.[31] In addition, limited experimental data for a small range in $\bar{z}$ can determine a_Q empirically,[31] and then (12) predicts Q over a wider range. While the full theory rigorously requires two phenomenological variables for $0.15 < \bar{z}$ <0.75, we find that (12a) consistently works well in this region, providing a theory with a single variable $\bar{z}$ for all $\bar{z}$.

An accurate treatment of the important polymer second virial coefficient A_2 requires at least a second-order description.[24,30] It is convenient to represent A_2 in terms of the dimensionless interpenetration function $\Psi(\bar{z})$ defined by[1]

$$A_2 = (4\pi\langle S^2 \rangle)^{3/2}(N_A/2M^2)\Psi(\bar{z}) \qquad (13)$$

with N_A Avogadro's number. The approximate second-order theory yields[31]

$$\Psi(\bar{z}) = \begin{cases} 0.207[(6.441\bar{z})/(1 + 6.441\bar{z})][1 + 1.93\bar{z}/ \\ \qquad\qquad (1 + 6.441\bar{z})], \quad \bar{z} < 0.15 \\ 0.269, \quad \bar{z} > 1.0 \end{cases} \qquad (14)$$

where the small $\bar{z}$ equation is found to be a good approximation for $0.15 < \bar{z} < 1.0$.

Dynamical polymer properties like the diffusion constant D and the intrinsic viscosity $[\eta]$ should, in principle, be evaluated by solving the appropriate dynamical equations with excluded volume present.[28] While some progress has been made in treating the full equations[37] or approximate models,[38] these equations are rather complicated by virtue of the long-range nature of hydrodynamic disturbances.[1] The polymer is modeled as moving in a continuum fluid. Motion of a chain segment exerts a frictional force on the fluid. This force is propagated through the fluid by hydrodynamics to other segments of the polymer, thereby altering their motion. These "hydrodynamic interactions" die off inversely with the distance from the source of friction, leading to long-range interactions in a system with long-range correlations.[1] In order to simplify this problem, Kirkwood introduced[1,39] the "preaveraging approximation" of replacing the instantaneous fluid velocity incident on a segment by the average velocity field much in the same spirit as Hartree's self-consistent field treatment of electrons in atoms. The preaveraging approximation for Gaussian chains is found to agree well with experiments in θ solvents apart from an overall multiplicative error of the order of 10% which appears to be independent of polymer, solvent, and molecular weight.[1] To date, no success has been made with analytical theories in describing corrections for the preaveraging approximation of Gaussian chains.[40]

(37) Shiwa, Y.; Kawasaki, K. *J. Phys. C* 1982, *15*, 5345.

(38) Oono, Y.; Kohmoto, M. *J. Chem. Phys.* 1983, *78*, 520; *Phys. Rev. Lett.* 1982, *49*, 1397. Oono, Y. *J. Chem. Phys.* 1983, *79*, 4629.

(39) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* 1948, *16*, 565; 1950, *18*, 512.

(40) Numerical simulations (Zimm, B. H. *Macromolecules* 1980, *13*, 592) give results for the nonpreaveraged Gaussian chain which are in agreement with experiment [for instance, Kawahara, K.; Norisuye, T.; Fujita, H. *J. Chem. Phys.* 1968, *49*, 4339.] Cherayil, B. J.; Douglas, J. F.; Freed, K. F., to be published: argue that ternary interactions also contribute.
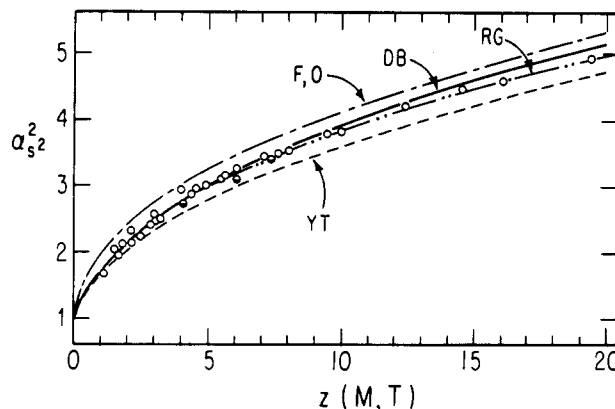

