

both components to the limits of present-day techniques; (2) estimated the presence of impurities in isobutyric acid by gas chromatography with different columns; (3) redetermined the coexistence curve using samples with different sealing techniques; (4) ascertained the stability of the system by reproducing phase-separation temperatures over a several months period; (5) avoided multiple scattering and gravitational effects by staying away from the very immediate neighborhood of the critical point; (6) reproduced our results using two separately prepared samples at the critical solution concentration; (7) ensured uniformity of temperature in the scattering cell by means of a massive copper shield; (8) studied the angular dissymmetry with visible light of different wavelengths and with different optical geometry, (9) used lasers excited by radio-frequency, direct current, and radiofrequency-direct current; (10) checked the frequency response of the spectrometer, the pick-up, vibration, and background problems; (11) calibrated the linearity of the analog squarer; (12) reduced the signal-to-noise ratio by means of a time-averaging computer, or a low pass filter; (13) examined the heating effect of the higher powered lasers, and (14) minimized the effects of stray light and reflections in our scattering measurements. We

worried about the effects of depolarization and rotational contributions because of the complexities of our molecules. So we tried to measure the line width at $\theta = 90^\circ$ with laser light polarized parallel to the direction of observation. Only a broad background was observed at $\Delta T = 0.5^\circ$. We then checked the depolarization by inserting an analyzer in our light-scattering photometer at $\Delta T \sim 0.1^\circ$. We found that the amount of depolarized light was about a few per cent, insufficient to account for any significant rotational contribution. What does $\gamma^* \approx 2/3$ and $\gamma \approx 5/4$ imply? If we take $(\partial\pi/\partial c)_T \propto (T - T_c)^\gamma$ and $\alpha^*(\partial\pi/\partial c)_T \propto (T - T_c)^{\gamma^*}$, we find for $T > T_c$, $\alpha^* \propto (T - T_c)^{\gamma^* - \gamma}$ with $\gamma^* - \gamma < 0$. This means that α^* has to increase as T approaches T_c . The self-diffusion coefficient decreases with increasing viscosity and the viscosity increases as T approaches T_c . The product, $\alpha^*(\partial\pi/\partial c)_T$, behaves within reason since it approaches zero as $T \rightarrow T_c$.

The discrepancy ($\gamma \neq \gamma^*$) in our light intensity and line-width studies implies that the transport coefficient α^* diverges as $(T - T_c)^{\gamma^* - \gamma}$ within the temperature range of our investigation.

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Translational Diffusion Constant of Polymer Chains^{1a}

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Abstract: The formal theory of the translational diffusion constant is reexamined in order to display in isolation the contributions from (a) the equilibrium average derived by Kirkwood, and (b) corrections due to distortion of the equilibrium segment distribution. The corrections are found to be small in good or poor solvents. The equilibrium contribution requires a calculation of $\langle 1/r_{ij} \rangle_{eq}$ for all pairs of segments i and j in the chain, and this calculation has been carried through on the basis of a boson operator formalism recently introduced. It is first shown that the boson formalism in lowest order gives a Gaussian distribution of r_{ij} , with a variance dependent on i and j and on the magnitude of the excluded volume. A calculation of the frictional expansion factor α_i shows that it increases much less rapidly with increasing goodness of solvent than other measures of chain dimension. However, the tentative conclusion is expressed that this behavior of α_i is due to the sensitivity of $\langle 1/r_{ij} \rangle_{eq}$ to non-Gaussian statistics, in comparison with $\langle r_{ij}^2 \rangle$. Methods for dealing with this sensitivity are outlined.

I. Introduction

The translational diffusion constant is conceptually the simplest transport coefficient of chain polymer molecules, and was one of the first to be investigated. Kirkwood² presented for the diffusion constant an expression involving just equilibrium averages of the reciprocal distances between segments. His expression was first regarded as exact but was later shown to be approximate, the corrections being identified by Ikeda³ and Erpenbeck⁴ (see also Saito⁵). Our goals here are

two: (1) to present explicitly the (small) correction to Kirkwood's formula and to examine the dependence of the correction on excluded volume forces; (2) to calculate the effect of excluded volume on the diffusion constants as given by Kirkwood's formula.

Regarding the first goal, the magnitude of the correction can be gauged in several ways, for example, by exact calculation for particular systems. Zwanzig⁶ has pointed out that the rigid ring has a diffusion constant smaller by the ratio 11/12 than that calculated from Kirkwood's formula. Approximate calculations are required for chain polymers, and our results, which reduce to those of Zimm⁷ at the θ temperature, indicate a

(1) (a) Supported in part by National Institutes of Health Research Grant GM 13556-03. (b) Fellow of Fundación Juan March.

(2) J. G. Kirkwood, *Rec. Trav. Chim.*, **68**, 649 (1949); (b) *J. Polymer Sci.*, **12**, 1 (1954).

(3) Y. Ikeda, *Kobayashi Rigaku Kenkyusho Hokoku*, **6**, 44 (1956).

(4) J. J. Erpenbeck and J. G. Kirkwood, *J. Chem. Phys.*, **38**, 1023 (1963).

(5) N. Saito, K. Okano, S. Iwayanagi, and T. Hideshima, *Solid State Phys.*, **14**, 343 (1963).

(6) R. Zwanzig, *J. Chem. Phys.*, **45**, 1858 (1966).

(7) B. H. Zimm, *ibid.*, **24**, 269 (1956).

discrepancy which is in the same direction but of smaller magnitude, and not much dependent on excluded volume effects. The possibility of a large dependence motivated our somewhat strenuous examination of the discrepancy.

Regarding the second goal, which is essentially the calculation of the frictional expansion factor α_i , we show that the boson formulation previously introduced⁸ is equivalent, in the low order of approximation considered here, to the use of modified Gaussian probability for intersegment distances. The Gaussian approximation has been introduced *ad hoc* in two previous studies of the diffusion constant by Kurata and Yamakawa,⁹ who calculated the "single contact" correction for excluded volume effects, and by Bloomfield and Zimm,¹⁰ who used the Peterlin¹¹ power law for the variance in their Gaussian distribution. The effect of any of the Gaussian approximations is to make α_i much smaller than α_R or α_L (the expansion factors for the radius of gyration and end-to-end distance, respectively), contrary to experiment¹² and exact single-contact theory.¹³ The source of the discrepancy is considered in the Discussion.

The plan of this work is as follows. In section II the equations of chain dynamics are specialized to motion of a single molecule in a constant external force field, and the equilibrium and nonequilibrium parts of the diffusion constant are isolated. In section III (and Appendix A) the nonequilibrium perturbation to the internal distribution function is calculated with the aid of one of Kirkwood's and Zimm's approximations, namely with the use of an averaged hydrodynamic interaction tensor. In section IV (and Appendix B) the equilibrium averages are first shown to reduce to Gaussian averages in the lowest order boson approximations, and the required averages are then computed. The detailed results for the friction constant are presented in section V.

