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Osmotic Pressure of Long Polymers in Good Solvents at Moderate Concentrations: A Comparison between Experiments and Theory

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ABSTRACT: Renormalization theory and experiments show that the osmotic pressure of dilute or semidilute solutions in good solvents obeys a scaling law; accordingly, its dependence on concentration can be represented by a universal function. This function has been measured (I.N. et al.) and quite independently, theoretical predictions concerning this function have been made (J.C.) in the framework of renormalization theory. It is shown that the theoretical predictions agree quantitatively with the measurements (with one exception).

I. Introduction

In this article, we deal with properties of solutions of long neutral polymers in good solvents. It is assumed that the polymer is approximately monodisperse and that the solutions are moderately concentrated, which means that the volume fraction of the polymer is small (the volume fraction of the solvent is nearly equal to one). It is expected[1,2] that in this case the properties of the polymers become universal. For instance, the critical indices can be measured and it has been shown that they depend neither on the solution nor on the solvent.[3] It is also expected that the osmotic pressure of solutions of long polymers should obey a scaling law that is also independent of the polymer and of the solvent.[2,4] However, it is still possible to do better. We may choose as a scale the size of an isolated polymer in solution, which can be defined, for instance, by its radius of gyration. Then, the osmotic pressure is determined by a universal function[2,5,6] that does not depend on any arbitrary constant. The aim of the present article is to show that recent theoretical predictions concerning this function[7] (for monodisperse systems) are in good agreement with the results of recent precise measurements.[6]

II. Osmotic Pressure: The Universal Function

The scaling law for the osmotic pressure Π of a solution of monodisperse polymers can be written in various ways. For the theoretician, the following form (in three dimensions) is convenient:

$$\Pi\beta = \mathbf{C}\, F(\mathbf{C}X^3) \qquad (1)$$

Here $\beta = 1/kT$, $\mathbf{C}$ is the number of polymers per unit volume, and X is a length related to the mean square end-to-end distance R^2 of a polymer in a very dilute solution by

$$R^2 = 3X^2 \qquad (2)$$

(If the space had dimension d, we would write $R^2 = dX^2$).

Usually the experimentalist uses a different form

$$\Pi/RT = \frac{C}{M}\, G\left(\frac{C}{C^*}\right) \qquad (3)$$

where C is the polymer concentration (mass per unit volume), M the molecular mass, and C^* a critical concentration defined by

$$C^* = M/(4/3)\pi R_G^3 N_A \qquad (4)$$

where R_G is the radius of gyration of a polymer in a dilute solution and N_A the Avogadro number. Equations 1 and 3 can be easily compared. We have

$$F(\mathbf{C}X^3) = G(C/C^*) \qquad (5)$$

with

$$F(0) = G(0) = 1$$

and, as $C = \mathbf{C}M/N_A$, we see immediately that

$$C/C^* = 4\pi\, 3^{1/2}(R_G/R)^3(\mathbf{C}X^3) \qquad (6)$$

In order to compare the theoretical predictions with the experimental results, we need the ratio R_G/R, which, for long polymers, is universal. This ratio is not known exactly but can be obtained in different ways.

A straightforward expansion of R^2 and $R_G{}^2$ in powers of the interaction, i.e., in powers of the classical dimensionless parameter[8] z gives[9]

$$R^2/(R^2)_0 = 1 + 1.333z - 2.075z^2 + ... \qquad (7a)$$

$$R_G{}^2/(R_G{}^2)_0 = 1 + 1.276z - 2.082z^2 + ... \qquad (7b)$$

and in the absence of any interaction, we know that $(R_G{}^2/R^2)_0 = 1/6$.

