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The second virial coefficient of polydisperse polymer samples in a good solvent

An analytical approach following the concept of interpenetrating chains

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Summary

In this paper we present analytical expressions for the osmotic and light–scattering second virial coefficients of polydisperse polymer samples in a good solvent. They are derived using the Schulz and the Lognormal molecular weight distribution respectively. The effect of interpenetrating coils is taken into account. Comparison is made with expressions already derived by Casassa using a hard sphere model. The reduction of the obtained expressions to simple scaling laws is discussed.

Introduction

One of the quantities playing a crucial part in the thermodynamics of polymer solutions is the second virial coefficient A_2. This quantity has been object of many theoretical and experimental studies. So far most of the theoretical calculations have only been concerned with monodisperse polymer solutions. For such solutions the following scaling law has been generally accepted (1,2)

$$A_2 = K_a M^{-a} = A_0 p^{-a} \tag{1}$$

where

$$A_0 = K_a M_0^{-a} \tag{2}$$

Here M is the molecular weight of the polymer, M_0 is the molecular weight of the repeating unit and p is the degree of polymerization ($p = M/M_0$). The constant K_a depends on the polymer–solvent system and the exponent a is only a function of the solvent quality. For monodisperse samples of a linear, coil–like polymer in a good solvent it has been shown theoretically that $0.2 \leq a \leq 0.25$ (1–3).

Despite advanced techniques of polymerization and fractionation one always deals in practice with polydisperse polymer fractions. At first instance this seems to enlarge enormously the difficulties in the theoretical calculations. For a polydisperse polymer solution Casassa (4) has proposed the following equations, which turned out to be consistent with experimental results (5–8).

$$(A_2)_{os} = \sum_{i=1}^{N} \sum_{j=1}^{N} A_{ij} w_i w_j \tag{3a}$$

$$(A_2)_{ls} = \frac{\sum_{i=1}^{N} \sum_{j=1}^{N} A_{ij} w_i w_j p_i p_j}{\left(\sum_{i=1}^{N} w_i p_i \right)^2} \tag{3b}$$

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*To whom offprint requests should be sent where os and ls refer to the osmotic and light scattering virial coefficients respectively, A_{ij} is the second virial coefficient determined by the interaction between two chains with degree of polymerization p_i and p_j respectively and w_i and w_j are their respective weight fractions. The indices i and j run over all the N different chain lengths in the polymer sample.

Following Casassa (9) we approximate these sums by integrals

$$(A_2)_{os} = \int_0^\infty dp\, w\{p\} \int_0^\infty dp'\, w\{p'\} A\{p,p'\} \tag{4a}$$

$$(A_2)_{ls} = \left(\bar{p}_w\right)^{-2} \int_0^\infty dp\, p\, w\{p\} \int_0^\infty dp' p' w\{p'\} A\{p,p'\} \tag{4b}$$

in which $\bar{p}_w$ stands for the weight averaged degree of polymerization of the sample and the second virial coefficients and the weight fractions appear as continuous functions.

Recently we have performed experiments to determine the behaviour of the coefficient A_{ij} (8,10). For this purpose the second virial coefficients of mixtures of two chemically identical polymers with different molecular weights in a good solvent have been measured. Ten combinations have been examined. The ratios of the molecular weights of both polymers have been varied from 1.8 to nearly 100. The system used in these measurements was polystyrene in toluene. Measurements have been performed both with osmometry and with light scattering at 25^{0}C. The polystyrene samples have been analyzed with GPC. It has been found that the molecular weight distributions of all these samples were very narrow ($\bar{M}_w/\bar{M}_n < 1.1$). In order to determine the values of the second virial coefficients A_i, A_j and A_{ij} the two fractions in each mixture were assumed to be monodisperse. With this assumption the values of A_i, A_j and A_{ij} were determined for each combination of two polymers fractions. For the range of molecular weigth ratios examined it has been found that the cross coefficient A_{ij} was approximately equal to the second virial coefficient of the smallest polymer

$$A_{ij} = A_{ii} \qquad \mathit{for:} \quad p_j \geq p_i \tag{5}$$

More precisely the values of the ratio A_{ij}/A_{ii} were found to increase slightly with increasing molecular weight ratio up to a constant value of 1.1 for $p_j/p_i \geq 20$. However, the deviations of the experimental values of the ratio A_{ij}/A_{ii} from 1 hardly exceed the experimental error. Moreover, even for samples with a broad molecular weight distribution the contribution to the second virial coefficient of the sample will mainly result from interactions between pairs of molecules, for which p_j/p_i is not extremely large.