II. Motion of the Polymer Molecule

We review here the different kinds of forces acting on the molecule as it moves through the solvent, obtain the equation of motion, and define the total friction coefficient. The polymer is represented by a chain of $N + 1$ segments, each of them being a point center of force interacting with all other segments and with the solvent. The model is the one used and described in greater detail in paper I.⁸

The total force acting on segment i of the molecule is

$$m \frac{d\mathbf{v}_i}{dt} = -\beta(\mathbf{v}_i - \mathbf{v}_i') - kT\nabla_i \ln \psi - \nabla_i U + \mathbf{F}_i \quad (1)$$

where \mathbf{v}_i is the segment velocity, \mathbf{v}_i' the solvent velocity at the position of i in the absence of the segment, β the friction constant, $-kT\nabla_i \ln \psi$ the entropic force with ψ the distribution function of segment coordinates, \mathbf{F}_i any force external to the solution, and U the chain potential which we shall specify shortly. For the moment

(8) Paper I: M. Fixman, *J. Chem. Phys.*, **45**, 785 (1966).

(9) M. Kurata and H. Yamakawa, *ibid.*, **29**, 311 (1958).

(10) V. Bloomfield and B. H. Zimm, *ibid.*, **44**, 315 (1966).

(11) A. Peterlin, *ibid.*, **23**, 2464 (1955).

(12) J. M. G. Cowie and E. L. Cussler, *ibid.*, **46**, 4886 (1967).

(13) W. H. Stockmayer and A. C. Albrecht, *J. Polymer Sci.*, **32**, 215 (1958).

we only require that $-\nabla_i U$ represent the force on segment i due to the adjacent ones and to interactions with all other segments.

The frictional force $-\beta(\mathbf{v}_i - \mathbf{v}_i')$ is given an explicit form by introducing the hydrodynamic interaction between segments i and j as expressed by the Oseen tensor

$$\begin{aligned} \mathbf{T}(\mathbf{r}_{ij}) &= (8\pi\eta_0)^{-1} \mathbf{r}_{ij}^{-3} (\mathbf{r}_{ij}^2 \mathbf{1} + \mathbf{r}_{ij} \mathbf{r}_{ij}) \quad \text{for } i \neq j \\ &= 0 \quad \text{for } i = j \end{aligned} \quad (2)$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$; \mathbf{r}_i is the position vector of segment i and η_0 is the solvent viscosity. This tensor is used to describe the perturbed flow of solvent at position i as

$$\mathbf{v}_i' = \mathbf{v}_i^0 + \beta \sum_{j=1}^{N+1} \mathbf{T}(\mathbf{r}_{ij}) \cdot (\mathbf{v}_j - \mathbf{v}_j') \quad (3)$$

where \mathbf{v}_i^0 is the unperturbed velocity of solvent at the position of i . Expressions 1 and 3 allow the equation of motion for segment i to be written in the form

$$\mathbf{v}_i = \mathbf{v}_i^0 - \sum_{j=1}^{N+1} \mathbf{D}_{ij} \cdot [\nabla_j (kT \ln \psi + U) - \mathbf{F}_j] \quad (4)$$

where we inserted the simplification of vanishing total force on the segment. The diffusion tensor \mathbf{D}_{ij} is defined by

$$\mathbf{D}_{ij} = \beta^{-1} \mathbf{1} + \mathbf{T}(\mathbf{r}_{ij}) \quad (5)$$

In order to simplify the description for translational motion of the polymer molecule subjected to a constant external force, we set our reference system of coordinates in such a way that \mathbf{v}_i^0 and \mathbf{F}_i have the form

$$\mathbf{v}_i^0 = 0 \quad (6)$$

$$\mathbf{F}_i = f \mathbf{e}_x$$

\mathbf{e}_x is a unit vector in the x direction and f is a constant equal to the magnitude of the external force per segment. This external force is assumed to remain constant over the domain of one polymer molecule and thus to be independent of i .

The ratio between the total external force acting on the macromolecule and the average velocity at its center of mass, under steady-state motion, defines the total friction coefficient B of the polymer chain

$$Nf\mathbf{e}_x = B \frac{1}{N} \sum_{i=1}^{N+1} \langle \mathbf{v}_i \rangle \quad (7)$$

where we assume all segments of the chain to have equal masses. Equations 4, 6, and 7 express the formal dependence of B on chain averages.

$$B = N^2 f \mathbf{e}_x \cdot \left\{ \sum_{i,j=1}^{N+1} \langle \mathbf{D}_{ij} [f \mathbf{e}_x - \nabla_j (kT \ln \psi + U)] \rangle \right\}^{-1} \quad (8)$$

With retention of only those contributions proportional to the external force, we can write the average inside the double sum as

$$\langle \mathbf{D}_{ij} \rangle_{\text{eq}} \cdot \mathbf{e}_x f - \langle \mathbf{D}_{ij} \cdot \nabla_j (kT \ln \psi + U) \rangle$$

where we designate equilibrium averages by the subscript "eq," thus differentiating these from the unsubscripted steady-state averages.

The contribution from $\langle \mathbf{D}_{ij} \cdot \nabla_j \ln \psi \rangle$ vanishes because we assume the solution to be incompressible. This requires

$$\sum_{j=1}^{N+1} \nabla_j \cdot \mathbf{D}_{ij} = 0 \quad (9)$$

and any reasonable ψ implies zero probability for the presence of polymer segments at infinity. The non-vanishing terms of eq 8 give

$$B = N^2 f \mathbf{e}_x \cdot \left[\sum_{i,j} \langle \mathbf{D}_{ij} \rangle_{\text{eq}} \cdot f \mathbf{e}_x - \langle \mathbf{D}_{ij} \cdot \nabla_j U \rangle \right]^{-1} \quad (10)$$

Further progress requires knowledge of the distribution function and an explicit form for the potential U . This potential includes, as we mentioned, two kinds of forces acting on each chain segment: backbone interactions with adjacent segments and excluded volume interactions with all others. We make for them the same choices as in paper I.

The backbone interactions are presumed to be due to "spring" forces connecting adjacent segments along the chain, and are derived from the potential S

$$S = \frac{3kT}{2b_0^2} \sum_{i=1}^N |\mathbf{r}_i - \mathbf{r}_{i+1}|^2 \quad (11)$$

where b_0 is a fixed length characteristic of the spring. The excluded volume interactions between any segments of the chain are taken as pairwise additive and derived from the potential E

$$E = kTX \sum_{i>j=1}^N \delta(\mathbf{r}_{ij}) \quad (12)$$

where δ stands for a Dirac δ function, and X is the excluded volume. The total potential of the chain is $U = S + E$.

We now turn our attention to the problem of determining the distribution functions.