Figure 1. Comparison of experimental data of Miyaki and Fujita[41] for the variation of α_{S^2} with $\bar{z}$ and the renormalization group predictions (RG) of (12), the Flory theory (F,O),[1,4] the Yamakawa–Tanka theory (YT),[1] and the Domb–Barrett (DB)[8c] equation. The symbols $\oplus$ designates data for polystyrene (PS) in benzene, O for PS in methyl ethyl ketone, and $\ominus$ for polyisobutylene (PIB) in cyclohexane. Our $\bar{z}$ is taken as 0.906 times the empirical z value of Miyaki and Fujita.[41]
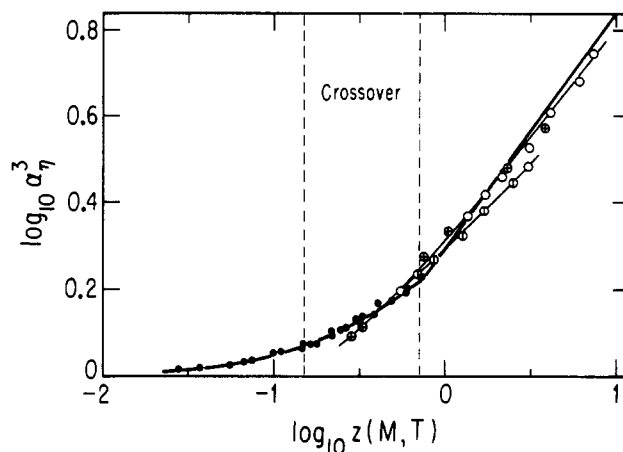

Figure 2. Experimental data[42] for log α_η^3 vs. log $\bar{z}$ taken from Miyaki and Fujita[41] with the RG prediction added. The symbols $\oplus$ and O for PIB in cyclohexane at 25 °C, $\odot$ for PIB in heptane at 25 °C, and $\bullet$ for PIB in isoamyl isovalerate. The RG curve uses $a_\eta = -0.274$ and is a parameter-free prediction since the same $\bar{z}$ is used as in Figure 1.

When excluded volume is incorporated and treated within this preaveraging approximation, the intrinsic viscosity and diffusion constant can be represented as equilibrium averages scaling as the properties Q in (12), provided we invoke the "nondraining" limit[1] wherein the fluid within the polymer coil remains entrapped inside it. Hence, we investigate this simplest approach to the excluded volume dependence of polymer dynamics by utilizing the preaveraging approximation and by only correcting the prefactors Q_0 for the inadequacies of this approximation for Gaussian chains. This approach is pursued because of its relative simplicity compared to an assault on the full dynamical equations, but even if successful, the latter must be studied to understand the approximations more thoroughly.

Figure 1 presents data of Miyaki and Fujita[41] $\alpha_{S^2}^2 \equiv \langle S^2 \rangle / \langle S^2 \rangle_0$ for various polymer solvent systems vs. an empirical z parameter which is found to be proportional to $M^{1/2}[1 - (\theta/T)]$. Their data are compared with the renormalization group prediction (12) by adjusting a

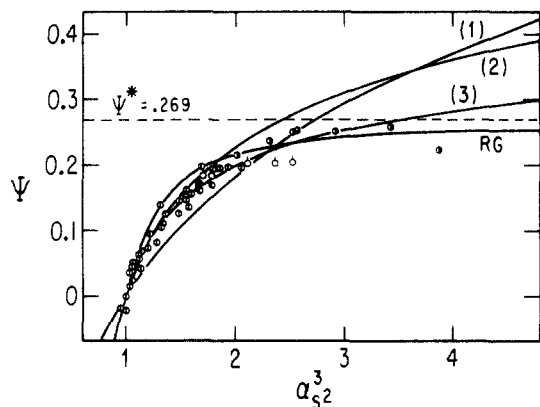(41) Miyaki, Y.; Fujita, H. *Macromolecules* 1981, *14*, 742.