Also results from other experiments (5,6,11–13) seem to confirm eq.(5), although the experimental errors in the values of A_{ij}/A_{ii} in these experiments were usually larger than those in ours.

Eq.(5) agrees in a first approximation with several theoretical predictions, based either on the two–parameter perturbation theory (8,14–20) or on the renormalization group approach (8,21–24). Particularly, eq.(5) results from the treatment of Witten and Prentis (8,20), who started from an interpenetration model, in which the smaller chain is assumed to interpenetrate into the larger.

Another equation follows from the hard sphere model proposed first by Casassa (9) and later by Yamakawa (1)

$$A_{ij} = \frac{A_{ii} p_i}{8 p_j} \left\{ 1 + \left(\frac{p_j}{p_i}\right)^{(2-a)/3} \right\}^3 \qquad \mathit{for:} \quad p_j \geq p_i \tag{6}$$

This equation greatly differs from eq.(5) and is confirmed by our experimental results only for $1 \leq p_j/p_i < 3$ (8).

The best quantitative agreement between a theoretical prediction and our experimental results is obtained with an equation proposed by Joanny, Leibler and Ball (24). According to this equation (see eq.(2.71) in chapter 2 of ref. 8) the ratio A_{ij}/A_{ii} does not differ appreciably from 1 within a large range of molecular weight ratios (i.e. $p_j/p_i \leq 10^6$).

Hence eq.(5) can be used as a good approximation to calculate the second virial coefficient of a polydisperse polymer sample. For that purpose we combine it first with eq.(1) and bring it in the appropriate form

$$A\{p,p'\} = A_0(p')^{-a} \qquad \textit{for:}\quad p' < p \tag{7a}$$

$$A\{p,p'\} = A_0 p^{-a} \qquad \textit{for:}\quad p' \geq p \tag{7b}$$

Using eqs.(7) the integrals in eqs.(4) can be reduced to

$$(A_2)_{os} = 2A_0 \int_0^\infty dp\, w\{p\} \int_0^p dp'\, (p')^{-a} w\{p'\} \tag{8a}$$

$$(A_2)_{ls} = 2A_0 \left(\bar{p}_w\right)^{-2} \int_0^\infty dp\, p w\{p\} \int_0^p dp'\, (p')^{1-a} w\{p'\} \tag{8b}$$

In the following these integrals will be further worked out for suitable forms for w{p} using two different molecular weight distribution functions, i.e. a Schulz function (25) and a Lognormal function (26). We will show that with these functions the double integrals can be solved analytically.

<u>Analytical solutions</u>

The Schulz distribution function (25) is given by

$$w^S\{p\} = \left\{(k/\bar{p}_n)^{k+1} p^k \exp\left[-p(k/\bar{p}_n)\right]\right\} / \,\Gamma(k+1) \tag{9}$$

Here Γ(k+1) is the Gamma function with argument k+1 and

$$k = \left((\bar{M}_w/\bar{M}_n) - 1\right)^{-1} = \left((\bar{p}_w/\bar{p}_n) - 1\right)^{-1} \tag{10}$$