III. Distribution Function

The equilibrium and steady-state distributions are needed. The procedure followed previously to determine steady-state distributions is based on the solution of the differential equation that arises when, in the equation of conservation of probability

$$\frac{\partial \psi}{\partial t} = - \sum_{i=1}^{N+1} \nabla_i \cdot (\mathbf{v}_i \psi) \quad (13)$$

the explicit form of \mathbf{v}_i is substituted. The resulting operator acting on ψ is modified under the factorization $\psi = \psi^\alpha \rho$, where ψ^α (a normalized zero-order approximation to the equilibrium distribution) is expressed in terms of an effective potential S^α

$$\psi^\alpha = \text{constant} \exp[-S^\alpha/kT] \quad (14)$$

The modified equation

$$\frac{\partial \rho}{\partial t} + \mathcal{L}\rho = 0 \quad (15)$$

determines the perturbed distribution ρ .

In our present problem the equation of motion giving the form of \mathbf{v}_i is expressed by (4) and (6). It produces for \mathcal{L}

$$\mathcal{L} = kT \sum_{i,j=1}^{N+1} [\nabla_i - \nabla_i S^\alpha/kT] \cdot \mathbf{D}_{ij} \cdot \{ \nabla_j + [\nabla_j U - S^\alpha]/kT - f \mathbf{e}_x/kT \} \quad (16)$$

According to the specifications in paper I, ψ^α is a modi-

fied Gaussian distribution with expansion factor α , and S^α ($S^\alpha \equiv \alpha^{-2}S$) comes to diagonal form under the normal coordinate transformation

$$\mathbf{r}_i = \sum_{l=0}^N Q_{il} \mathbf{q}_l \quad \mathbf{q}_l = \sum_{i=1}^{N+1} \tilde{Q}_{li} \mathbf{r}_i$$

$$Q_{il} = N^{-1/2} (2 - \delta_{il})^{1/2} \cos(il\pi/N) \quad (17)$$

where δ_{il} is the Kronecker δ .

The equation $\mathcal{L}\rho = 0$ determines the time-independent perturbed distribution. With \mathcal{L} written in terms of these normal coordinates the equation reads

$$\mathcal{L}\rho = -kT \sum_{k,l=1}^N \left(\frac{\partial}{\partial \mathbf{q}_k} - 2\alpha_k^2 \mathbf{q}_k \right) \cdot \mathbf{F}_{kl} \cdot \left[\frac{\partial}{\partial \mathbf{q}_l} + \frac{1}{kT} \frac{\partial}{\partial \mathbf{q}_l} (U - S^\alpha) - \frac{N^{1/2}}{kT} f \mathbf{e}_x \delta_{il} \right] \rho = 0 \quad (18)$$

where the motion of the center of mass has been eliminated. \mathbf{F}_{kl} is defined by

$$\mathbf{F}_{kl} = \sum_{i,j=1}^{N+1} Q_{ik} Q_{jl} \mathbf{D}_{ij} \quad (19)$$

and α_l by

$$\alpha_l^2 = \frac{6}{b_0^2 \alpha^2} \sin^2(l\pi/2N) \quad (20)$$

The solution of eq 18 is described in Appendix A where it is carried out in terms of the boson operator representation introduced previously for polymer flow problems. The result is

$$\rho = \exp \left[\left(\frac{N}{2} \right)^{1/2} \frac{f}{kT} \sum_{l=1}^N \frac{\langle F_{0l} \rangle_{\text{eq}}}{\langle F_{ll} \rangle_{\text{eq}}} \frac{b_{lx}^+}{\alpha_l (1 + G_l)} \right] \rho_{\text{eq}} \quad (21)$$

Here b_{lx}^+ is a boson operator creating an excitation of the l th mode of motion in the x direction relative to the ground state ψ^α . G_l is the same force constant that was introduced in previous papers. Its definition is reproduced in Appendix A, formula A.5. Of course the distribution function for steady state given in (21) reduces to the equilibrium one when the external force f is zero. The equilibrium distribution, as found in paper I, is given by

$$\rho_{\text{eq}} = \exp \left[- \frac{1}{2} \sum_{l=1}^N \frac{G_l}{1 + G_l} \mathbf{b}_l^+ \cdot \mathbf{b}_l^+ \right] |0\rangle \quad (22)$$

where $\mathbf{b}_l^+ = b_{lx}^+ \mathbf{e}_x + b_{ly}^+ \mathbf{e}_y + b_{lz}^+ \mathbf{e}_z$, and $|0\rangle$ represents, in the boson language, the unexcited ground state ψ^α .

In the derivation of eq 21, \mathbf{D}_{ij} has been replaced by its equilibrium average, as in almost all prior work. Use of this approximation again in the calculation of the steady-state average, $\langle \mathbf{D}_{ij} \cdot \nabla_j U \rangle$, reduces the average to its simplified form, $\langle \mathbf{D}_{ij} \rangle_{\text{eq}} \cdot \langle \nabla_j U \rangle$. Appendix C describes the use of (21) to find $\langle \nabla_j U \rangle$, with the result

$$\langle \nabla_j U \rangle = N^{1/2} f \mathbf{e}_x \sum_{l=1}^N Q_{jl} \frac{\langle F_{0l} \rangle_{\text{eq}}}{\langle F_{ll} \rangle_{\text{eq}}} \quad (23)$$

Substitution of this result into eq 10 gives

$$B = N^2 \left(\sum_{i,j=1}^{N+1} \langle D_{ij} \rangle_{\text{eq}} - N \sum_{l=1}^N \frac{\langle F_{0l} \rangle_{\text{eq}}^2}{\langle F_{ll} \rangle_{\text{eq}}} \right)^{-1} \quad (24)$$

The numerical evaluation of this formula for B requires only the average behavior of the diffusion tensor

in equilibrium. We consider equilibrium averages in the next section.

The contribution $\langle v_j U \rangle$ due to the average force acting on segment j , because of its interaction with all others, is absent in the classical Kirkwood and Riseman paper.¹⁴ Its appearance in the present work is not caused by the introduction of the excluded volume potential. Indeed, for $E = 0$ our treatment ought to reproduce Zimm's result, which also differed from that of Kirkwood and Riseman. We shall show in section V, dedicated to numerical results, that the contribution of F_{j0} to the total friction coefficient is, however, very small if not negligible. The consideration of the excluded volume does not alter this result appreciably.

