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LETTER TO THE EDITOR

Scaling laws for the internal energy and the heat of dilution of a polymer solution

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Abstract. We relate the internal energy of a polymer solution to a field-theoretic vertex function, differentiated with respect to the coupling constant. Renormalization group arguments yield the scaling law which has a simple physical interpretation. Application of our result to an evaluation of the heat of dilution shows a close relation between this quantity and the osmotic pressure.

Recently it has been shown (de Gennes 1972, des Cloizeaux 1975) that a dilute solution of long chain molecules can be described within the framework of renormalized field theory. The problem has been reduced to the treatment of a classical field with local four-point coupling. One important result of that approach is a scaling law for the osmotic pressure P_c :

$$P_c/k_B T = c_p(1 + P(N^{\nu d} c_p S)). \quad (1)$$

Here c_p and N denote the number density of the polymer chains and the number of links per chain, respectively. $d = 3$ is the dimensionality of the system and $\nu \sim 0.6$ is a universal exponent. The scale factor S depends on the special features (density ρ , temperature T , etc) of the system considered. The function $P(x)$ is universal, and can be calculated from a renormalized field theory. For small arguments, one obtains $P(x) \sim x$ and this yields a simple power law for the N dependence of the second virial coefficient $P_2(N)$ defined by

$$P_c = k_B T c_p + P_2(N) c_m^2 + O(c_m^3) \quad (2)$$

$$c_m = N c_p. \quad (3)$$

For large values of $N^{\nu d} c_p$, one obtains the asymptotic form

$$P_c = P_\infty c_m^{\nu d / (\nu d - 1)}. \quad (4)$$

To derive these results, des Cloizeaux (1975) started from the ratio \mathcal{Z} of the grand canonical partition function of the solution to that of the pure solvent. He showed that \mathcal{Z} is given by a field-theoretic vertex function. It is obvious that from this starting point we can calculate other thermodynamic quantities like the entropy of mixing, the chemical potential of the solvent, or the excess of the internal energy due to the presence of polymer molecules. We here present the results for the excess energy

$$\Delta u = -k_B T^2 \frac{\partial}{\partial T} \ln \mathcal{Z}. \quad (5)$$

In equation (5) the partial derivative with respect to the temperature T has to be taken with fixed activities for both the solvent and the polymer. As a consequence, in the field-theoretic model only the bare coupling constant g_0 (and an additive contribution to the bare mass) are varied, and thus the problem of calculating Δu is essentially reduced to that of calculating the derivative of a vertex function with respect to g_0 . It is well known (Brézin *et al* 1974) that this yields a linear combination of several renormalized vertex functions, the different terms having an appealing interpretation in our problem. We find

$$\Delta u = \alpha_1 c_m + \alpha_2 c_p + \alpha_3 [c_p - (P_c/k_B T)] + \alpha_4 u_c \quad (6)$$

$$u_c = c_p N^{-\nu\omega} U_c(N^{\nu d} c_p S). \quad (7)$$

Here $\omega \sim 0.75$ is another universal exponent. The coefficients α_1 to α_4 are independent of N and c_p . For later use we note the expression for α_3 :

$$\alpha_3 = k_B T^2 \frac{\partial}{\partial T} \ln S. \quad (8)$$

The derivation of equations (6) to (8) will be given elsewhere. Here we want to discuss some implications and point out the relevance for the interpretation of some experiments.

Equation (6) splits nicely into a sum of different contributions, which can be interpreted in physical terms. In the isolated chain limit we find

$$\lim_{c_p \rightarrow 0} \Delta u/c_p = \alpha_1 N + \alpha_2 + \alpha_4 N^{-\nu\omega} U_c(0). \quad (9)$$

Obviously α_1 is the average energy of solvation of one link and α_2 represents an additional contribution from the ends of the chain. Close contacts of different parts of the chain give rise to the α_4 term. The decrease with N of this contribution is noticeable. A naive estimate yields an increasing result: neglecting correlations we find for the number n of close pairs $n \sim N^2 R^{-3}$, where the radius R of the chain increases like N^ν (de Gennes 1972). Consequently we estimate $n \sim N^{0.2}$. The difference compared to the correct result $n \sim N^{-0.5}$ stresses the 'strong effective repulsion' among different parts of the same chain, which is due to the 'self-avoiding' aspects of the problem.

