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# Renormalisation group calculation of the second virial coefficient of a polymer solution to order $\epsilon^2$ in $d = 4 - \epsilon$ dimensions

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**Abstract.** Field theory renormalisation group methods are used to describe the crossover behaviour of the second virial coefficient  $A_2$  of the osmotic pressure for a monodisperse polymer solution as a function of temperature and molecular weight to second order in  $\epsilon = 4 - d$ . The results are in significantly better agreement with experiment than previous renormalisation group calculations.

## 1. Introduction

Following the pioneering work of de Gennes (1972), Burch and Moore (1976) have shown how multipolymer properties may be calculated using a particular  $O(n)$  symmetric field theory in the limit  $n \rightarrow \infty$ . Close links exist between the Green functions of the following  $O(n)$  symmetric theory, in the limit  $n = 0$  and various correlation functions of the polymer problem:

$$\mathcal{H} = \frac{1}{2} \sum_{\alpha=1}^m \sum_{i=1}^n [(\nabla \phi_{i\alpha})^2 + \Lambda^{-2}(\nabla^2 \phi_{i\alpha})^2 + M_{OC}^2(\phi_{i\alpha})^2] + \frac{1}{2} \sum_{\alpha=1}^m \sum_{i=1}^n t_{\alpha}(\phi_{i\alpha})^2 + \frac{u\Lambda^{\epsilon}}{4!} \left( \sum_{\alpha=1}^m \sum_{i=1}^n (\phi_{i\alpha})^2 \right)^2 + \sum_{\alpha=1}^m \sum_{i=1}^n h_{i\alpha} \phi_{i\alpha}. \quad (1.1)$$

Here  $\phi_{i\alpha}$  is an  $(n \times m)$ -component field and the bare mass has been split into  $M_{OC}^2 + t_{\alpha}$ ,  $\alpha = 1, 2, \dots, m$ , where  $M_{OC}^2$  is the bare mass of the critical theory. The cut-off  $\Lambda$  which reflects the finite size of the monomers is implemented by the fourth-order derivatives in (1.1); henceforth we choose units in which  $\Lambda = 1$ . The higher symmetry,  $O(nm)$ , of the interaction term reflects the inability of the monomers to distinguish between inter- and intra-polymer contacts, whilst phenomenologically the coupling  $u$  takes the form  $u \sim (1 - \Theta/T)$  where  $\Theta$  is the Flory temperature. We do not consider the collapsed phase  $u < 0$ .

In this paper we consider only monodisperse solutions, i.e. each polymer has the same molecular weight  $M$ , corresponding to  $N$  flexible units and investigate the crossover from the Wilson-Fisher to Gaussian fixed point exhibited by the second virial coefficient  $A_2$  as the temperature  $T$  approaches the Flory temperature  $\Theta$ . Burch and Moore (1975, to be referred to as BM) have performed a similar calculation using a phenomenological approach due to Wegner and Reidel (1973); their renormalisation

group equations have the same form as an order  $\epsilon$  calculation but additional terms are present at order  $\epsilon^2$ .

The virial coefficients of the osmotic pressure (Yamakawa 1971) are described within the polymer model due to Edwards (1966) by the multi-dimensional inverse Laplace transform of connected Green functions computed from the above field theory in the limit  $n = 0$ . In particular the second virial coefficient  $A_2$  is of the form

$$A_2 = P_{NN}/(P_N)^2 \tag{1.2}$$

where  $P_N$  and  $P_{NN}$  are given in terms of Green functions by:

$$G^{4(2,2)}(t_\alpha, t_\beta, u, 1) \equiv \lim_{n \rightarrow 0} \frac{1}{V} \int d^d x \int d^d y \int d^d z \int d^d w \frac{\partial^4 \ln Z(\mathbf{h})}{\partial h_{\alpha 1}(x) \partial h_{\alpha 1}(y) \partial h_{\beta 1}(z) \partial h_{\beta 1}(w)} \Big|_{\mathbf{h}=0} \tag{1.3}$$

$$= \int_0^\infty \int_0^\infty dN dM \exp(-Nt_\alpha - Mt_\beta) P_{NM} \quad (\alpha \neq \beta)$$

$$G^2(t_\alpha, u, 1) \equiv \lim_{n \rightarrow 0} \frac{1}{V} \int d^d x \int d^d y \frac{\partial^2 \ln Z(\mathbf{h})}{\partial h_{\alpha 1}(x) \partial h_{\alpha 1}(y)} \Big|_{\mathbf{h}=0} \tag{1.4}$$

Here  $Z$  is the partition function and  $V$  the volume of space. In the  $n = 0$  limit it is straightforward to show that Green functions will depend only on the fields which appear in external legs. (Fields with other values of  $\alpha$  appear only in closed loops, giving a factor of  $n$ .) Thus, for convenience, one chooses a ‘minimal’ theory when calculating any particular correlation function; for example whilst  $G^{4(2,2)}$  may be calculated for any theory for which  $m \geq 2$ , the minimal theory has  $m = 2$ .