By combining the preceding equations, we can write the ratio $R_G{}^2/R^2$ as a Padé approximant

$$R_G{}^2/R^2 = \frac{1 + 1.153z}{6(1 + 1.210z)}$$

and for $z \to \infty$, we find the asymptotic value

$$R_G{}^2/R^2 = \tfrac{1}{6}(1 - 0.047) \qquad (8)$$

It is known, however, that $R_G{}^2$ and R^2 are given by series expansion in z, which are not convergent. Thus the preceding estimate of $R_G{}^2/R^2$ is not very reliable.

This ratio can be obtained in a different way. We know that the theory applies to fictitious polymers immersed in a space of arbitrary dimension d. Thus renormalization theory shows how to find expansions of universal quantities in terms of $\epsilon = 4 - d$. An expansion of the universal ratio $R_G{}^2/R^2$ (when $z \to \infty$) gives[7,10] to first order in ϵ

$$R_G{}^2/R^2 = \tfrac{1}{6}(1 - \epsilon/96 + ...) \qquad (9)$$

and for $d = 3$ ($\epsilon = 1$) we obtain

$$R_G{}^2/R^2 = \tfrac{1}{6}(1 - \tfrac{1}{96}) = \tfrac{1}{6}(1 - 0.010) \qquad (10)$$

a result that certainly is not very good.

A better value can be obtained by using the fact that for $d = 1$ (rigid rods), we have

$$R_G{}^2/R^2 = \tfrac{1}{12}$$

The semiempirical formula

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$$\frac{R_G^2}{R^2} = \frac{1}{6}\left(\frac{1 - 31\epsilon/96}{1 - 30\epsilon/96}\right)$$

is compatible with eq 9 and 10 and gives for $d = 3$

$$R_G^2/R^2 = \tfrac{1}{6}(1 - \tfrac{1}{66}) = \tfrac{1}{6}(1 - 0.015) \qquad (11)$$

As eq 9 is exact in the limit $z \rightarrow \infty$, it seems more reasonable to adopt the preceding value eq 11 than the value given by eq 8. In any case[16] by comparing eq 8, 10, and 11, we see that the error is of the order of a few percent.

Finally, eq 11, 6, and 5 give the conversion formulas

$$C/C^* = 1.448(\mathbf{C}X^3) \qquad (12a)$$

$$F(x) = G(1.488x) \qquad (12b)$$

III. Experimental and Theoretical Results

The function $F(x)$ has not been calculated for all values of x, but we know how it behaves for small and large x and we can compare the experimental and the theoretical results in these regions.

The experiments conducted by Noda and collaborators[6] give for small values of C/C^*

$$\Pi M/CRT = 1 + 1.12(C/C^*)[1 + 0.28(C/C^*) + ...] \qquad (13a)$$

$$G'_{\text{exptl}}(0) \simeq 1.12 \qquad x = 0 \qquad (13b)$$

and for large values of C/C^*

$$\Pi M/CRT = 1.5_0(C/C^*)^{1.32_5} \qquad (14a)$$

$$G_{\text{exptl}}(x) \propto 1.5_0 x^{1.32_5} \qquad x \gg 0 \qquad (14b)$$

The theory of direct renormalization developed by des Cloizeaux[6] gives for small $\mathbf{C}X^3$

$$\Pi\beta/\mathbf{C} = 1 + \tfrac{1}{2}(2\pi)^{d/2}g^*(\mathbf{C}X^3) + ... \qquad (15)$$

and the expansion of g^* to second order in $\epsilon = 4 - d$ is

$$g^* = \frac{\epsilon}{8} + \frac{\epsilon^2}{16}\left(\frac{25}{16} + \ln 2\right) + ... \qquad (16)$$