IV. Diffusion Tensor Equilibrium Average

The diffusion tensor \mathbf{D}_{ij} , as defined by (5) is considered only in the nondraining limit. That is, our interest centers on the case of long macromolecular chains, where the inner part of the molecule is completely shielded by the outer regions from any hydrodynamic interaction with the solvent. Inclusion of draining would be relatively trivial compared to the treatment of shielding. In the nondraining limit only the interaction tensor $\mathbf{T}(\mathbf{r}_{ij})$ needs to be considered. A δ function representation will be used for $\mathbf{T}(\mathbf{r}_{ij})$ through

$$\mathbf{T}(\mathbf{r}_{ij}) = \int d\mathbf{r} \mathbf{T}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_{ij}) \quad (25)$$

We require then the equilibrium average of $\delta(\mathbf{r} - \mathbf{r}_{ij})$. After this, the integration over \mathbf{r} is performed. The equilibrium average of the δ function is found in appendix B by means of boson operator techniques. The result is in terms of the f_i 's defined in eq A.7

$$\langle \delta(\mathbf{r} - \mathbf{r}_{ij}) \rangle_{\text{eq}} = \left[2\pi \sum_{l=1}^N \frac{f_l^2}{1 + G_l} \right]^{-1/2} \times \exp \left[- \frac{r^2}{2 \sum_{l=1}^N \frac{f_l^2}{1 + G_l}} \right] \quad (26)$$

which shows that a Gaussian distribution for the separation between segments is obtained for equilibrium. The interaction tensor equilibrium average is then

$$\langle \mathbf{T}(\mathbf{r}_{ij}) \rangle_{\text{eq}} = \int d\mathbf{r} \mathbf{T}(\mathbf{r}) \langle \delta(\mathbf{r} - \mathbf{r}_{ij}) \rangle_{\text{eq}} \quad (27)$$

with $\mathbf{T}(\mathbf{r})$ defined by (2) and $\langle \delta(\mathbf{r} - \mathbf{r}_{ij}) \rangle_{\text{eq}}$ given by (26). The integration over r finally produces

$$\langle \mathbf{T}(\mathbf{r}_{ij}) \rangle_{\text{eq}} = (6\pi^{3/2}\eta_0)^{-1} \left[\frac{1}{2} \sum_{l=1}^N \frac{f_l^2}{1 + G_l} \right]^{-1/2} \mathbf{1} \quad (28)$$

V. Friction Coefficient and Excluded Volume

The dependence of the friction coefficient on the excluded volume is contained in expression 24. In the nondraining limit, $\mathbf{T}(\mathbf{r}_{ij})$ replaces \mathbf{D}_{ij} . In this section we present the numerical results obtained for B and its variation with excluded volume.

First, in part I, we find the contribution from each of the two terms

$$\sum_{i \neq j} \langle \mathbf{T}(\mathbf{r}_{ij}) \rangle \quad (29)$$

(14) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565 (1948).

and

$$N \sum_{l=1}^N \frac{\left(\sum_{i \neq j} Q_{i0} Q_{jl} \langle \mathbf{T}(\mathbf{r}_{ij}) \rangle_{\text{eq}} \right)^2}{\sum_{i \neq j} Q_{i0} Q_{jl} \langle \mathbf{T}(\mathbf{r}_{ij}) \rangle_{\text{eq}}} \quad (30)$$

Especially we compare them and show that the magnitude of (30) is below 2% of the value of (29). The interaction tensor is then the main term in the friction coefficient, and its contribution to the variation of B with the excluded volume is computed. In part II we give the coefficient of the single contact term in the perturbation expansion of B .

1. General Results. We begin substituting for the symbol f_i in formula 28 its detailed meaning.

$$\frac{1}{2} \sum_{l=1}^N \frac{f_l^2}{1 + G_l} = \frac{1}{4} \sum_{l=1}^N \frac{(Q_{li} - Q_{jl})^2}{\alpha_i^2 (1 + G_l)} \simeq \frac{N b_0^2}{6} \alpha^2 \frac{2}{\pi^2} \sum_{l=1}^N \frac{[\cos(il\pi/N) - \cos(jl\pi/N)]^2}{l^2 (1 + G_l)} \quad (31)$$

To evaluate the sums over segment coordinates in (28) we introduce a continuous variable approximation valid for large N .

$$i = Nx; \quad j = Ny; \quad \sum_{i \neq j} \simeq N^2 \int_0^1 dx \int_0^1 dy \quad (32)$$

Spurious singularities at $x = y$ are easily handled.

We abbreviate (31) by defining

$$\sigma_l(x, y) = \frac{2(\cos l\pi x - \cos l\pi y)^2}{\pi^2 l^2} \quad (33)$$

so that

$$\frac{1}{2} \sum_{l=1}^N \frac{f_l^2}{1 + G_l} = \alpha^2 \frac{N b_0^2}{6} \sum_{l=1}^N \frac{\sigma_l(x, y)}{1 + G_l} \quad (34)$$

and

$$\sum_{l=1}^N \sigma_l(x, y) = |x - y| \quad (35)$$

For tabulation purposes we give the integrals to be evaluated the symbol

$$E_{kl} = \int_0^1 dx \int_0^1 dy \cos k\pi x \cos l\pi y \times \left[\sum_{m=1}^N \frac{\sigma_m(x, y)}{1 + G_m} \right]^{-1/2} \quad (36)$$

Then the expressions involving the interaction tensor average are

$$\sum_{i \neq j} \langle \mathbf{T}(\mathbf{r}_{ij}) \rangle_{\text{eq}} = \frac{N^{3/2}}{(6\pi^3)^{1/2} b_0 \eta_0} E_{00} \quad (37)$$

$$N \sum_{i \neq j} Q_{ik} Q_{jl} \langle \mathbf{T}(\mathbf{r}_{ij}) \rangle_{\text{eq}} =$$

$$(2 - \delta_{k0})^{1/2} (2 - \delta_{l0})^{1/2} \frac{N^{3/2}}{(6\pi^3)^{1/2} b_0 \eta_0} E_{kl} \quad (38)$$

and eq 24 reads

$$B = (6\pi^3 N)^{1/2} b_0 \eta_0 \left[E_{00} - \sum_{l=1}^N \frac{E_{0l}^2}{E_{ll}} \right]^{-1} \quad (39)$$

For θ conditions $G_l = 0$, (35) applies, and the E_{kl} 's are then easily expressed in terms of Fresnel integrals and their value obtained from tables. For the cases where

the excluded volume is not zero, numerical quadrature has been used. In these cases the sum over m in (36) needs to be evaluated for every k and l . We performed it by summing correctly the first 14 terms and extrapolating the remainder to $m = \infty$. Simpson's rule integration with 61 points has produced the results shown in Tables I and II for E_{00} , E_{0l} , and E_{1l} , E_{0l}

Table I

z	0.0000	0.0747	0.2432	0.6574	1.7644	4.947	14.658
E_{00}	2.6667	2.6002	2.5080	2.3909	2.2520	2.1010	1.9487
α_f	1.000	1.026	1.063	1.115	1.184	1.269	1.368
α_{L^a}	1.000	1.044	1.111	1.213	1.361	1.572	1.864

^a α_L values from M. Fixman, *J. Chem. Phys.*, **45**, 793 (1966).