After substituting this distribution function in eqs.(8) and performing some algebra, which is summarized in Appendix A, we arrive at

$$(A_2)_{os} = A_0(\bar{p}_n)^{-a} Q^S_{os}\{k,a\} = K_a \bar{M}_n^{-a} Q^S_{os}\{k,a\} \tag{11a}$$

$$(A_2)_{ls} = A_0(\bar{p}_w)^{-a} Q^S_{ls}\{k,a\} = K_a \bar{M}_w^{-a} Q^S_{ls}\{k,a\} \tag{11b}$$

with

$$Q^S_{os}\{k,a\} = k^a \frac{\Gamma(k+1-a)}{\Gamma^2(k+1)} \sum_{n=0}^{\infty} \frac{\Gamma(2k+2+n-a)}{\Gamma(k+2+n-a)} 2^{a-2k-1-n} \tag{12}$$

and

$$Q^S_{ls}\{k,a\} = Q^S_{os}\{k+1,a\} \tag{13}$$

The Lognormal distribution function (26) is given by

$$w^{LN}\{p\} = (\pi)^{-1/2}(p\beta)^{-1} \exp\left\{-(\ln p\, /\ln p_m)^2/\beta^2\right\} \tag{14}$$

with

$$\beta^2 = 2\ln(\bar{p}_w/\bar{p}_n) = 2\ln(1+k^{-1}) \tag{15}$$

and

$$p_m = (\bar{p}_w \bar{p}_n)^{1/2} \tag{16}$$

Using this distribution function the integrals in eqs.(8) can be calculated. The derivation is given in Appendix B. The results are

$$(A_2)_{os} = A_0(\bar{p}_n)^{-a} Q^{LN}_{os}\{\beta, a\} = K_a \bar{M}_n^{-a} Q^{LN}_{os}\{\beta, a\} \tag{17a}$$

$$(A_2)_{ls} = A_0(\bar{p}_w)^{-a} Q^{LN}_{1s}\{\beta, a\} = K_a \bar{M}_w^{-a} Q^{LN}_{1s}\{\beta, a\} \tag{17b}$$

with

$$Q^{LN}_{os}\{\beta, a\} = Q^{LN}_{1s}\{\beta, a\} = 1 + (2\pi)^{-1/2} a\beta + \frac{1}{4}(a^2 - a)\beta^2 + \frac{1}{24}(2\pi)^{-1/2}(5a^3 - 6a^2)\beta^3 + \frac{1}{32}(a^2 - a)^2\beta^4 + \ldots \tag{18}$$

Note that eqs.(11) and (17) have been written such that they may be considered as extensions of the corresponding scaling relations for polydisperse polymers

$$(A_2)_{os} = A_0 \bar{p}_n^{-a} = K_a \bar{M}_n^{-a} \tag{19a}$$

$$(A_2)_{ls} = A_0 \bar{p}_w^{-a} = K_a \bar{M}_w^{-a} \tag{19b}$$

The coefficients Q appearing in eqs.(11) and (17) indicate the deviations of the values of the second virial coefficients from the above scaling behaviour. Obviously it is of interest to investigate further under which conditions eqs.(19) are reasonable approximations of eqs.(11) and (17).

Hard sphere analogs of eqs.(11) to (13) have been derived by Casassa (9,1). They are represented by eqs.(11) and (13), but with eq.(12) replaced by

$$Q^{S}_{os} = \left\{k^a/4\left(\Gamma(k+1)\right)^2\right\} \times \left\{\Gamma(k-a+2)\Gamma(k) + 3\Gamma\left(k-\frac{2}{3}a+\frac{4}{3}\right)\Gamma\left(k-\frac{1}{3}a+\frac{2}{3}\right)\right\} \quad \textit{(Hard Sphere Model)} \tag{20}$$

This variant for which explicitly use has been made of eq.(6) instead of eq.(5) will also be discussed.

Results and discussion

In Fig.1 $(A_2)_{os}$ and $(A_2)_{ls}$ are plotted against $\bar{M}_w/\bar{M}_n$ ($= \bar{p}_w/\bar{p}_n$) together with the plots obtained from the scaling relations (19). For the sake of convenience $(A_2)_{os}$ originating from eq.(19a) was arbitrarily chosen equal to 1. The plots have been prepared with $a = 0.217$, i.e. the experimental value found for polystyrene in toluene at 25°C from a double logarithmic plot of $(A_2)_{os}$ versus M_n (8).