The Green functions  $G^N$  are of the general scaling form:

$$G^N = t^{d - \frac{1}{2}(2+d)N} f(x) \tag{1.5}$$

Here  $x \sim ut^{-\epsilon/2}$  and  $f(x)$  is regular except at  $\infty$  ( $x \geq 0$ ). One observes a crossover from Gaussian behaviour ( $x \ll 1$ ) to the full critical behaviour described by the Wilson–Fisher fixed point of the renormalisation group ( $x \gg 1$ ) as the temperature is raised. Explicitly

$$f(x) = \begin{cases} 1 + O(x) & x \ll 1 \\ x^{a_N} [1 + O(x^{-2\omega/t})] & x \gg 1 \end{cases}$$

Now the Laplace transform of  $N^\theta$  is simply

$$\int_0^\infty N^\theta e^{-Nt} dN = \Gamma(\theta + 1)t^{-(\theta+1)}$$

so that the associated functions  $P^N$  passes the same qualitative structure in terms of the polymer scaling variable  $z \sim uN^{\epsilon/2}$ . The polymer situation ( $N \gg 1$ ) thus corresponds exactly to the approach of the critical temperature ( $t \ll \Lambda^2$ ) in the magnetic analogue. In this sense the problem is critical so the properties of scaling and universality characteristics of the latter system appear naturally in the polymer problem. For example the second virial coefficient  $A_2 \sim uN^2 f(z)$ , where the crossover scaling function  $f(z)$  describes the crossover from a system characterised by swelled chains ( $z \gg 1$ ) to random

walk behaviour ( $z \ll 1$ ) as the  $\theta$  temperature is approached:

$$A_2 \sim \begin{cases} uN^2[1 + O(z)] & z \ll 1 \\ uN^2z[1 + O(z^{-2\omega/\epsilon})] & z \gg 1. \end{cases}$$

Since the mean square size of a single polymer  $\langle R^2 \rangle \sim N^{2\nu}$  ( $z \gg 1$ ) then  $A_2$  is proportional to the excluded volume as expected.

To calculate correlation functions for the polymer system we shall clearly need to evaluate Green functions deep in the critical regime  $t \ll \Lambda^2$ . We are therefore led to use the renormalisation group in  $d = 4 - \epsilon$  dimensions in order to control the corrections to mean-field theory. Using the renormalisation group one may relate the singular part of a Green function ( $t \ll \Lambda^2$ ) to its value outside the critical regime ( $t \approx \Lambda^2$ ), where straightforward perturbation theory may be trusted. We follow the approach of Bruce and Wallace (1976, to be referred to as BW) who worked within the formalism developed by Zinn-Justin (1973).

The broad outline of the paper is as follows: § 2 introduces and solves the renormalisation group equation, then § 3 describes the calculation of  $P_N$  and  $P_{NN}$ . Finally the second virial coefficient is constructed and compared with experimental data.

## 2. The renormalisation group

Using the renormalised perturbation theory developed by Brézin *et al* (1973) it is straightforward to show that the  $N$ -point connected Green functions  $G^N(t_1, \dots, t_m; u, \Lambda)$  satisfy the following simple renormalised group equation in the limit  $n \rightarrow 0$ :

$$\left\{ \Lambda \frac{\partial}{\partial \Lambda} + W(u) \frac{\partial}{\partial u} - \left( \frac{1}{\nu(u)} - 2 \right) \sum_{\alpha} t_{\alpha} \frac{\partial}{\partial t_{\alpha}} + \frac{L}{2} \eta(u) \right\} G^L(t_1, \dots, t_m; u, \Lambda) = \Delta G^L \quad (2.1)$$

where  $\Delta G^N$  is smaller than  $G^N$  by terms of order  $t/\Lambda^2$  up to powers of  $\ln(t/\Lambda^2)$ , in an  $\epsilon$  expansion. The functions  $W(u)$ ,  $[(1/\nu(u)) - 2]$ ,  $\eta(u)$  are determined solely by the massless theory, i.e.  $t_{\alpha} = 0$  for all  $\alpha = 1, 2, \dots, m$ , so that they coincide with those of BW since the same ultraviolet regularisation is used. Introducing new variables,  $T, T_{\beta}$ ,  $\beta = 1, 2, \dots, m - 1$ , defined by

$$T = \left( \prod_{\alpha=1}^m (t_{\alpha}) \right)^{1/m} \quad (2.2)$$

$$T_{\beta} = \frac{1}{t_{\beta}} \left( \prod_{\substack{\alpha=1 \\ \alpha \neq \beta}}^m (t_{\alpha}) \right)^{1/m} \quad \beta = 1, 2, \dots, m - 1$$

we obtain finally a renormalisation group equation similar in form to that of BW:

$$\left( \Lambda \frac{\partial}{\partial \Lambda} + W(u) \frac{\partial}{\partial u} - \left( \frac{1}{\nu(u)} - 2 \right) T \frac{\partial}{\partial T} + \frac{L}{2} \eta(u) \right) G^2(T, T_{\beta}, u, \Lambda) = \Delta G^L \quad (2.3)$$

where to second order in a simultaneous power series expansion in  $(u, \epsilon)$  for  $0 < u < u^* = O(\epsilon)$  one has:

$$W(u) = -\epsilon u + \frac{8}{3}u^2(1 + \frac{1}{2}\epsilon) - \frac{14}{3}u^3 + O(u, \epsilon)^4 \quad (2.4)$$

$$\left(\frac{1}{\nu(u)} - 2\right) = -\frac{2}{3}u(1 + \frac{1}{2}\epsilon) + \frac{5}{9}u^2 + O((u, \epsilon)^3) \tag{2.5}$$

$$\eta(u) = \frac{1}{9}u^2 + O((u, \epsilon)^3). \tag{2.6}$$

As usual a factor  $K_d = \pi^{d/2}\Gamma(d/2)^{-1}(2\pi)^{-d}$  has been absorbed in  $u$ . It should be remarked that except for the  $O(nm)$  symmetric case ( $t_\alpha = t$  for all  $\alpha$ ), the  $n = 0$  limit is essential to the existence of such a simple renormalisation group equation; for non-zero  $n$  the scalar group equation; for non-zero  $n$  the scalar equation (2.1) is replaced by a matrix equation in the spin indices. Only in the limit  $n = 0$  are these matrices proportional to the identity so that (2.1) is resurrected.