Table II

	l	$-E_{0l}$	E_{1l}	$\frac{E_{0l}^2}{E_{1l}}$	$\frac{E_{0l}^2}{E_{1l}E_{00}}$
$z = 0.0000$	2	0.10931	0.4609	0.02592	0.00972
$\alpha = 1.000$	4	0.04366	0.3395	0.00561	0.00210
	6	0.02501	0.2810	0.00223	0.00084
	8	0.01673	0.2450
	10	0.01221	0.2200
$z = 0.2432$	2	0.10216	0.4550	0.02294	0.00915
$\alpha = 1.123$	4	0.04094	0.3370	0.00497	0.00198
	6	0.02346	0.2796	0.00197	0.00078
$z = 4.947$	2	0.07929
$\alpha = 1.642$	4	0.03355
	6	0.01937

vanishes for l odd. The strength of the excluded volume effect is gauged by means of the dimensionless parameter z

$$z = N^{1/2} \left(\frac{6}{b_0^2} \right)^{3/2} \frac{X}{8\pi^{3/2}} \quad (40)$$

For θ conditions we sum the values of the five E_{0l}^2/E_{1l}^2 's that appear on Table II, and extrapolate the sum to $l = \infty$ getting

$$\sum_{l=1}^{\infty} \frac{E_{0l}^2}{E_{1l}^2} = 0.0375 \quad (41)$$

Comparing this with $E_{00} = 8/3$ we see that (30) brings in a contribution which is only 1.40% of the value of (29). The last column in Table II represents the relative magnitude of each l th summand in (41), as compared to the magnitude of (29). We see that for $z = 0.2433$ (a moderately low excluded volume) the values in this column for each l are smaller than the ones for θ conditions. An increase in excluded volume decreases the relative importance of (30), and, thus, 1.40% is its largest contribution. We have computed E_{0l} for the higher value $z = 4.950$ also, to be sure that no unexpected increase occurs for large excluded volumes. The last row of Table I shows the values of the dimensionless quantity α_f

$$\alpha_f = B/B_{z=0} \quad (42)$$

when B is given only by E_{00} with neglect of the small $E_{0l}\alpha_f$ is a measure of the expansion of the macromolecule over its unperturbed hydrodynamic dimensions. From the table we see that our results make this expansion

factor for friction phenomena a slower increasing function of z than the corresponding one for the end-to-end distance, α_L .

Finally we give the total diffusion coefficient D of the macromolecule, for θ conditions

$$D = kT/B = 0.1928kT/N^{1/2}b_0\eta_0 \quad (43)$$

It is in good accord with the constant 0.192 given by Zimm.⁷ The value 0.1955 obtained by Kirkwood and Riseman¹⁴ is found when only (29) is considered. The inclusion of the average internal forces of the polymer chain lowers this diffusion coefficient by 1.4% for θ conditions, and by a smaller proportion when excluded volume effects are present.

2. Perturbation Series. Linear Term. We present now the expansion of α_f in powers of the excluded volume parameter z . Only the linear term is known in the series, the value of its coefficient having been calculated exactly by Stockmayer and Albrecht.¹³ The form that we use for α_f , according to its definition in part I of this section, is

$$\alpha_f = \frac{E_{00(z=0)}}{E_{00}} = \frac{8}{3} E_{00}^{-1} \quad (44)$$

with E_{00} given by (36). The perturbation series reads then

$$\alpha_f = 1 - \frac{3}{8} \left(\frac{\partial E_{00}}{\partial z} \right)_{z=0} z + O(z^2) \quad (45)$$

where

$$\left(\frac{\partial E_{00}}{\partial z} \right)_{z=0} = -\frac{1}{2} \int_0^1 dx \int_0^1 dy |x - y|^{-3/2} \sum_{l=1}^N \sigma_l(x, y) \left[\frac{\partial}{\partial z} \left(\frac{\alpha^2}{1 + G_l} \right) \right]_{z=0} \quad (46)$$

and

$$\left[\frac{\partial}{\partial z} \left(\frac{\alpha^2}{1 + G_l} \right) \right]_{z=0} = g_l \quad (47)$$

The quantity g_l , independent of excluded volume, was defined in paper I in terms of the symbols introduced in eq A.6 and A.7

$$g_l = \frac{1}{4} \left(\frac{\alpha^2 b_0^2}{6} \right)^{3/2} N^{-1/2} \sum_{i \neq j} C_{ij}^{-5/2} f_i^2 \quad (48)$$

which, with the continuous variable approximation (32), can be written as

$$g_l = \frac{1}{2} \int_0^1 dx \int_0^1 dy |x - y|^{-5/2} \sigma_l(x, y) \quad (49)$$

If, similarly, we define the quantity p_l to be

$$p_l = \frac{1}{2} \int_0^1 dx \int_0^1 dy |x - y|^{-3/2} \sigma_l(x, y) \quad (50)$$

the perturbation series (45) reads finally

$$\alpha_f = 1 + \frac{3}{8} \sum_{l=1}^N g_l p_l z + O(z^2) \quad (51)$$

Both g_l and p_l can be expressed in terms of Fresnel integrals. For g_l this was already done in paper I where a table of its first 12 values was also given. For

p_l we have

$$p_l = \frac{1}{2} l^{-5/2} (8\sqrt{2}/\pi^2) \{ (l/2)^{1/2} [(-1)^l - 2] + l\pi S_2(l\pi) + 3C_2(l\pi)/2 - C_2(2l\pi)/\sqrt{2} \} \quad (52)$$

The Fresnel integrals S_2 and C_2 have here the same meaning as before. In Table III we present the first 12 values of p_l .

Table III

l	p_l	l	p_l
1	0.32658	7	0.03382
2	0.15600	8	0.02838
3	0.09786	9	0.02427
4	0.06900	10	0.02108
5	0.05218	11	0.01854
6	0.04132	12	0.01649

For l greater than 12 we use the asymptotic form of the Fresnel integrals to compute the g_i 's and p_i 's needed in (51). We then sum these values up to $l = 500$ and extrapolate the remaining part of the sum to $l = \infty$. The result is

$$\alpha_f = 1 + 0.415z + O(z^2) \quad (53)$$

which gives a value too low for the coefficient of the term linear in z , when compared with the exact one 0.609.¹³ On the other hand, our result is very close to the 0.416 given by Kurata and Yamakawa.⁹ Their use of a Gaussian distribution for r_{ij} is undoubtedly the cause of this coincidence.

VI. Discussion

We conclude that deviations from the Kirkwood formula for the friction constant of chain polymers are small in all solvents, good or poor. However, an application of the Kirkwood formula requires the calculation of $\langle 1/r_{ij} \rangle_{\text{eq}}$, an average for which the Gaussian approximation is probably inadequate. The inadequacy is theoretically established for small z where the effect of the Gaussian approximation is large, according to eq 53, and the comments below it. At moderate and large z , experiment and Monte Carlo calculations show that α_f , α_L , and α_R (expansion of radius of gyration) lie much closer to each other than our calculation of α_f would indicate. The defect in our calculation cannot be blamed on our formula for $\alpha_{ij}^2 = \langle r_{ij}^2 \rangle_{\text{eq}} / \langle r_{ij}^2 \rangle_{\theta}$, for which the various theories are in relatively close agreement, compared to the discrepancy in question.