Figure 3. Comparison of theories and experiment for variation of Ψ with α_{S^2}. The data in the figure is taken from Yamakawa[1] with the parameter-free RG predictions added. Data points from Norisuye et al.[45] are $\mathbb{O}$ for polychloroprene (PC) in CCl_4 at 25 °C, Φ for PC in n-butyl acetate at 25 °C, and $\mathbb{O}$ for PC in *trans*-decalin at various temperatures. Similar data[35,46,47] and fits are available for PIB, PS, and poly(p-methylstyrene) (PPMS) in various solvents. The curves (1)–(3) represent older theories as reviewed by Yamakawa.[1]

Figure 4. Experimental data of Yamakawa,[46] Fujita,[47] and their respective co-workers for $A_2M/[\eta]$ vs. $\alpha_{S^2} - 1$ compared with the parameter-free RG predictions. The data points are $\mathbb{O}$ for PC in CCl_4 at 25 °C, Φ for PC in n-butyl acetate at 25 °C, $\mathbb{O}$ for PC in *trans*-decalin, $\bullet$ for PPMS in toluene at 30 °C, $\oplus$ for PPMS in dichloroethane at 30 °C, $\ominus$ for PPMS in cyclohexane at 30 °C, $\odot$ for PPMS in methyl ethyl ketone at 30 °C, $\mathbb{O}$ for PPMS in diethyl succinate at various temperatures. The theoretical calculations use the value of $\Phi_0 = 2.51 \times 10^{23}$ to correct Gaussian chain theory of $[\eta]_0$ for preaveraging,[40] and the experimental data are reproduced from Yamakawa[1] with the RG predictions appended.

single overall proportionality factor between their z parameter and $\bar{z}$ in (12). Also plotted are the Domb–Barrett (DB)[7c] equation, an interpolation formula based on lattice calculations, the original Flory theory (F,O),[1,4] and the Yamakawa–Tanaka (YT) theory.[1]

Miyaki and Fujita[41] have also studied the intrinsic viscosity $[\eta]$ as a function of their z parameter using the same z variable as in Figure 1. Hence, the comparison between theory and experiment[42] for $[\eta]$ has no adjustable parameters. This comparison is presented in Figure 2 where the RG predictions are the only theoretical ones available over the whole range of excluded volume, i.e., of $\bar{z}$. Some polymer–solvent dependence is apparent for larger $\bar{z}$ in the good solvent regime. An approximate treatment[43] shows that this dependence is likely a result of the breakdown of the nondraining approximation inherent in the predicted curve. Thus, as suggested by Berry,[44] the fluid begins to flow through the polymer coil as the chain swells. The tendency toward draining in good solvents is quite polymer dependent[43] and deserves further theoretical and experimental study.

Polymer scientists consider various universal ratios of polymer properties such that the power law portions cancel and only the prefactor part remains. One example is the penetration function Ψ of (13). Equation (14) for Ψ does not have the large $\bar{z}$ power law behavior of (12), so Ψ approaches a constant asymptotic value Ψ^* as $\bar{z} \to \infty$. Figure 3 presents a comparison of the RG theory, some older theories described by Yamakawa,[1] and the experimental data of Norisuye et al.[46] for Ψ of polychloroprene in various solvents. Some of the older theories[1] are incapable of predicting the constant asymptote for large α_{S^2}, while the RG theory gives a good fit to this and similar data by other workers.[35,46,47] Note

that because Figure 3 plots observables against each other, the RG predictions *have no adjustable parameters.*

Another universal ratio of interest is $A_2M/[\eta]$, and data for this ratio of Yamakawa,[46] Fujita,[45] and their respective co-workers for various polymer–solvent systems is presented in Figure 4 along with the *parameter-free* RG predictions. In both Figures 3 and 4 the Gaussian chain $[\eta]_0$ is corrected for the preaveraging approximation,[40] and this appears to be adequate in also describing the excluded volume dependence for nondraining polymers.