It is of interest to observe that for $\bar{M}_w/\bar{M}_n < 2$ ($k > 1$, $\beta < 1.18$) the second virial coefficients obtained with eq.(5) follow closely (within 4%) the plots predicted by the scaling relations. Even for $\bar{M}_w/\bar{M}_n > 2$ the second virial coefficients are reasonably represented by the scaling–law plots, that is, in the case of the Lognormal distribution the agreement is excellent, however, in the case of the Schulz distribution deviations from the scaling law are seen for $(A_2)_{os}$. Obviously the influence of the type of distribution becomes observable in the range $\bar{M}_w/\bar{M}_n > 2$.

The plots in Fig.1 based on the hard sphere model (eq.(6)) only tend to the scaling law curves in the rather restricted range $\bar{M}_w/\bar{M}_n < 1.25$ ($k > 4$, $\beta < 0.67$). Bearing in mind that eq.(5) is more realistic than eq.(6) (see above) it must be concluded that the values of the second virial coefficients are overestimated by the hard sphere model in the range $\bar{M}_w/\bar{M}_n > 1.25$.

Fig.2 shows the curves of the ratio $(A_2)_{os}/(A_2)_{ls}$ versus $\bar{M}_w/\bar{M}_n$ for $a = 0.217$. Again the overestimation effect of the hard sphere model is seen. For comparison some experimental points have been added in the figure, all referring to polystyrene samples in toluene at 25°C. Measured data of $\bar{M}_w$, $\bar{M}_n$, $(A_2)_{ls}$ and $(A_2)_{os}$ for the samples P2, PS90 and PS300

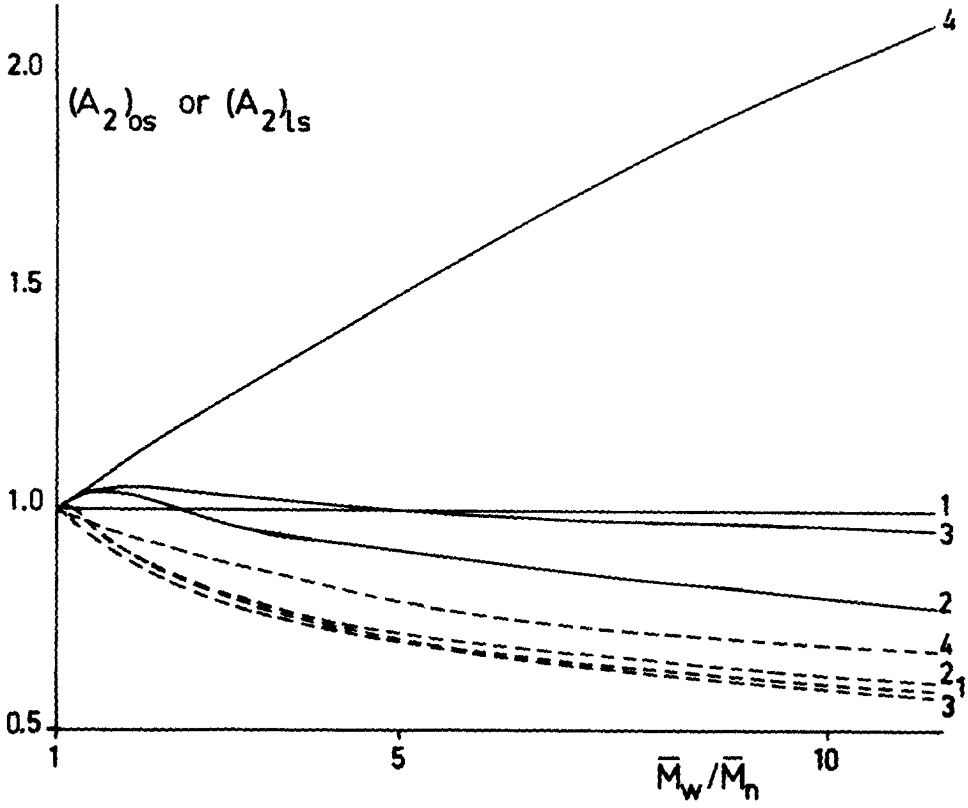

Figure 1 $(A_2)_{os}$ *(full curves) and* $(A_2)_{ls}$ *(dashed curves) plotted against* $\overline{M}_w/\overline{M}_n$ *according to 1: eqs.(19), 2: eqs.(11) to (13), 3: eqs.(17) and (18) and 4: eqs.(11),(13) and (20). The value of the exponent a is 0.217 for all cases.*

have been determined by ourselves (8), whereas those of PSLustrex have been reported (27). The molecular weight distributions were previously known from GPC measurements and satisfied more or less Schulz distributions. The experimental points fall rather well on the theoretical curve 2 but deviate significantly from the hard sphere curve 4.