For $d = 3$ ($\epsilon = 1$) this formula gives

$$g^* = 0.266$$

A better value can be obtained by noting that for $d = 1$ (rigid rods), we would get

$$\Pi\beta/\mathbf{C} = 1/(1 - \mathbf{C}X) \qquad (17)$$

and therefore that

$$g^* = (2/\pi)^{1/2} \qquad \text{for } d = 1\ (\epsilon = 3) \qquad (18)$$

Thus g^* can be calculated by using the interpolating formula

$$g^* = \frac{\epsilon}{8} + \frac{\epsilon^2}{16}\left(\frac{25}{16} + \ln 2\right) + \frac{\epsilon^3}{27}\left[(2/\pi)^{1/2} - \frac{321}{256} - \frac{9}{16}\ln 2\right]$$

which is compatible with eq 16 and 18. For $d = 3$ ($\epsilon = 1$), this formula gives

$$g^* = 0.233 \qquad (19)$$

a value that will be adopted here. Now eq 15 reads

$$\Pi\beta/\mathbf{C} = 1 + 1.835(\mathbf{C}X^3) + ...$$

$$F'_{\text{theor}}(x) = 1.835$$

and using the conversion formulas (12), we obtain

$$G'_{\text{theor}}(0) = 1.448^{-1}F'_{\text{theor}}(0) = 1.26 \qquad (20)$$

This value is not far from the experimental result (13), and the difference can be explained by theoretical and experimental uncertainties.

Let us now consider the third virial coefficient. We might compare its experimental and theoretical values but it is better to consider the invariant ratio

$$\rho = \frac{1}{2}\frac{F''(0)}{[F'(0)]^2} = \frac{1}{2}\frac{G''(0)}{[G'(0)]^2} = \frac{A_3}{A_2^2M} \qquad (21)$$

where A_2 and A_3 are the second and the third virial coefficients.

A first-order calculation in ϵ gives[11]

$$\rho = \epsilon(8 \ln 2 - \tfrac{9}{2} \ln 3 - \tfrac{1}{6}) + ...$$

and therefore for $d = 3$

$$\rho \simeq 0.435 \qquad (22)$$

This value is rather crude; a better approximation can be obtained by remarking that for $d = 1$, according to eq 17 we have $\rho = 1$. Thus ρ can be calculated by using the interpolating formula

$$\rho = 0.435[\epsilon/(1 + 0.102\epsilon)]$$

which is compatible with the preceding results. For $d = 3$, this formula gives

$$\rho_{\text{theor}} = 0.39 \qquad (23)$$

This value is substantially larger than the value

$$\rho_{\text{exptl}} = 0.25$$

which was used in the so-called square root plot fitting the experimental data.[5,6] A similar result[12] was obtained by applying the method of Stockmayer and Casassa[13] to the same data. Using the data of α - 104[6] and plotting directly Π vs. C in regions where $C < C^*$, Jannink[14] found

$$\rho_{\text{exptl}} = 0.30$$

but this value is still far from the theoretical estimate.

The origin of this discrepancy is unknown. The procedures for evaluating ρ_{exptl} may markedly affect the results, owing to experimental errors. There are reasons to believe that the fourth virial coefficient is negative and the fourth-order term may give contributions that are of the same magnitude as the third-order term. The polydispersity effects also may be important. Moreover, the observed value of ρ may be smaller than the asymptotic value of ρ, valid for very long chains. Incidentally, we note that for hard spheres we would get $\rho = 0.625$ and that the values of ρ obtained from the old (and not very reliable) theory of Stockmayer and Casassa[13] are comparable to 0.25 in regions of excluded volume for the experimental data.

For large values of $\mathbf{C}X$ (semidilute regime), $\Pi\beta$ should depend only on $\mathbf{C}X^{1/\nu}$, which is proportional to the concentration of monomers

$$\Pi\beta/\mathbf{C} \simeq F(\mathbf{C}X^{1/\nu})^{1/(\nu d-1)} \qquad (24a)$$

$$F(x) \simeq {}^0F x^{1/(\nu d-1)} \qquad (24b)$$

The theoretical value[3,14] of ν for $d = 3$ is

$$\nu_{\text{theor}} = 0.588 \pm 0.001$$

which gives

$$1/(\nu d - 1) = 1.309 \pm 0.006 \qquad \text{for } d = 3 \qquad (25)$$

A crude estimation of ${}^0F$ can also be found. We note that for $d = 4$, we have $\nu = 1/2$ and $1/(\nu d - 1) = 1$. This means that in the limit $d \rightarrow 4$, the asymptotic term coincides with the second virial coefficient. Therefore, for small ϵ