The concentration dependence of equilibrium properties can be treated by similar chain conformation space RG method[27] for concentrations well into the semidilute region where the polymers are substantially mutually interpenetrating. This extension is conveniently developed by directly incorporating Edwards's theory[48] of the screening of excluded volume interactions in semidilute and concentrated solutions. Comparison of predicted universal plots for the osmotic compressibility with experimental data[49] shows excellent agreement, and further studies should be pursued. Technical problems still preclude the treatment of excluded volume effects on polymer dynamics in semidilute solutions. Nevertheless our infinite dilution results imply that draining effects will play a role here.

Concluding Remarks

This brief qualitative overview of some recent advances in the chain conformation space (RG) description of polymer excluded volume is designed, in part, to exhibit how large length scale polymer properties can be explained in terms of rather simple coarse grained models of polymer structure and dynamics. The RG

(42) Fox, T., Jr.; Flory, P. J. *J. Phys. Colloid Chem.* **1949**, *53*, 197. Matsumoto, T.; Nishioka, N.; Fujita, H. *J. Polym. Sci.* **1972**, *10*, 23.
(43) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 2354.
(44) Berry, G. C. *J. Chem. Phys.* **1967**, *46*, 1338.
(45) Norisuye, T.; Kawahara, K.; Teramoto, A.; Fujita, H. *J. Chem. Phys.* **1968**, *49*, 4330. Kawahara, K.; Norisuye, T.; Fujita, H. *J. Chem. Phys.* **1968**, *49*, 4339.
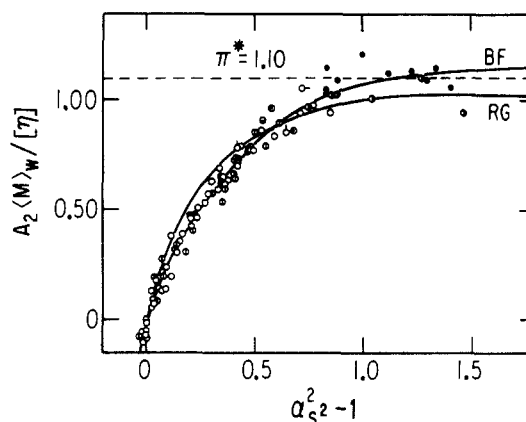(46) Tanaka, G.; Imai, S.; Yamakawa, H. *J. Chem. Phys.* **1970**, *52*, 2639.

(47) Matsumoto, T.; Nishioka, N.; Fujita, H. *J. Polym. Sci.* **1972**, *10*, 23.
(48) Edwards, S. F. *Proc. Phys. Soc., London* **1966**, *88*, 265; *J. Phys. A* **1975**, *10*, 1670.
(49) Wiltzius, P.; Haller, H. R.; Cannell, D. S.; Schaefer, D. W. *Phys. Rev. Lett.* **1983**, *51*, 1183.

theory is based on simple physical considerations that large length scale polymer properties must provide universal laws embodying the long chainlike character of polymers. These laws are represented in terms of scaling laws and their generalization to the important regions of intermediate excluded volume where the power law exponents are no longer universal constants. A motivation is provided for the ϵ-expansion methods. The procedures for performing the ϵ-expansion calculations, evaluating the renormalization constants, and determining the generalized scaling functions are beyond the scope of this article. However, we summarize some of the major results for the excluded volume dependence of a variety of equilibrium and dynamic properties of polymers at infinite dilution in terms of the same variables employed to analyze experimental data. The agreement between theory and experiment is very good especially for the crossover regime which is inaccessible to previous theories. It will be of interest to extend these theoretical methods to more complicated polymer systems[50,51] where there are too many relevant parameters for simple scaling[13b] arguments to provide an adequate zeroth order description.