In the critical regime  $t \ll \Lambda^2$  by ignoring  $\Delta G^L$  we obtain a homogeneous equation for the leading terms of  $G^L$  in the critical regime. Although the solution for  $G^L$  which follows involves the perturbative regime  $t \approx \Lambda^2$ , for which  $\Delta G^L$  may certainly not be neglected, the homogeneous form may be retained with the understanding that it applies only to the ‘leading terms’ in the above sense. The final form of the renormalisation group equation is therefore:

$$\left[ \Lambda \frac{\partial}{\partial \Lambda} + W(u) \frac{\partial}{\partial u} - \left(\frac{1}{\nu(u)} - 2\right) T \frac{\partial}{\partial T} + \frac{L}{2} \eta(u) \right] G^L(T, T_\beta, u, \Lambda) = 0. \tag{2.7}$$

This homogeneous equation is solved using the method of characteristics, one simply writes  $\tau = \ln \Lambda$  and introduces functions  $u(\tau)$ ,  $T(\tau)$  such that:

$$\frac{d}{d\tau} u(\tau) = W(u(\tau)) \tag{2.8}$$

$$\frac{d}{d\tau} \ln T(\tau) = 2 - \frac{1}{\nu(u)} \tag{2.9}$$

$$\frac{d}{d\tau} T_\gamma(\tau) = 0 \quad \gamma = 1, 2, \dots, M - 1. \tag{2.10}$$

With the initial conditions  $u(0) = u$ ,  $T(0) = T$ , ( $\Lambda = 1$ ) then (2.7) has the formal solution

$$G^L(T, u, 1) = \left( e^{L/2} \int_0^\tau \Lambda(u(\tau')) d\tau' \right) G^L(T(\tau), u(\tau), e^\tau). \tag{2.11}$$

Solving (2.8), (2.9) for  $u(\tau)$ ,  $T(\tau)$  one finds that:

$$\left(\frac{u^* - u(\tau)}{u^* - u}\right)^{-\epsilon\nu/\omega} \frac{u(\tau)}{u} = e^{-\epsilon\tau} \tag{2.12}$$

$$T(\tau) = T \left(\frac{u^* - u(\tau)}{u^* - u}\right)^\rho \left(1 + \frac{11}{48}(u(\tau) - u)\right) \tag{2.13}$$

such that differentiation resurrects (2.8), (2.9) up to terms of  $O((u, \epsilon)^4)$ . Here  $u^*$  is the Wilson-Fisher fixed point coupling:

$$u^* = \frac{3}{8}\epsilon(1 + \frac{5}{32}\epsilon) + O(\epsilon^3). \tag{2.14}$$

Further  $\nu \equiv \nu(u^*)$  and  $\omega \equiv -\nu W'(u^*)$  are respectively the usual correlation length and crossover exponents, whilst  $\rho$  satisfies the relation:

$$\rho\omega = 2\nu - 1 + O(\epsilon^3). \tag{2.14}$$

In the next section the equations (2.10) to (2.14) are exploited in order to determine the two- and four-point connected Green functions required to evaluate the second virial coefficient  $A_2$ . By a suitable choice of  $\tau$ ,  $T(\tau) = e^{2\tau}$ , one puts the Green function  $G^L(\tau)$  into the perturbative regime, where the standard graphical expansion may be used. Equations (2.10)–(2.14) then yield the full critical Green functions  $G^L(0)$  to within terms of  $O((u, \epsilon)^3)$ . This matching procedure produces systematic corrections to the results of BM who assume that one may choose a  $\tau$  such that  $G^L(\tau)$  is proportional to the zeroth-order term of its perturbation expansion in  $u(\tau)$  for all  $N$ .

### 3. The calculation of Green functions

#### 3.1. The two-point function

It is convenient to use the minimal Hamiltonian  $m = 1$  ( $n = 0$ ) and instead of calculating perturbatively  $G^2(\tau)$  with a propagator  $|q^2 + \Lambda^{-2}q^4 + t(\tau)|^{-1}$ , vertices  $m_{0c}^2$  and  $u(\tau)e^{\epsilon\tau}$ , to use a propagator  $|q^2 + \Lambda^{-2}q^4 + r(\tau)|^{-1}$  where  $r^{-1}$  is the exact susceptibility. One then obtains  $r$  as a function of  $t$  by using the following self-consistency equation for the self-energy:

$$r = t + \Sigma(0, r) - \Sigma(0, 0). \tag{3.1}$$

Following BW one obtains,

$$r(\tau) = t(\tau)\{1 + \frac{1}{3}u(\tau)[\ln(t(\tau)e^{-2\tau}) + 1]\} + O((u, \epsilon)^2) \tag{3.2}$$

