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Evaluation of Thermodynamic and Hydrodynamic Parameters of Polymer Molecules

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Summary

A numerical regression method, assisted by a least squares technique, is proposed to obtain thermodynamic and hydrodynamic parameters of polymer molecules via a direct comparison between experimental data and theoretical functions. This comparison is independent of the number of the experimental variables. The method also enables to decide if a selected set of theoretical equations fits satisfactorily the experimental results.

Introduction

The thermodynamic and hydrodynamic treatment of macromolecular solutions is a very active field of investigation. When attention is directed to very dilute solutions of random coiled linear polymer molecules a lot of experimental results (molecular weight, radius of gyration, second virial coefficient, intrinsic viscosity, etc.) are available to be analyzed by means of different theoretical approaches which have the same underlying purpose: to describe equilibrium and transport solution properties in terms of polymer-solvent and polymer-polymer interaction parameters. To obtain these parameters one has to take sufficient experimental values (which may be measured with different reliability) of a number of variables which are connected to each other by different systems of equations (explicitly or not) and decide which of these systems, if any, give a satisfactory fit to the experimental results.

It is well known that dilute polymer solution theory has to account not only for the interaction between its constituents as any other solution theory but also for the average dimensions of the macromolecules in solution. This feature leads to the so called two parameter theory (YAMAKAWA, 1971). The manipulation of the experimental data to show how the different theoretical approaches work has to meet therefore the simultaneous verification of both the thermodynamic and transport

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aspects , based on the situation that there are enough experimental data appropriately distributed in the measured molecular weight range.

To this end several procedures were proposed in the literature: for example to group some experimental results to make a comparison with the theoretical functions possible (YAMAKAWA, 1968); to linearize these functions allowing an easy grphical analysis (NORISUYE et al., 1968; BERRY, 1966); to use graphical methods based on empirical laws (GLÖCKNER, 1980); etc. All these methods have to circumvent the difficulty which prevents a direct comparison between measurements and theory. Generally they are bounded to some requisites which depend on the particular mathematical form of the equations used.

Here we propose a numerical method (Gauss' method, BARD, 1974) by which this direct comparison is possible without necessity of any change in the theoretical equations or use of any additional relationship and by simultaneous use of all experimental results.

Outlines of the method

Let us assume that for a solution of a linear polymer the experimental values of the radius of gyration $Rg,e = \langle Rg^2 \rangle^{1/2}$, the second virial coefficient A2,e and the intrinsic viscosity $[\eta],e$ are known as a function of the molecular weight M. Within the frame of the two parameter model theory calculated values Rg,c , A2,c and $[\eta],c$ may be derived from the following structural equations:

$$\begin{aligned} Rg,c &= R(Ko,B,M) \\ A2,c &= A(Ko,B,M) \qquad\qquad (1) \\ [\eta],c &= E(Ko,B,\Phi o,M) \end{aligned}$$

where $Ko^2 = \langle Rg^2 \rangle o/M$ and $B = \beta/ms^2$ are the two parameters to be determined. Φo is Flory's viscosity constant which we take as a third parameter, $\langle Rg^2 \rangle o$ is the square of the unperturbed radius of gyration, and β is the binary cluster integral of interaction between chain segments of molecular weight ms. The explicit form of eqs.(1) depend on each theory but are always non linear.

With initial assumed values of the parameters Ko, B and Φo we may calculate Rg,ci , $A2,ci$ and $[\eta],ci$ for each molecular weight Mi with the help of eqs.(1). The Gauss method considers that the differences between the experimental and calculated values of Rg, A2 and $[\eta]$ arise from the errors (δKo, δB and $\delta \Phi o$) in the assumed values of the three parameters.

According to a one term Taylor development the relations between the above differences and the parameter errors are given by

$$
\begin{aligned}
\Delta R_i &= \left.\frac{\partial R}{\partial Ko}\right)_i \delta Ko + \left.\frac{\partial R}{\partial B}\right)_i \delta B \\
\Delta A_i &= \left.\frac{\partial A}{\partial Ko}\right)_i \delta Ko + \left.\frac{\partial A}{\partial B}\right)_i \delta B \qquad\qquad (2) \\
\Delta E_i &= \left.\frac{\partial E}{\partial Ko}\right)_i \delta Ko + \left.\frac{\partial E}{\partial B}\right)_i \delta B + \left.\frac{\partial E}{\partial \Phi o}\right)_i \delta \Phi o
\end{aligned}
$$

Eqs.(2) provide the new values of the parameters ($Ko + \delta Ko$, $B + \delta B$, $\Phi o + \delta \Phi o$). With these a new set of calculated values (Rg,c , $A2,c$ and $[\eta],c$) are obtained through eqs.(1) and the procedure repeated until the parameter values show no significant change.