(50) Miyaki, A.; Freed, K. F. *Macromolecules* **1983,** *16,* 1228; **1984,** *17,* 678.

(51) Freed, K. F. *J. Chem. Phys.* **1983,** *79,* 3121. Nemirovsky, A.; Freed, K. F., to be published.

Local Mode Overtone Spectra

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The concept of a normal mode plays an important part in vibrational theory whether for molecules, musical instruments, or engineering structures. In molecules certain vibrational modes are localized. A familiar example is a bond vibration with a frequency so disparate from others in the molecule that it is effectively uncoupled from other degrees of freedom, such as the ν_1 C–H stretching mode of $CHCl_3$. The success of infrared spectroscopy as an analytical tool depends on recognition of characteristic local bond or local group frequencies of this type. This Account deals with a more sophisticated form of localization that can develop in molecules for which the forms of coupled normal modes are determined by symmetry. The meaning of the term "local" has subtleties attached to it in this context, but there is no doubt that the concept has had signal success in the interpretation of multiquantum (overtone) absorption spectra, which are now becoming accessible by laser spectroscopy.[1,2]

In order to explain this new kind of localization it is convenient to start from a classical model. Imagine a molecule containing two equivalent bonds with a common frequency ω_0. Oscillations in one of them will be resonantly excited by vibrations in the other and energy will flow between them at a frequency ω_1 governed by the strength of interbond coupling. The ensuing motion may then be decomposed into two concerted normal mode motions[3] with frequencies $\omega_0 \pm \omega_1$. This normal mode picture depends however on the harmonic approximation—Namely that ω_0 and ω_1 are independent of energy. In a more realistic anharmonic model the individual bond frequencies will vary with energy, typically decreasing, for stretching vibrations, as the energy increases. This means that highly excited bonds will have a different natural frequency ω_0' from one that is unexcited. The coupling between them will therefore be effectively quenched if this anharmonic detuning is large and the interbond coupling is relatively weak. Classical studies on a realistic potential function confirm that one can observe a permanent imbalance between the two local bond excitation states of H_2O for example.[4] More detailed analysis of this classical situation may be found in papers by Lawton and Child,[5] Jaffé and Brumer,[6] and Sibert et al.[7] We note here two important observations. First, that the conditions of large anharmonicity and weak interbond coupling are most easily satisfied by the stretching of X–H bonds. Second, the two possible distributions of separate quanta in the two bonds gives rise to a twofold classical local mode degeneracy, with higher degeneracies if the number of equivalent bonds is increased.

The main purpose of this Account is to outline the quantum-mechanical analogue of this picture. One important change is that the quantum-mechanical states must of course carry the proper symmetry labels for the system. Thus the theory is developed in terms of symmetry adapted local mode states, given, in the case of two oscillations, by

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(1) J. S. Wong and C. B. Moore in "Frontiers of Chemistry", K. J. Laidler, Ed., Pergamon., Oxford, 1982, p 353.

(2) M. E. Long, R. L. Swofford, and A. C. Albrecht, *Science (Washington D.C.),* 191, 183 (1976).

(3) See G. Herzberg, "Infra-red and Raman Spectra", Van Nostrand-Reinhold, New York, 1945.

(4) R. T. Lawton and M. S. Child, *Mol. Phys.,* 37, 1799 (1979).

(5) R. T. Lawton and M. S. Child, *Mol. Phys.,* 44, 709 (1981).

(6) C. Jaffé and P. Brumer, *J. Chem. Phys.,* 73, 5646 (1980).

(7) E. L. Sibert, W. P. Reinhardt, and J. T. Hynes, *J. Chem. Phys.* 77, 3583 (1982).