Despite the fact that we require the two-point function correct to  $O(\epsilon^2)$  the  $O((u, \epsilon)^2)$  corrections to (3.2) may be neglected, for at this order they only contribute to a non-universal prefactor  $Z_2(u)$  which is a harmless scale factor. Using the matching condition  $T(\tau) \equiv t(\tau) = e^{2\tau}$ , equations (2.10)–(2.14) and the following additional information, the result of  $G^2$  may then be calculated:

$$\exp\left(-\int_0^\tau \eta(\tau') d\tau'\right) = \left(\frac{u^* - u(\tau)}{u^* - u}\right)^\phi \left[1 - \frac{1}{24}(u(\tau) - u)\right] + O((u, \epsilon)^2) \tag{3.3}$$

$$\phi\omega = \nu\eta \tag{3.4}$$

where  $\eta$  is the usual Wilson–Fisher exponent.

The two-point function has the following simple form:

$$G^2(t, u, 1) \equiv r^{-1} = Z_2(u)t^{-1} \left(\frac{u^* - u(\tau)}{u^* - u}\right)^{\rho_2} \left(1 - \frac{25}{48}u(\tau)\right) \tag{3.5}$$

where

$$\rho_2\omega = 1 - \gamma + O(\epsilon^3);$$

$\gamma$  is the usual susceptibility exponent.

The non-universal prefactor  $Z_2(u)$  having absorbed the non-universal factors to  $O(\epsilon^2)$ , then (3.5) constitutes a representation of the two-point function in terms of  $u(\tau)$ . Using the matching conditions and equations (2.11), (2.12) one may obtain the following compact parametric description for  $u(\tau) = pu^*$ :

$$(1 - p)^{-\epsilon/2\omega} p = x \tag{3.6}$$

where

$$x \equiv \frac{u}{u^*} \left( 1 - \frac{u}{u^*} \right)^{-\epsilon/2\omega} t^{-\epsilon/2}.$$

Unfortunately one cannot carry this description through the process of Laplace inversion. Instead (3.6) must be solved separately in the perturbative ( $x \ll 1$ ) and asymptotic ( $x \gg 1$ ) regimes or the crossover variable,  $x$ .

For  $x \ll 1$ , equations (3.5) and (3.6) yield:

$$G^2(t, u, 1) = Z_2(u) t^{-1} \left[ 1 + \frac{1}{4} \left( 1 - \frac{7}{32} \epsilon \right) x + O(x^2) \right] \tag{3.7}$$

where  $Z_2(u)$  has absorbed additional non-universal factors.

For  $x \gg 1$ , first eliminating  $u(\tau)$  in terms of  $(p, t)$ , (3.5) and (3.6) give:

$$G^2(t, u, 1) = Z_2(u) t^{-1} x^{2\rho_2\omega/\epsilon} \left( 1 - \frac{25}{128} \epsilon \right) \left[ 1 + \frac{1}{4} \left( 1 - \frac{3}{8} \epsilon \right) x^{-2\omega/\epsilon} + O(x^{-4\omega/\epsilon}) \right]. \tag{3.8}$$

Finally  $P_N$  is generated by Laplace inversion; the results are:

$$P_N = \begin{cases} Z_2(u) \left[ 1 + \frac{1}{4} \left( 1 - \frac{7}{32} \epsilon \right) z + O(z^2) \right] & z \ll 1 \tag{3.9} \\ \frac{Z_2(u)}{\Gamma(\gamma)} \left( 1 - \frac{25}{128} \epsilon \right) z^{2\rho_2\omega/\epsilon} \left[ 1 + \frac{1}{4} \frac{\Gamma(\gamma)}{\Gamma(\gamma - \omega)} \left( 1 - \frac{3}{8} \epsilon \right) z^{-2\omega/\epsilon} + O(z^{-4\omega/\epsilon}) \right] & z \gg 1 \tag{3.10} \end{cases}$$

where

$$z \equiv \frac{u}{u^*} \left( 1 - \frac{u}{u^*} \right)^{-\epsilon/2\omega} N^{\epsilon/2}. \tag{3.11}$$

### 3.2. The four-point Green function

For the four-point function, the minimal Hamiltonian has  $m = 2$  ( $n = 0$ ) so that there are now two propagators in the problem  $(q^2 + \Lambda^{-2} q^4 + r_\alpha(\tau))^{-1}$  and  $(q^2 + \Lambda^{-2} q^4 + r_\beta(\tau))^{-1}$  where  $r_\alpha\{r_\beta\}$  is given in terms of  $t_\alpha\{t_\beta\}$  by (3.2) as before. Unfortunately the procedure is not as straightforward as before, for even at the one-loop level in the perturbation expansion of  $G^{4(2,2)}(\tau)$  we have ‘mixed diagrams’. With the obvious notation, examples are given in figure 1. Again up to the non-universal prefactor  $Z_4(u)$  which will now be a function of  $M/N$  at  $O(\epsilon^2)$  if  $P_{NM}$  is calculated, attention may be restricted to the  $O(u, \epsilon)$  corrections. The only mixed diagram of first order (see figure 1(a)) has the following form:

$$X(t_\alpha, t_\beta) \simeq \left( \frac{\lambda + 1}{\lambda - 1} \right) \ln \lambda + O(\epsilon) \tag{3.12}$$

where  $\lambda = t_\alpha/t_\beta$  and the matching condition  $T(\tau) = e^{2\tau}$  has been employed. However, Laplace inverting quantities of the general form  $t_\alpha^{-\phi} t_\beta^{-\psi} X(t_\alpha, t_\beta)$  will clearly be difficult. This problem may however be sidestepped for the important case  $M = N$  by effectively commuting the operation of Laplace inversion ( $L^{-1}$ ) with the momentum integrations as follows.