Another conclusion which may be drawn from Fig.2 is that within the domain of normal experimental errors the curve 1 corresponding to the scaling relations already forms a rather good approximation for the Schulz distribution, whereas it is even exact for the Lognormal distribution. This implies that the ratio $(A_2)_{os}/(A_2)_{ls}$ may rather well be estimated by $(\overline{M}_w/\overline{M}_n)^a$ (8).

Finally we remark that the global picture arising from Fig.1 or Fig.2 does not change much if at least the exponent a varies between 0.2 and 0.3, which is the typical range found experimentally for linear, coil-like polymers in good solvents (28). Thus our findings are expected to be valid more generally for linear coils in a good solvent.

Conclusions

With eqs.(11) to (13) and (17) to (18) we have the disposal of analytical expressions for $(A_2)_{os}$ and $(A_2)_{ls}$ for polydisperse polymers in a good solvent. These equations are based on a Schulz and a Lognormal molecular weight distribution respectively and account for the

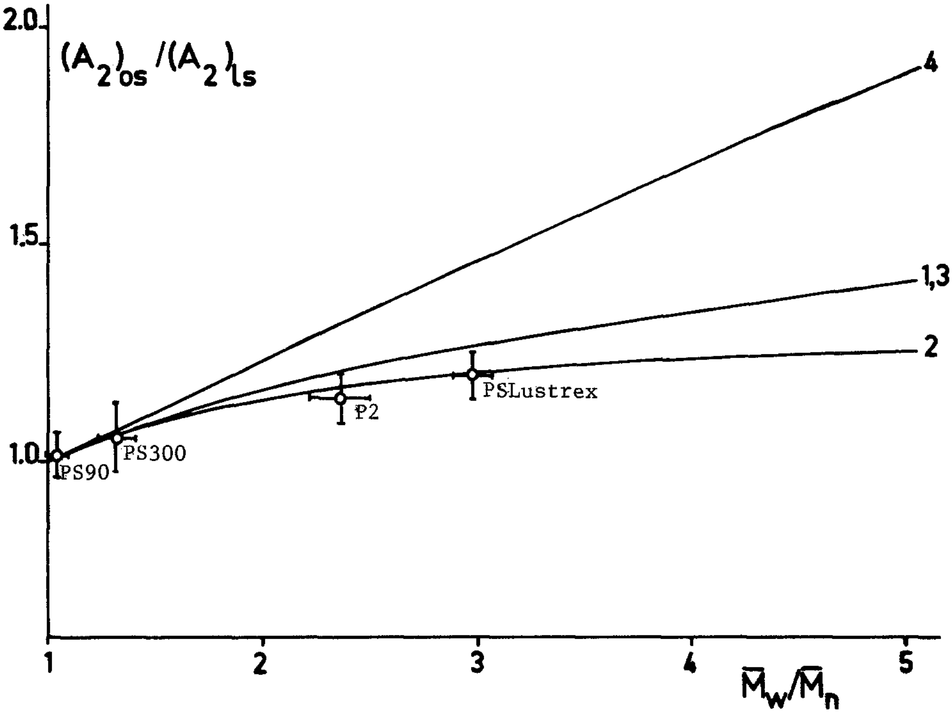

Figure 2 $(A_2)_{os}/(A_2)_{ls}$ *plotted against* $\overline{M}_w/\overline{M}_n$ *according to different treatments for* $a = 0.217$. *The meaning of the numbers is the same as in Fig.1. Experimental points including error bars are indicated with* o.

effect of interpenetration. For the case of the Schulz distribution analogous analytical expressions originating from the hard sphere model have been shown to yield too high estimates for the second virial coefficients above the value $\overline{M}_w/\overline{M}_n = 1.25$.