Actually there are N sets of experimental values and n parameters (here $n = 3$) to be determined ($N > n$). Therefore it is necessary to use a regression method assisted by a least squares technique. In other words we try to minimize the sum of the squares of the differences given by eqs.(2). Such a sum has an unsatisfactory property because we add rather different entities. To solve this problem it is only necessary to minimize the sum of the squares of the relative differences, i.e.:

$$S = \sum_{i=1}^{N} \left\{ h_R \left(\frac{Rg,e - Rg,c}{Rg,e} \right)_i^2 + h_A \left(\frac{A2,e - A2,c}{A2,e} \right)_i^2 + h_E \left(\frac{[\eta],e - [\eta],c}{[\eta],e} \right)_i^2 \right\} \quad (3)$$

where h_R, h_A and h_E are numerical coefficients which, in a relative scale, allow to correct in case that some kind of measurement (say a) may be experimentally more reliable than other (say b) by putting $h_a > h_b$.

Using the abbreviations $F_k = R, A$ or E, with $k = 1,..,L$ P_j = Ko, B or Φo, with $j = 1,,..,n$; eq.(3) may be written in a very general way,

$$S = \sum_{i=1}^{N} \sum_{k=1}^{L} h_k \left(\frac{\Delta F_k}{F_{k,e}} \right)_i^2 \qquad (4)$$

(L is the number of measured dependent variables), the condition for a minimum being n equations of the form

$$0 = \frac{\partial S}{\partial P_j} = -2 \sum_{i=1}^{N} \sum_{k=1}^{L} \left. h_k \frac{\Delta F_k}{F_{k,e}^2} \right)_i \left. \frac{\partial F_k}{\partial P_j} \right)_i \qquad (5)$$

Introducing eqs.(2) in (5)

$$\sum_{i=1}^{N} \sum_{k=1}^{L} \left. \left. h_k \frac{\Delta F_k}{F_{k,e}^2} \right)_i \frac{\partial F_k}{\partial P_j} \right)_i = \sum_{i=1}^{N} \sum_{k=1}^{L} \left. \left. \frac{h_k}{F_{k,e}^2} \right)_i \frac{\partial F_k}{\partial P_j} \right)_i \sum_{\ell=1}^{n} \frac{\partial F_k}{\partial P_\ell} \delta P_\ell \qquad (6)$$

($\ell = 1,..,j,..,n$). The n eqs.(6) allow to calculate the n values δP_ℓ with which a new set of parameters ($P_\ell + \delta P_\ell$) are calculated to make a new iteration step as outlined before.

For a specific application see the Appendix.

Application to some experimental results.

We applied the method to data from several polymer-solvent systems found in the literature and compared the values of the parameters Ko and Φo to those measured experimentally under theta conditions. Only self-consistent combinations of equations for the expansion factor α and the interpenetration function $\bar{z}\ h(\bar{z})$ were used (YAMAKAWA, 1971; GLOCKNER, 198o). For each variable we also calculated the standard error of estimate

$$s'_k = \left\{ \frac{1}{N} \sum_{i=1}^{N} \left(\frac{F_{k,e} - F_{k,c}}{F_{k,e}} \right)_i^2 \right\}^{1/2} \qquad (7)$$

which can be compared to the mean experimental relative error e_{rel} with which $F_{k,e}$ was measured. $s'_k \lesssim e_{rel}$ means that the theoretical curve fits appropriately to the experimental values. See table I.

In table I it is seen that for some systems the values of the parameters obtained agree with those determined experimentally but for others a somewhat too high difference is found. This is probably because the theories are not valid for high values of the excluded volume parameter z.

As an example we plotted in fig. I $[\eta]$,e , A2,e and Rg,e against the molecular weight M of very high molecular weight Polystyrene in benzene (MIYAKI et al., 1978; EINAGA et al., 1979), together with their experimental errors and the theoretical curves that best fitted the experimental data. A quite good adjustment is found for $[\eta]$ and Rg but for A2 a clear bias between theoretical curve and experimental values is found. This differences do not dissappear by use of reasonable values for the statistical weights h_k. This means that the theoretical equations are incapable to describe appropriately the A2 - M relationship.

We also applied this method but taking only Rg and A2 values. The parameters Ko and B calculated were similar to those obtained by GLOCKNER (1980) by use of his graphical procedure.

Naturally the method may be extended so as to embrace any other experimental variable adequately described by theory (for example the diffusion and sedimentation coefficients, etc.).