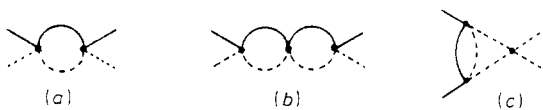


Figure 1. A selection of mixed diagrams; only (a) need be evaluated.

The first step is to replace the smoothly cut off integral of our theory by a dimensionally regularised equivalent. To do this one notes that (appendix 1),

$$\int_0^\infty \frac{dx x^{1-\epsilon/2}}{[x(1+x)+t_\alpha][x(1+x)+t_\beta]} = -\left(\frac{2}{\epsilon}+1\right) + \int_0^\infty \frac{dx x^{1-\epsilon/2}}{(x+t_\alpha)(x+t_\beta)} + O(t_\alpha, t_\beta) \quad (3.13)$$

where the left-hand side is smoothly cut off and the right hand side is to be dimensionally regularised. The problem is thus reduced to the Laplace inversion of the simpler, dimensionally regularised form. One may of course replace  $r_\alpha(\tau)$  and  $t_\alpha(\tau)$  by  $t_\alpha$  at this order. Writing

$$Y \equiv (t_\alpha, t_\beta)^{-\phi} e^{\epsilon\tau} \int_0^\infty \frac{dx x^{1-\epsilon/2}}{(x+t_\alpha)(x+t_\beta)} \quad (3.14)$$

and re-arranging using the identity

$$\frac{1}{\lambda} = \int_0^\infty dy e^{-\lambda y}$$

gives

$$Y = \int_0^\infty dx x^{1-\epsilon/2} \int_0^\infty d\lambda_1 \int_0^\infty d\lambda_2 e^{-(\lambda_1+\lambda_2)x} (t_\alpha^{-\phi} e^{-\lambda_1 t_\alpha}) (t_\beta^{-\phi} e^{-\lambda_2 t_\beta}).$$

One now recalls that  $t^{-\phi} e^{-\lambda t}$  is the Laplace transform of a function  $f(N)$  defined as follows:

$$f(N) = \begin{cases} 0 & 0 < N < \lambda \\ \frac{(N-\lambda)^{\phi-1}}{\Gamma(\phi)} & N > \lambda \end{cases} \quad (3.15)$$

where  $\phi - 1 > 0$ . Laplace inverting  $Y$  under the integral sign, we therefore obtain:

$$L^{-1}(Y) \stackrel{M=N}{=} N^{2(\phi-1)} \frac{\Gamma(d/2)}{\Gamma(\phi - \epsilon/\Delta)^2} \int_0^1 \int_0^1 d\lambda_1 d\lambda_2 \frac{[(1-\lambda_1)(1-\lambda_2)]^{\phi-1}}{(\lambda_1 + \lambda_2)^{2-\epsilon/2}}. \quad (3.16)$$

In particular for  $\phi = 2 + O(\epsilon)$  evaluating the integrals on  $\lambda_1$  and  $\lambda_2$  to order  $\epsilon$ , we have the result

$$L^{-1}(Y) = [(2/\epsilon) + (\frac{1}{2} - 2 \ln 2) + O(\epsilon)] L^{-1}((t_\alpha t_\beta)^{-\phi}). \quad (3.17)$$

Finally, then for  $M = N$ ,  $\phi = 2 + O(\epsilon)$  one may effectively pre-invert the contribution from the mixed diagram by using:

$$L^{-1}((t_\alpha t_\beta)^{-\phi} X(t_\alpha, t_\beta)) = -(2 \ln 2 + \frac{1}{2}) L^{-1}((t_\alpha t_\beta)^{-\phi}) + O(\epsilon). \quad (3.18)$$

Up to this pre-inversion, the calculation now follows the previous path, yielding the following results:

$$P_{NN} = \begin{cases} Z_4(u) N^2 \left( 1 + \frac{5}{16} (1 - \frac{6}{4\epsilon} A) \epsilon z + O(z^2) \right) & z \ll 1 \quad (3.19) \\ Z_4(u) \frac{1 - \frac{3}{8} A \epsilon}{\Gamma^2(\gamma + \frac{1}{2} \nu d)} N^2 z^{2\rho_4 \omega/\epsilon} \left[ 1 - \frac{5}{32} \left( \frac{\Gamma(\gamma + \frac{1}{2} \nu d)}{\Gamma(\gamma + \frac{1}{2} \nu d - \frac{1}{2} \omega)} \right)^2 \left( 1 - \frac{12}{5} A \epsilon \right) z^{-2\omega/\epsilon} \right. \\ \left. + O(z^{-4\omega/\epsilon}) \right] & z \gg 1 \quad (3.20) \end{cases}$$



where

$$\rho_4\omega = 2(2 - \gamma) - d\nu + O(\epsilon^3) \quad A = -0.424.$$

**4. The construction of  $A_2$**

$A_2$  is calculated in the poor-solvent region ( $z \ll 1$ ) by inserting (3.9) and (3.19) into (1.2). Thus near the  $\Theta$  point:

$$A_2 = uN^2[1 - Bz + O(z^2)] \quad z \ll 1 \tag{4.1}$$

where

$$B \equiv \frac{5}{16} \frac{(1 - \frac{6}{5}A)\epsilon}{\Gamma^2(2 + \frac{1}{4}\epsilon)} - \frac{1}{2} \frac{(1 - \frac{7}{32}\epsilon)}{\Gamma(1 + \frac{1}{2}\epsilon)}.$$