We have begun an investigation of the difference between $\langle 1/r_{ij} \rangle_{\text{eq}}$ and $\langle r_{ij}^2 \rangle_{\text{eq}}^{-1/2}$ on the basis of perturbation theory applied to a modified boson formalism. In this modified formalism the basis set differs from the previous one in that each normal mode is assigned a different excluded volume expansion factor. As a consequence all excluded volume effects studied in this paper and paper I are absorbed into the (Gaussian) ground state. What remains is treated as a perturbation, which, it can be shown, must give the linear term in z exactly, for the average of any function of coordinates. Hopefully the perturbation theory will also provide satisfactory estimates of non-Gaussian behavior at

moderate z . The numerical work required to apply the modified boson formalism appears to be tractable but has not been completed at the time of writing.

Appendix A

We solve here eq 18 using the same boson operator representation described previously.⁸ It was introduced *via* the matrix elements of normal coordinates and their derivatives formed with the set of eigenfunctions for the free-draining operator. The same matrix elements are obtained with an occupation number representation for the eigenfunctions in which the normal coordinates and their derivatives are properly represented by boson operators. The normalized ψ^α constitutes then the ground state or vacuum $|0\rangle$ of the system. The reader is directed to section III.B of paper I for the definitions of creation and annihilation operators (\mathbf{b}_i^+ and \mathbf{b}_i for each normal mode) and we give here only the final relations establishing the equivalence between coordinate and boson operator language

$$\frac{\partial}{\partial \mathbf{q}_i} = \sqrt{2}\alpha_i \mathbf{b}_i \quad (A.1)$$

$$\mathbf{q}_i = \frac{1}{\sqrt{2}\alpha_i} (\mathbf{b}_i^+ + \mathbf{b}_i)$$

(18) translates then into

$$\mathcal{L}\rho = \sum_{k,l} \mathbf{b}_k^+ \cdot \mathbf{A}_{kl} \cdot \{ \mathbf{b}_l + \frac{1}{kT} [\mathbf{b}_l (U - S^\alpha)] - \left(\frac{N}{2} \right)^{1/2} \frac{f}{kT} \frac{\delta_{l0}}{\alpha_l} \mathbf{e}_z \} |\rho\rangle = 0 \quad (A.2)$$

where

$$\mathbf{A}_{kl} = 2kT\alpha_k\alpha_l \mathbf{F}_{kl} \quad (A.3)$$

and $|\rho\rangle$ is the occupation number representative of ρ . Only a quadratic boson expansion of $U - S^\alpha$ allows an easy solution of (A.2). With that simplification

$$(U - S^\alpha)/kT = \frac{1}{2} \sum_{l=1}^N G_l (\mathbf{b}_l^+ + \mathbf{b}_l) \cdot (\mathbf{b}_l^+ + \mathbf{b}_l) \quad (A.4)$$

The force constant G_l was defined in paper I

$$G_{kl} = \alpha^2 - 1 - \frac{X}{32\pi^{3/2}} \sum_{i \neq j} C_{ij}^{-1/2} f_k f_l \quad (A.5)$$

with

$$C_{ij} = \frac{1}{2} \sum_{l=1}^N f_l^2 \quad (A.6)$$

and

$$f_l = \frac{Q_{jl} - Q_{il}}{\sqrt{2}\alpha_l} \quad (A.7)$$

Nondiagonal terms (G_{kl} , $k \neq l$) were shown to be extremely small.

The commutator

$$[\mathbf{b}_l (U - S^\alpha)/kT] = G_l (\mathbf{b}_l^+ + \mathbf{b}_l) \quad (A.8)$$

introduced in (A.2) yields

$$\sum_{k,l} \mathbf{b}_k^+ \cdot \mathbf{A}_{kl} \cdot \left\{ G_l \mathbf{b}_l^+ + (1 + G_l) \mathbf{b}_l - \left(\frac{N}{2} \right)^{1/2} \frac{f}{kT} \frac{\delta_{l0}}{\alpha_l} \mathbf{e}_z \right\} |\rho\rangle = 0 \quad (A.9)$$

The approximation

$$\Lambda_{kl} \simeq \langle \Lambda_{kl} \rangle_{\text{eq}} \delta_{kl} \quad (\text{A.10})$$

which has been discussed already reduces the equation to be solved to

$$\sum_{i=1}^N \mathbf{b}_i^+ \cdot (\mathbf{U}_i \cdot \mathbf{b}_i + \mathbf{V}_i \cdot \mathbf{b}_i^+ - \mathbf{W}_i \cdot \mathbf{e}_z) |\rho\rangle = 0 \quad (\text{A.11})$$

where

$$\begin{aligned} \mathbf{U}_i &= \langle \Lambda_{ii} \rangle_{\text{eq}} (1 + G_i) \\ \mathbf{V}_i &= \langle \Lambda_{ii} \rangle_{\text{eq}} G_i \\ \mathbf{W}_i &= \langle \mathbf{F}_{i0} \rangle_{\text{eq}} (2N)^{1/2} \alpha_i f \end{aligned} \quad (\text{A.12})$$

The three dyads \mathbf{U}_i , \mathbf{V}_i , \mathbf{N}_i , are proportional to the idem factor since $\langle \mathbf{D}_{ij} \rangle_{\text{eq}}$ is diagonal in the space coordinates (as shown in section IV). We try a solution of the form

$$|\rho\rangle = M|0\rangle$$

$$M = \exp \left[\sum_{i=1}^N M_i \mathbf{b}_i^+ \cdot \mathbf{b}_i^+ \right] \exp \left[\sum_{i=1}^N \mathbf{b}_i^+ \cdot \mathbf{a}_i \right] \quad (\text{A.13})$$

where \mathbf{a}_i is an arbitrary vector that commutes with \mathbf{b}_i^+ and \mathbf{b}_i . M has only creation operators and eq A.11 holds after we multiply by M^{-1} on the left. That is

$$M^{-1} \mathcal{L} M |0\rangle = \sum_{i=1}^N \mathbf{b}_i^+ \cdot (\mathbf{U}_i \cdot \mathbf{b}_i^M + \mathbf{V}_i \cdot \mathbf{b}_i^+ - \mathbf{W}_i \cdot \mathbf{e}_z) |0\rangle = 0 \quad (\text{A.14})$$

where

$$\mathbf{b}_i^M = M^{-1} \mathbf{b}_i^M \quad (\text{A.15})$$

The same technique, used in previous instances to evaluate operators having the form that \mathbf{b}_i^M has, is now followed for this one. Consider the more general $\mathbf{b}_i^M(\lambda)$