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$$ {}^0F \simeq \tfrac{1}{2}(2\pi)^{d/2} \tag{26a} $$

$$ g^* \simeq (\pi^2/4)\epsilon \tag{26b} $$

and for $d = 3$, we obtain the crude result

$$ {}^0F \simeq 2.46 $$

Thus for large x, we find

$$ F_{\text{theor}}(x) = 2.46x^{1.309\pm0.006} \tag{27} $$

and, using the conversion formula (12) we obtain in this way

$$ G_{\text{theor}}(x) \simeq 1.51x^{1.309\pm0.06} \qquad x \gg 1 \tag{28} $$

Again, we see that there is a good agreement between this expression and the experimental result (14). The experimental value of ν obtained by writing $1/(3\nu - 1) = 1.32_5$, namely

$$ \nu_{\text{exptl}} = 0.585 \tag{29} $$

is slightly smaller than expected, but crossover effects or polydispersity effects may well explain this fact.

IV. Conclusion

The predictions of renormalization theory concerning the behavior of the osmotic pressure of long chains in good solvents seem to agree with the experimental results, with one exception concerning the ratio ρ of the third virial coefficient to the square of the second virial coefficient. Polydispersity effects or the fact that the polymer is not infinitely long may explain this discrepancy. Anyway, more work is needed to obtain a really precise description of the universal function that describes the asymptotic behavior of the osmotic pressure.

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$$ R_G{}^2/R^2 = 0.157 \pm 0.002 = \tfrac{1}{6}(1 - 0.06 \pm 0.01) \quad \text{(Wall and Erpenbeck}^{17}\text{)} $$

$$ R_G{}^2/R^2 = 0.155 \pm 0.001 = \tfrac{1}{6}(1 - 0.07 \pm 0.01) \quad \text{(Domb}^{18}\text{)} $$

More recently, similar results have been found by McCrackin, Mazur, and Guttman.[19] These values are smaller than the theoretical values (see eq 8 and 11). However, these "experimental values" are not completely reliable. Weill and des Cloizeaux[20] have shown that R_G approaches the asymptotic limit more slowly than R. This effect appears clearly in the results of McCrackin, Mazur, and Guttman,[19] who have found different (effective) indices for R and R_G. Owing to this fact, the ratio $R_G{}^2/R^2$ is probably, in many cases, underestimated.
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Thermodynamics of Crystallization in a Model Polymer Network

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ABSTRACT: A new thermodynamic theory of crystallization in polymer networks subjected to a constant deformation was formulated. Many drastic model assumptions used by other authors were abandoned, and the effect of junction displacement caused by crystallization was taken into account. A variety of crystallite types with respect to morphology size and orientation were allowed to coexist in a partially crystalline network. The free energy of such a network was calculated on the basis of the rubber elasticity theory, and the equilibrium state of the network was found by minimization of the free energy with respect to crystallinity variables. The average equilibrium degree of crystallinity and a change in stress due to equilibrium crystallization were determined. Example computations were performed for a uniaxial deformation and a tetrafunctional regular network composed of Gaussian chains of equal contour lengths.

Introduction

Polymer crystallization seems to be one of the most important problems in polymer physics. It has been established that in the case of un-cross-linked polymers, kinetic factors play a dominant role in crystallization.[1] On the contrary, it is usually presumed that crystallization of polymer networks is mostly controlled by thermodynamics. We have made an attempt to formulate a new thermodynamic theory of crystallization in polymer networks subjected to a constant deformation. Several theories on this subject have been published. The most fundamental paper was presented by Flory in 1947.[2]

A few drastic assumptions were involved in the original Flory theory. All crystallites were assumed to have the

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