TABLE I

Polymer - solvent system	Molecular weight range ($M\,10^{-6}$) (cgs units)	Range of z values		Calculated parameters Ko_8 10^8	B_{27} 10^{27}	Φ_o 10^{-23}	Expt. param. Ko_8 10^8	Φ_o 10^{-23}	Syst. of theor. equations (+)	St. error of estimate s'_R (%)	s'_A (%)	s'_E (%)	Ref.
				(cgs units)			(cgs units)						
Polystyrene (benzene)	57 - 8.8	1.8	0.71	0.47	1.1	1.7	0.30	2.3	KYYT	2 (20)*	8 (5)	5 (1)	5 9
Poly-α-methyl-styrene (toluene)	7.5 - 0.20	2.5	0.41	0.33	1.5	1.9	0.29	2.0	KYYT	3	17	5	7 10
Poly-α-methyl-styrene (toluene)	4.1 - 0.19	1.5	0.33	0.37	1.7	1.6	"	"	KYYT	3	10	5	12
Poly-methyl methacrylate (acetone)	7.8 - 0.34	2.2	0.45	0.31	1.1	1.5	0.22 0.25	2.7	FKO,m	6	10	10	4 13
Poly-chloro-prene (n-butil-acetate)	3.2 - 0.16	1.1	0.25	0.34	1.1	2.1	0.32	2.3	FKO,m KYYT	5	11	8	11
Poly-chloro-prene ($C\ Cl_4$)	3.2 - 0.16	2.0	0.44	0.36	2.3	2.0	0.32	2.3	FKO,m	7	15	7	11
Amylose Tri-acetate (nitro-methane)	3.1 - 0.15	1.0	0.22	0.34	1.0	2.1	-	-	FKO,o	3	5	6	1

* experimental mean relative errors as given by the authors.

\+ system of theoretical equations that best fit the experimental results. FKO,o/m: Flory-Krigbaum-Orofino, original and modificated; KYYT: Kurata-Yamakawa/Yamakawa-Tanaka (YAMAKAWA, 1971).

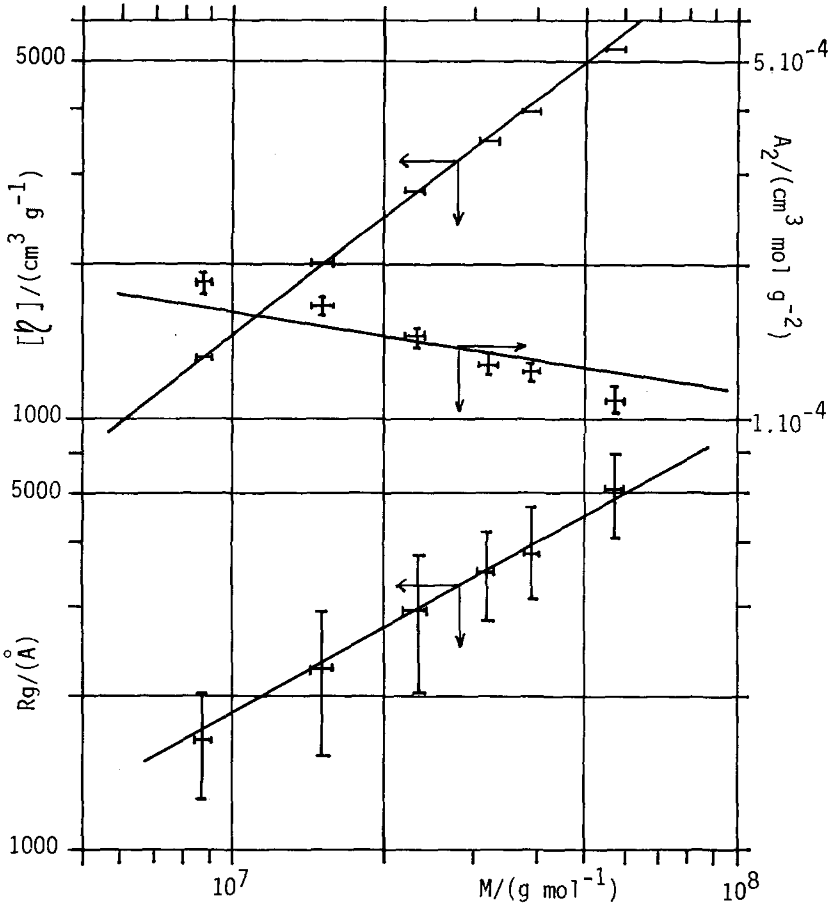

FIGURE I.- Intrinsic viscosity, second virial coefficient, radius of gyration of Polystyrene in benzene and the theoretical curves that best fit the experimental data.