In the good-solvent region (3.10), (3.20) and (1.2) yield

$$A_2 = CuN^2 z^{2\theta/\epsilon} [1 + Dz^{-2\omega/\epsilon} + O(z^{-4\omega/\epsilon})] \quad z^{-2\omega/\epsilon} \ll 1 \tag{4.2}$$

where

$$C \equiv \left( \frac{\Gamma(\gamma)}{\Gamma(\gamma + \frac{1}{2}\nu d)} \right)^2 \frac{(1 - \frac{3}{8}A\epsilon)^2}{-\frac{25}{128}\epsilon}$$

$$D \equiv \left( \frac{\Gamma(\gamma + \frac{1}{2}\nu d)}{\Gamma(\gamma + \frac{1}{2}\nu d - \frac{1}{2}\omega)} \right)^2 \frac{5}{16} (1 - \frac{6}{5}A)\epsilon - \frac{\Gamma(\gamma)}{\Gamma(\gamma - \omega)} \frac{1}{2} (1 - \frac{3}{8}\epsilon)$$

$$\theta \equiv d\nu - 2 + O(\epsilon^3)$$

(the interesting non-universal prefactor  $Z_4 Z_2^{-2}$  having been scaled out).

The equations (4.1), (4.2) constitute a representation of the crossover from the Gaussian to Wilson-Fisher fixed points in  $d = 4 - \epsilon$  dimensions, correct to  $O(\epsilon^2)$ . It should be remarked that  $A_2 \sim N^{\nu d}$  ( $z \gg 1$ ), i.e. is proportional to the excluded volume as expected.

In order to predict physics one must work in  $d = 3$  dimensions ( $\epsilon = 1$ ) so that one must decide at which point to introduce  $\epsilon = 1$  into our expressions. Solving for  $u(\tau)$  as a function of the crossover scaling parameter  $\chi$  we used the exponential form of the parametric equation, thus the only consistent point of view, if we wish to retain the exponential forms (4.1) and (4.2) is to take  $\epsilon = 1$  before expanding in  $x$  (or  $x^{-2\omega}$ ). One therefore simply introduces  $\epsilon = 1$  into (4.1) and (4.2); giving for the poor-solvent region:

$$A_2 = uN^2[1 - 0.075z + O(z^2)] \quad z \ll 0.1 \tag{4.3}$$

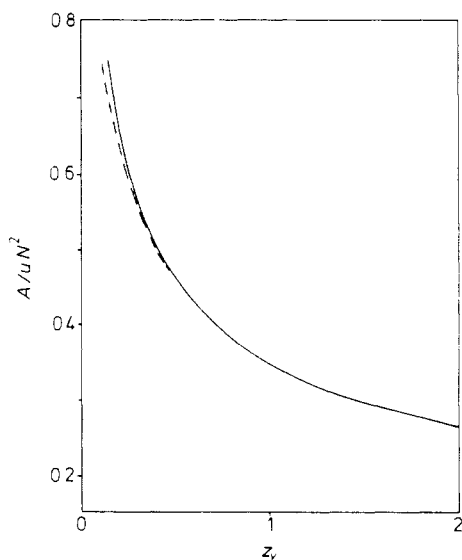
and for the good-solvent region

$$A_2 = 1.432uN^2 z^{-0.390} [1 + 0.241z^{-y} + O(z^{-2y})] \quad z^{-y} \ll 1.2 \tag{4.4}$$

where  $y$  is determined by  $\omega$ , which has a particularly badly behaved  $\epsilon$  expansion:

$$\omega = \frac{1}{2}\epsilon (1 - \frac{17}{32}\epsilon) + O(\epsilon^3) \equiv \begin{cases} \frac{1}{2} & \text{zeroth order} \\ 0.234 & \text{first order,} \end{cases}$$

whilst the recent work of Le Guillou and Zinn-Justin (1977) suggests that  $\omega = 0.465 \pm 0.010$  in three dimensions. Fortunately the results are insensitive to this difference; in figure 2  $A_2$  is plotted for  $\omega = 0.234$  and  $\omega = 0.465$  to illustrate this.



**Figure 2.** Plots of  $A_2/uN^2$  against  $z_y$  for  $\omega = 0.234$  (broken curve) and  $\omega = 0.465$  (full curve).