$$\begin{aligned} \mathbf{b}_i^M(\lambda) &= \exp \left[-\lambda \sum_{k=1}^N \mathbf{b}_k^+ \cdot (M_k \mathbf{b}_k^+ + \mathbf{a}_k) \right] \mathbf{b}_i \times \\ &\quad \exp \left[\lambda \sum_{k=1}^N \mathbf{b}_k^+ \cdot (M_k \mathbf{b}_k^+ + \mathbf{a}_k) \right] \\ \frac{\partial \mathbf{b}_i^M(\lambda)}{\partial \lambda} &= M^{-1} [\mathbf{b}_i, \mathbf{b}_i^+ (M_i \mathbf{b}_i^+ + \mathbf{a}_i)] M \end{aligned}$$

$$[\mathbf{b}_i, \mathbf{b}_i^+ (M_i \mathbf{b}_i^+ + \mathbf{a}_i)] = 2M_i \mathbf{b}_i^+ + \mathbf{a}_i$$

$$\mathbf{b}_i^M(\lambda) = 2M_i \mathbf{b}_i^+ + \mathbf{a}_i + \mathbf{c}$$

and \mathbf{c} is determined by the identity $\mathbf{b}_i^M(0) = \mathbf{b}_i$

$$\mathbf{b}_i^M = 2M_i \mathbf{b}_i^+ + \mathbf{b}_i + \mathbf{a}_i \quad (\text{A.16})$$

Substitution into eq A.14 gives

$$\sum_{i=1}^N \mathbf{b}_i^+ \cdot [(2M_i \mathbf{U}_i + \mathbf{V}_i) \cdot \mathbf{b}_i^+ + \mathbf{U}_i \cdot \mathbf{b}_i + \mathbf{U}_i \cdot \mathbf{a}_i - \mathbf{W}_i \cdot \mathbf{e}_z] |0\rangle = 0 \quad (\text{A.17})$$

which is satisfied by the simultaneous vanishing of

$$\begin{aligned} 2M_i \mathbf{U}_i + \mathbf{V}_i &= 0 \\ \mathbf{U}_i \cdot \mathbf{a}_i - \mathbf{W}_i \cdot \mathbf{e}_z &= 0 \end{aligned} \quad (\text{A.18})$$

for every l . With substitution of \mathbf{U}_i , \mathbf{V}_i , and \mathbf{W}_i by their values given in (A.12), eq A.18 now require

$$\begin{aligned} 2M_i(1 + G_i) + G_i &= 0 \\ 2kT\alpha_i(1 + G_i)\langle F_{il} \rangle_{\text{eq}} \mathbf{a}_i &= (2N)^{1/2} f \langle F_{0l} \rangle_{\text{eq}} \mathbf{e}_z \end{aligned} \quad (\text{A.19})$$

or

$$\begin{aligned} M_i &= -\frac{1}{2} \frac{G_i}{1 + G_i} \\ \mathbf{a}_i &= \left(\frac{N}{2}\right)^{1/2} \frac{f}{kT} \alpha_i^{-1} (1 + G_i)^{-1} \frac{\langle F_{0l} \rangle_{\text{eq}}}{\langle F_{il} \rangle_{\text{eq}}} \mathbf{e}_z \end{aligned} \quad (\text{A.20})$$

Thus, the steady-state distribution has the form

$$|\rho\rangle = \exp \left\{ -\frac{1}{2} \sum_{i=1}^N \frac{\mathbf{b}_i^+}{1 + G_i} \cdot \left[G_i \mathbf{b}_i^+ - \frac{(2N)^{1/2} f \langle F_{0l} \rangle_{\text{eq}}}{kT \alpha_i \langle F_{il} \rangle_{\text{eq}}} \mathbf{e}_z \right] \right\} |0\rangle \quad (\text{A.21})$$

Appendix B

The occupation number representative of the perturbed distribution for equilibrium $|\rho\rangle_{\text{eq}}$ is

$$\begin{aligned} |\rho\rangle_{\text{eq}} &= M_0 |0\rangle \\ M_0 &= \exp \left[-\frac{1}{2} \sum_{i=1}^N \frac{G_i}{1 + G_i} \mathbf{b}_i^+ \cdot \mathbf{b}_i^+ \right] \end{aligned} \quad (\text{B.1})$$

Since only creation operators are contained in M_0 , the average of the δ function can be written as

$$\langle 0 | \delta(\mathbf{r} - \mathbf{r}_{ij}) | \rho \rangle_{\text{eq}} = \langle 0 | M_0^{-1} \delta(\mathbf{r} - \mathbf{r}_{ij}) M_0 | 0 \rangle = \langle 0 | \delta(\mathbf{r} - \mathbf{r}_{ij}^{M_0}) | 0 \rangle \quad (\text{B.2})$$

where

$$\begin{aligned} \mathbf{r}_{ij}^{M_0} &= \sum_{i=1}^N f_i (\mathbf{b}_i^+ + \mathbf{b}_i^{M_0}) \\ \mathbf{b}_i^{M_0} &= M_0^{-1} \mathbf{b}_i M_0 \end{aligned} \quad (\text{B.3})$$

$\mathbf{b}_i^{M_0}$ equals (compare with (A.16) for $\mathbf{a}_i = 0$)

$$\mathbf{b}_i^{M_0} = \mathbf{b}_i - \frac{G_i}{1 + G_i} \mathbf{b}_i^+ \quad (\text{B.4})$$

Then

$$\mathbf{r}_{ij}^{M_0} = \sum_{i=1}^N f_i [\mathbf{b}_i + \mathbf{b}_i^+ (1 + G_i)^{-1}] \quad (\text{B.5})$$

and eq B.2 becomes

$$\begin{aligned} \langle 0 | \delta(\mathbf{r} - \mathbf{r}_{ij}) | \rho \rangle_{\text{eq}} &= (2\pi)^{-3} \int d\mathbf{w} \langle 0 | \exp \times \\ &\quad [i\mathbf{w} \cdot (\mathbf{r}_{ij}^{M_0} - \mathbf{r})] | 0 \rangle = (2\pi)^{-3} \int d\mathbf{w} \exp[-i\mathbf{w} \cdot \mathbf{r}] \prod_{i=1}^N \langle 0 | \times \\ &\quad \exp\{if_i \mathbf{w} \cdot [\mathbf{b}_i + \mathbf{b}_i^+ (1 + G_i)^{-1}]\} | 0 \rangle \end{aligned} \quad (\text{B.6})$$