The α_3 term vanishes in the isolated-chain limit, but it dominates the α_4 term in the limit of large overlap among chains (i.e. $N \rightarrow \infty$, c_m fixed, small):

$$\Delta u = \alpha_1 c_m - \frac{\alpha_3 P_\infty}{k_B T} c_m^{\nu d/(vd-1)} + \alpha_4 U_{c,\infty} c_m^{\nu(d+\omega)/(vd-1)}. \quad (10)$$

In deriving this equation we assume that the limit $N \rightarrow \infty$, c_m fixed, exists (des Cloizeaux 1975, § VI). It is suggestive that the α_3 term represents the energy of interaction among different chains. Its close relation to the osmotic pressure is quite understandable since it is the interaction among different chains which gives rise to $P_c - k_B T c_p \neq 0$.

From these equations we can derive scaling expressions for various thermodynamic quantities. We here concentrate on the heat of dilution which has been of some interest experimentally (Flory 1970, Lichtenthaler and Heintz 1976, private communication). We start with a volume V containing solvent of density ρ and polymer of density c_p . We add a volume ΔV of solvent of density ρ_0 . As a result we find a change in volume, accompanied by the production of an amount ΔQ of heat. During this process the pressure (and the temperature) are held fixed, and this yields an equation for $\rho = \rho(T, P, c_p)$ which can be evaluated for small $\rho - \rho_0$, $\rho_0 = \rho(T, P, 0)$. Using this result

together with equations (1) and (6) we can calculate $\Delta Q/\Delta V$. We here give the results for the two limiting cases discussed throughout this letter.

(i) N fixed, $c_p \rightarrow 0$

$$\lim_{c_p \rightarrow 0} \frac{1}{c_m^2} \lim_{\Delta V \rightarrow 0} \frac{\Delta Q}{\Delta V} = P_2(N) \chi_1 + \text{constant} \times N^{\nu(d-\omega)-2} + O(N^{-1}). \quad (11)$$

(ii) $c_m \neq 0$ fixed, $N \rightarrow \infty$

$$\frac{1}{c_m^2} \lim_{\Delta V \rightarrow 0} \frac{\Delta Q}{\Delta V} = \frac{\chi_1}{\nu d - 1} P_\infty c_m^{2-\nu d/(\nu d-1)} [1 + \text{constant} \times c_m^{\nu\omega/(\nu d-1)} + O(c_m)] \quad (12)$$

$$\chi_1 = \left. \frac{T}{\rho_0} \frac{\partial \rho_0}{\partial T} \right|_{p \text{ fixed}} - \frac{\alpha_3}{k_B T} \quad (13)$$

Note that in both limits the leading contribution is determined completely by the osmotic pressure and by χ_1 . From its definition (8) α_3 can be fixed by a measurement of the osmotic pressure as a function of T . *So the leading terms in equations (11) and (12) can in principle be fixed by an independent measurement, and results for the heat of dilution can be analysed to yield the first correction, and thus the exponent ω .*

A quantitative test of equation (11) may be difficult, since it involves an extrapolation to $c_p = 0$ of heat-of-dilution data, which are taken at sizable values of c_p . From its derivation, equation (12) is restricted to small concentrations, too. The actual range of applicability of this approach, however, depends on the system and can be very large ($c_m \rho^{-1} \sim 0.5$), as has been found in scattering experiments (Daoud *et al* 1975, Schäfer and Witten 1976). Thus an experimental test is not inconceivable. A comparison with existing data (Flory 1970, Lichtenthaler and Heintz 1976, private communication) shows satisfactory qualitative agreement.

Finally we want to note that the scaling laws for other quantities like entropy of mixing etc take the structure of equation (6), but with different constants α_1 to α_4 . Experimental information on these quantities therefore could also be included into a test of the theory.

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