Appendix A

We want to calculate the double integral in eq.(8a) by applying a Schulz distribution function, which is given by eq.(9). First we define

$$t = kp/\overline{p}_n \qquad \text{and} \qquad t' = kp'/\overline{p}_n \tag{A1}$$

Substituting eq.(9) into eq.(8a) and introducing the variables t and t' we find

$$(A_2)_{os} = \frac{2A_0(\overline{p}_n/k)^{-a}}{\Gamma^2(k+1)} \int_0^\infty dt\; t^k e^{-t} \int_0^t dt'\; (t')^{k-a} e^{-t'} \tag{A2}$$

The second part of the integral is an incomplete Gamma function, for which we use the following series expansion

$$\int_0^t dt'\; (t')^{k-a} e^{-t'} = \Gamma(k+1-a)\, t^{k+1-a} e^{-t} \sum_{n=0}^{\infty} \frac{t^n}{\Gamma(k+2-a+n)} \tag{A3}$$

After substitution of this equation into eq.(A2) a sum of Gamma functions is obtained, which is given by eq.(12) in the main text. The derivation for $(A_2)_{ls}$ from eq.(8b) is analogous. In this derivation the parameter k should be replaced by k+1.

Appendix B

In order to solve the double integral in eq.(8a) with the Lognormal distribution function, given by eq.(14), we first introduce the following variables

$$z = \frac{\ln(p/p_m)}{\beta}, \quad z' = \frac{\ln(p'/p_m)}{\beta}, \quad y = z + \tfrac{1}{2}a\beta, \quad y' = z' + \tfrac{1}{2}a\beta \tag{B1}$$

Then the distribution function can be rewritten as

$$w\{p\}dp = \pi^{-1/2}e^{-z^2}dz = \pi^{-1/2}e^{-(y-a\beta/2)^2}dy \tag{B2}$$

A similar equation exists for w{p'}dp'. Substitution of the eqs.(B1) and (B2) in the seond integral in eq.(8a) leads to

$$\int_0^p dp'\ (p')^{-a}w\{p'\} = A_0\pi^{-1/2}p_m{}^{-a}e^{a^2\beta^2/4}\int_{-\infty}^{y} dy'e^{-(y')^2} =$$
$$\tfrac{1}{2}A_0p_m{}^{-a}e^{a^2\beta^2/4}(1 + \mathrm{erf}\{y\}) \tag{B3}$$

where erf{y} is the error function.
Using eqs.(B1), (B3), (15) and (16) we find from eq.(8a)

$$(A_2)_{os} = A_0\bar{p}_n{}^{-a}e^{(a^2-a)\beta^2/4}\left\{1 + \pi^{-1/2}\int_{-\infty}^{\infty} dz\ e^{-z^2}\mathrm{erf}\left(z+\tfrac{1}{2}a\beta\right)\right\} \tag{B4}$$

Further

$$\int_{-\infty}^{\infty} dz\ e^{-z^2}\mathrm{erf}\left(z+\tfrac{1}{2}a\beta\right) = \int_0^{\infty} dz\ e^{-z^2}\left\{\mathrm{erf}\left(z+\tfrac{1}{2}a\beta\right) - \mathrm{erf}\left(z-\tfrac{1}{2}a\beta\right)\right\} \tag{B5}$$

For $a \leq 0.3$ and $\overline{M}_w/\overline{M}_n \leq 10$ the value of $a\beta/2$ is small enough to expand the error functions in Taylor series. Taking all terms up to third order in $a\beta$ we then find for the integral

$$\pi^{-1/2}\int_0^{\infty} dz\ e^{-2z^2}(a\beta - \tfrac{1}{12}a^3\beta^3 + \tfrac{1}{3}a^3\beta^3z^2 + \ldots) \tag{B6}$$

This integral is easily solved. The result is substituted in eq.(B5) and thereafter in eq.-(B4). The factor $\exp\{(a^2-a)\beta^2/4$ in this equation is also expanded in a Taylor series. Then eq.(B4) can be rearranged to eq.(18). The derivation of the equation for $(A_2)_{ls}$ from eq. (8b) is analogous. In this derivation the parameter a should be replaced by a–1.

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