We now factor the exponential containing boson operators into an ordered product in which the annihilation operators always stay to the right of the creation operators

$$\begin{aligned} \exp\{if_i \mathbf{w} \cdot [\mathbf{b}_i + \mathbf{b}_i^+ (1 + G_i)^{-1}]\} &= \\ \exp \left[-\frac{1}{2} f_i^2 (1 + G_i)^{-1} w^2 \right] \exp[if_i (1 + G_i)^{-1} \mathbf{w} \cdot \mathbf{b}_i^+] &\times \\ \exp[if_i \mathbf{w} \cdot \mathbf{b}_i] & \quad (\text{B.7}) \end{aligned}$$

where the first exponential in the right-hand member of this formula arises from the commutator

$$[\mathbf{w} \cdot \mathbf{b}_i, \mathbf{w} \cdot \mathbf{b}_i^+] = w^2 \quad (\text{B.8})$$

Recalling (B.5) we find

$$\prod_{i=1}^N \exp\{if_i \mathbf{w} \cdot [\mathbf{b}_i + \mathbf{b}_i^+(1 + G_i)^{-1}]\} = \exp\left[-\frac{1}{2} \sum_{i=1}^N f_i^2 (1 + G_i)^{-1} w^2\right] \theta \exp[i\mathbf{w} \cdot \mathbf{r}_{ij}^{M_0}] \quad (\text{B.9})$$

where θ designates an ordering operator whose action is to place, in the boson expansion of $\mathbf{r}_{ij}^{M_0}$, every \mathbf{b}_i on the right of every \mathbf{b}_i^+ . The average is then

$$\prod_{i=1}^N \langle 0 | \exp\{if_i \mathbf{w} \cdot [\mathbf{b}_i + \mathbf{b}_i^+(1 + G_i)^{-1}]\} | 0 \rangle = \exp\left[-\frac{1}{2} \sum_{i=1}^N f_i^2 (1 + G_i)^{-1} w^2\right] \quad (\text{B.10})$$

and

$$\langle 0 | \delta(\mathbf{r} - \mathbf{r}_{ij}) | \rho \rangle_{\text{eq}} = (2\pi)^{-3} \int d\mathbf{w} \times \exp\left[-i\mathbf{w} \cdot \mathbf{r} - \frac{w^2}{2} \sum_{i=1}^N f_i^2 (1 + G_i)^{-1}\right] \quad (\text{B.11})$$

Integration over \mathbf{w} gives

$$\langle 0 | \delta(\mathbf{r} - \mathbf{r}_{ij}) | \rho \rangle_{\text{eq}} = \left[2\pi \sum_{i=1}^N f_i^2 (1 + G_i)^{-1}\right]^{-3/2} \times \exp\left[-\frac{r^2}{2 \sum_{i=1}^N f_i^2 (1 + G_i)^{-1}}\right] \quad (\text{B.12})$$

Appendix C

The average $\langle \nabla_j U \rangle$ translates into boson language as

$$\langle \nabla_j U \rangle = \sum_{i=1}^N Q_{ji} \left\langle \frac{\partial U}{\partial \mathbf{q}_i} \right\rangle = \sqrt{2} \sum_{i=1}^N Q_{ji} \alpha_i \langle 0 | [(\mathbf{b}_i, U)] | \rho \rangle \quad (\text{C.1})$$

where the commutator is

$$[\mathbf{b}_i, U] = kT(1 + G_i)(\mathbf{b}_i^+ + \mathbf{b}_i) \quad (\text{C.2})$$

Then

$$\begin{aligned} \langle 0 | (\mathbf{b}_i^+ + \mathbf{b}_i) | \rho \rangle &= -\frac{1}{2} (1 + G_i)^{-1} \langle 0 | (\mathbf{b}_i^+ + \mathbf{b}_i) \mathbf{b}_i^+ \\ &\left[G_i \mathbf{b}_i^+ - \frac{(2N)^{1/2} f \langle F_{0i} \rangle_{\text{eq}}}{kT \alpha_i \langle F_{ii} \rangle_{\text{eq}}} \mathbf{e}_z \right] | 0 \rangle = \\ &\left(\frac{N}{2}\right)^{1/2} (1 + G_i)^{-1} \frac{f \langle F_{0i} \rangle_{\text{eq}}}{kT \alpha_i \langle F_{ii} \rangle_{\text{eq}}} \mathbf{e}_z \quad (\text{C.3}) \end{aligned}$$

since $[\mathbf{b}_i, \mathbf{b}_i^+ \cdot \mathbf{e}_z] = \mathbf{e}_z$. Combining (C.2) and (C.3) we get

$$\langle \nabla_j U \rangle = N^{1/2} f \mathbf{e}_z \sum_{i=1}^N Q_{ji} \frac{\langle F_{0i} \rangle_{\text{eq}}}{\langle F_{ii} \rangle_{\text{eq}}} \quad (\text{C.4})$$

Conductance of the Alkali Halides. XI. Cesium Bromide and Iodide in Water at 25°¹

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Abstract: The conductances at 25° in water of cesium bromide and cesium iodide have been determined over the range $0.003 \leq c \leq 0.10 N$. About 65 sets of data are given for each salt, sufficient to permit a statistical analysis of the differences $\delta\Lambda$ between calculated and observed values of the conductance. The semiempirical screening equation $\Lambda = \Lambda_0 - Sc^{1/2} + E'c \ln c + Ac + Bc^{3/2}$ accurately reproduces the data within about 0.01%, with a random pattern of $\delta\Lambda$'s, and the constants are independent of the concentration range, provided c_{min} does not exceed 0.01. The explicit equation $\Lambda = \gamma(\Lambda_0 - \Delta\Lambda)(1 + \Delta X/X)/(1 + 3\varphi/2)$ reproduces the data over the same range, and with the same precision. The distribution of $\delta\Lambda$'s is likewise random, independent of concentration. The values of the parameters Λ_0 = limiting conductance, K_A = association constant, and \hat{a} = contact distance are independent of the upper limit of the concentration range, provided c_{max} does not exceed 0.10 N . Deviations between Λ_{calcd} and Λ_{obsd} are very nearly proportional to c^2 in the range $0.10 \leq c \leq 1.0$. The following values summarize the results: for cesium iodide, $\Lambda_0 = 154.17$, $K_A = 0.93$, $\hat{a} = 5.49$; for cesium bromide, $\Lambda_0 = 155.37$, $K_A = 1.07$, $\hat{a} = 5.55$.

Association of 1:1 electrolytes in water has not been seriously considered since the advent of the Debye-Hückel theory of electrolytes in 1923. This theory was so successful in accounting for the limiting behavior of dilute solutions of strong electrolytes in water that the Arrhenius hypothesis was completely

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rejected for such systems. In 1926, Bjerrum revived the idea that less than the stoichiometric concentration of electrolyte functioned as free ions, by proposing ion pairs to account for the activity coefficients of 2:2 electrolytes in water. In 1933, Fuoss and Kraus combined the Debye and the Bjerrum theories to obtain a conductance equation which accurately reproduced observations in solvents of dielectric constant of about 25 or less, where the conductance curve lies well below