Appendix

By use of vectorial notation and introducing the approximation

$$\frac{\Delta F_k}{F_{k,e}} \simeq \ln \frac{F_{k,e}}{F_{k,c}} \qquad (A1)$$

the n eqs. (6) may be written

$$\vec{\delta} = \vec{v} \cdot (\vec{\vec{Q}})^{-1} \qquad (A2)$$

where $\vec{\delta} = \left\{ \delta P_j \right\}$

$$\vec{v} = \left\{ \sum_{i=1}^{N} \sum_{k=1}^{L} h_k \ln\left(\frac{F_{k,e}}{F_{k,c}}\right)_i \left.\frac{\partial \ln F_k}{\partial P_j}\right)_i \right\} \qquad (A3)$$

and $\vec{\vec{Q}}$ is a n x n matrix whose elements are

$$\vec{\vec{Q}} = \left\{ \sum_{i=1}^{N} \sum_{k=1}^{L} h_k \left.\frac{\partial \ln F_k}{\partial P_j}\right)_i \left.\frac{\partial \ln F_k}{\partial P_\ell}\right)_i \right\} \ell = 1, \ldots, j, \ldots, n$$

As an example we take Flory-Krigbaum-Orofino (FKO) self consistent system of equations for the expansion factor α and the interpenetration function $\bar{z}\, h(\bar{z})$ (YAMAKAWA, 1971)

$$\begin{aligned} \alpha^5 - \alpha^3 &= c\, z \\ \bar{z}\, h(\bar{z}) &= \frac{\ln(1 + c' z)}{c'} \end{aligned} \qquad (A4)$$

and a first term perturbative series for the viscosity expansion factor (YAMAKAWA and TANAKA, 1967)

$$\alpha_\eta^3 = 1 + c_1 z + \ldots \qquad (A5)$$

where z is the well known excluded volume parameter defined by $z = (4\Pi)^{-3/2} B\, Ko^{-3} M^{1/2}$ and $\bar{z} = z/\alpha^3$.- (A6)

Given the following relationships (YAMAKAWA, 1971)

$$\begin{aligned} \langle Rg^2 \rangle &= \alpha^2 \langle Rg^2 \rangle_o \\ A2 &= B \frac{Na}{2} h(\bar{z}) \\ [\eta] &= [\eta]_\Theta\, \alpha_\eta^3 = 6^{3/2} \Phi o\, Ko^3 \alpha_\eta^3 M^{1/2} \end{aligned} \qquad (A7)$$

we derive

$$\begin{aligned} Rg,c &= Ko\, M^{1/2} (1 + c\, \bar{z})^{1/2} \\ A2,c &= B\, Na \frac{\ln(1 + c' \bar{z})}{2\, c'\, \bar{z}} \\ [\eta],c &= 6^{3/2} \Phi o\, Ko^3 (1 + c_1 z)\, M^{1/2} \end{aligned} \qquad (A8)$$

and the following derivative equations:

$$\frac{\partial \ln R}{\partial Ko} = \frac{1}{Ko}\left[1 - \frac{3\, c\, \bar{z}}{2 + 5\, c\, \bar{z}}\right] \qquad \frac{\partial \ln R}{\partial B} = \frac{1}{B}\left[\frac{c\, \bar{z}}{2 + 5\, c\, \bar{z}}\right]$$

$$\frac{\partial \ln A}{\partial Ko} = \frac{3(1 + c\, \bar{z})}{Ko(1 + 2.5\, c\, \bar{z})}\left[1 - \frac{1}{h(\bar{z})\, (1 + c' \bar{z})}\right]$$

$$\frac{\partial \ln A}{\partial B} = \frac{1}{B(1 + 2.5\, c\, \bar{z})}\left[\frac{1 + c\, \bar{z}}{h(\bar{z})(1 + c' \bar{z})} + \frac{3\, c\, \bar{z}}{2}\right] \qquad (A9)$$

$$\frac{\partial \ln R}{\partial \Phi o} = \frac{\partial \ln A}{\partial \Phi o} = 0 \qquad \frac{\partial \ln E}{\partial \Phi o} = \frac{1}{\Phi o}$$

$$\frac{\partial \ln E}{\partial Ko} = \frac{(-3)}{Ko}\left[1 + \frac{c_1 z}{1 + c_1 z}\right] \qquad \frac{\partial \ln E}{\partial B} = \frac{1}{B}\left[\frac{c_1 z}{1 + c_1 z}\right]$$

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