Berry (1966) who measured the second virial coefficient  $A_2$  for a solution of polystyrene in decalin presents his results in terms of the Yamakawa (1971) perturbation expansion:

$$A_2 = uN^2[1 - 2.865z_y + O((z_y)^2)]. \quad (4.5)$$

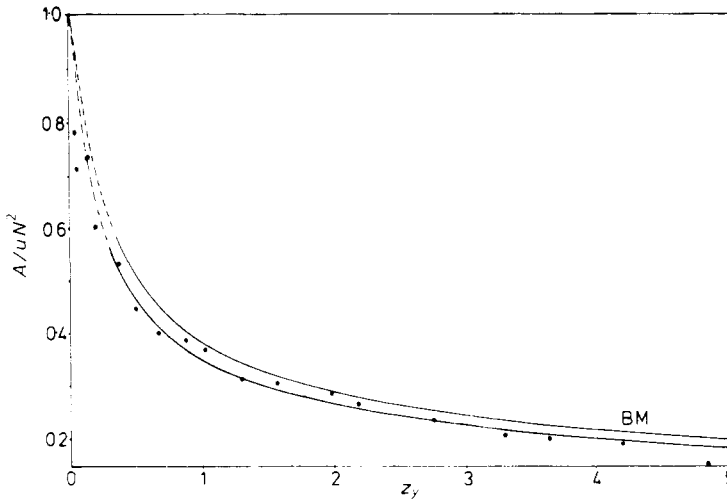
Scaling  $Z$  to reproduce (4.5) from (4.3) one may obtain a convenient comparison with this experimental data. In the good-solvent region one has the final result ( $z = 38.20z_y$ ):

$$A_2 = 0.344uN^2z_y^{-0.390}[1 + 0.0082z^{-0.930} + O(z^{-1.06})] \quad (4.6)$$

with  $z_y \gg 0.03$ . This region of validity of the expansion was determined by computing the first correction to (4.5). Figure 3 is plot of  $A_2/uN^2$  against  $z$  predicted by (4.5), compared with the experimental data of Berry and the phenomenological result of Burch and Moore. The most probable source of the small discrepancy at large  $z$  is the failure of the relation  $u \approx 1 - \Theta/T$  when  $T$  is not close to  $\Theta$  (Yamakawa 1971, p 375). In addition marginal operators, like  $\phi^6$  in  $d = 3$  which produces logarithmic corrections, should strictly be included, particularly in the region of the Flory temperature. However, the present experimental data do not warrant the introduction of these extra degrees of freedom.

## 5. Conclusions

The calculation of the second virial coefficient of the osmotic pressure appears to reproduce the experimental data of Berry extremely well, making a significant improvement to the result of Burch and Moore. After tying down the functional form for  $z \ll 1$  no further free parameters exist, whilst the exponents, given to  $O(\epsilon^2)$  compare well with experiment ( $\epsilon = 1$ ).



**Figure 3.** Plot of  $A_2/uN^2$  against  $z$ , the data points are for polystyrene in decalin (Berry 1966). The broken curve is an interpolation of (4.5) and (4.6). Also shown for comparison is the result of Burch and Moore (1976).

The method generates the leading terms of polymer correlation functions within the homogeneity assumption; (2.7) and preceding paragraph, to  $O(\epsilon^2)$ . For the sceptical it should be remarked that one may obtain an identical homogeneous equation in terms of renormalised parameters without this assumption (Bruce and Wallace 1976). A distinct advantage over the method of Burch and Moore is that corrections to their simple boundary conditions may be systematically included, their choice corresponding exactly to retaining only the lowest-order term of a perturbation expansion in  $u(\tau)$  for each  $G^L(\tau)$ . Whilst the  $\Theta$  temperature has been taken to be analogous to a Gaussian fixed point, one should strictly use a tricritical description by including the  $\phi^6$  coupling. In  $d = 3$  dimensions,  $\phi^6$  operators are marginal at the  $\Theta$  temperature so one would therefore expect logarithmic corrections to our results for  $z \ll 1$ . However, the present experimental data do not warrant the introduction of this extra degree of freedom.

To solve the problems presented by the mixed diagrams we have had to use an alternative inversion technique to Burch and Moore; however, the diagrams still constitute a considerable nuisance. Work is currently in progress to formulate the renormalisation group equations directly for polymer properties in order to further simplify this problem. It is hoped that we may then tackle the polydisperse problem; for example one could calculate the generalised second virial coefficient  $A_2(M, N)$  to  $O(\epsilon^2)$ .

Further a parametric description would then be obtained directly in terms of the polymer variables allowing a discussion of the convergence of the  $\epsilon$  expansion within this exact representation (to  $O(\epsilon^2)$ ). One would also be in an ideal position to determine the convergence of the power series representation.

### Acknowledgments

I would like to thank Professor M A Moore for introducing me to the problem, my supervisor Dr D J Wallace for his encouragement and the SRC for a maintenance grant.

**Appendix 1**

Equation (3.13) may be simply derived as follows:

$$\begin{aligned}
 & \int_0^\infty \frac{dx x^{1-\epsilon/2}}{[x(1+x)+t_\alpha][x(1+x)+t_\beta]} \\
 &= \frac{1}{t_\alpha - t_\beta} \int_0^\infty dx x^{1-\epsilon/2} \left( \frac{1}{x(x+1)+t_\beta} - \frac{1}{x(x+1)+t_\alpha} \right) \\
 &= \frac{1}{t_\alpha - t_\beta} \int_0^\infty dx x^{1-\epsilon/2} \left[ \left( \frac{1}{x(x+1)+t_\beta} - \frac{1}{x(x+1)} \right) - \left( \frac{1}{x(x+1)+t_\alpha} - \frac{1}{x(x+1)} \right) \right] \\
 &= \frac{1}{t_\alpha - t_\beta} \left[ t_\beta \left( 1 + \frac{2}{\epsilon} (1 - t_\beta^{-\epsilon/2}) \right) - t_\alpha \left( 1 + \frac{2}{\epsilon} (1 - t_\alpha^{-\epsilon/2}) \right) \right] + O(t_\alpha, t_\beta) \\
 &= - \left( 1 + \frac{2}{\epsilon} \right) + \frac{1}{t_\alpha - t_\beta} \left( \frac{2}{\epsilon} \right) (t_\alpha^{1-\epsilon/2} - t_\beta^{1-\epsilon/2}) + O(t_\alpha, t_\beta) \\
 &= - \left( 1 + \frac{2}{\epsilon} \right) + \frac{1}{t_\alpha - t_\beta} \left[ \int_0^\infty dx x^{1-\epsilon/2} \left( \frac{1}{x+t_\beta} - \frac{1}{x+t_\alpha} \right) \right] + O(t_\alpha, t_\beta, \epsilon) \\
 &= - \left( 1 + \frac{2}{\epsilon} \right) + \int_0^\infty \frac{dx x^{1-\epsilon/2}}{(x+t_\alpha)(x+t_\beta)} \tag{3.13}
 \end{aligned}$$

**Appendix 2**

For easy reference we list the  $\epsilon$  expansions of various quantities defined in the text:

$$\begin{aligned}
 \nu &= \frac{1}{2} \left( 1 + \frac{1}{8}\epsilon + \frac{15}{256}\epsilon^2 \right) + O(\epsilon^3) \\
 \gamma &= 1 + \frac{1}{8}\epsilon + \frac{13}{256}\epsilon^2 + O(\epsilon^3) \\
 \eta &= \frac{1}{64}\epsilon^2 + O(\epsilon^3) \\
 \omega &= \frac{1}{2}\epsilon \left( 1 - \frac{17}{32}\epsilon \right) + O(\epsilon^3) \\
 \rho &= \frac{1}{4}(1 + \epsilon) + O(\epsilon^2) \\
 \rho_2 &= -\frac{1}{4} \left( 1 + \frac{15}{16}\epsilon \right) + O(\epsilon^2) \\
 \rho_4 &= -\frac{15}{16}\epsilon + O(\epsilon^2) \\
 \theta &= -\frac{1}{4}\epsilon \left( 1 - \frac{7}{32}\epsilon \right) + O(\epsilon^3).
 \end{aligned}$$

Of course only  $\omega$  and any other two quantities are independent, the relations are:

$$\begin{aligned}
 \gamma &= \nu(2 - \eta) & \rho\omega &= 2\nu - 1 & \rho_2\omega &= 1 - \gamma \\
 \rho_4\omega &= 2(2 - \gamma) - d\nu & \theta &= d\nu - 2.
 \end{aligned}$$

**Appendix 3**

Burch and Moore write phenomenological renormalisation group equations for their

scaling fields  $\mu_i, i = 1, 2, \dots, M$  and  $\mu_2$

$$\frac{d\mu_i}{dl} = 2\mu_i - A\mu_i\mu_2 \quad i = 1, 2, \dots, M$$

$$\frac{d\mu_2}{dl} = \mu_2(1 - \mu_2)$$

which correspond exactly to our equations (2.8), (2.9) if the  $O(\epsilon^2)$  corrections are ignored and one takes:

$$A = \frac{1}{4} \quad l = -\tau \quad \mu_i = t_i/\Lambda^2 \quad (i = 1, 2, \dots, M) \quad \mu_2 = \frac{3}{8}u$$

for  $\epsilon = 1$ . Whilst Burch and Moore choose  $A = \frac{1}{3}$  rather than the latter value in order to obtain the experimental value  $\nu = \frac{3}{5}$  for the correlation length exponent we have  $(2 - A)^{-1} = \frac{4}{7}$ , a small difference.

Now the Green functions  $G^{2M}$  have the general form

$$G^{2M}(t_i, u, \Lambda) = \Lambda^{d-M(2+d)} f(x_i, u)$$

where the function  $f(x_i, u)$  ( $x_i \equiv t_i/\Lambda^2$ ) satisfies the following renormalisation group equation:

$$\left( W(u) \frac{\partial}{\partial u} - \frac{1}{\nu(u)} \sum_{i=1}^M x_i \frac{\partial}{\partial x_i} + d - M(d+2) + M\eta(u) \right) f(x_i, u) = 0.$$

Solving this renormalisation group equation as usual ( $\Lambda = 1$ ), with initial condition  $x_i(0) = t_i, u(0) = u$  one has

$$G^{2M}(t, u, 1) = \exp\left( [d - M(d+2)]\tau + \int^\tau \eta(u(\tau')) d\tau' \right) G^{2M}(x_i(\tau), u(\tau)).$$

Since  $\Lambda(u) = O(\epsilon^2)$  we see that at first order in  $\epsilon$  we reproduce the homogeneous form quoted by Burch and Moore for the Green functions  $G^{2M}$ . Thus it is clear that the phenomenological calculation of Burch and Moore closely resembles an  $O(\epsilon)$  calculation, extra terms being present at  $O(\epsilon^2)$ . Of course it could be argued that instead of our simple correspondence one should allow  $(\mu_1, \mu_2)$  to be non-linear functions of  $(t_i, u)$ , however it is then difficult to set up a consistent approximation system in order to obtain systematic corrections to the Burch and Moore calculation.

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