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# A non-ideal polymer chain interacting with a penetrable surface

Marios K Kosmas

Chemistry Department, University of Ioannina, Ioannina, Greece

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**Abstract.** We study the conformational properties of a polymer chain in the presence of both excluded volume interactions and interactions with a penetrable surface. The coexistence of two different kinds of interaction brings new features to the behaviour of the chain, beyond those coming from the two interactions acting independently. We follow an analysis which can find application to the study of problems with more than one interaction parameter.

## 1. Introduction

The probability distribution for the positions  $\mathbf{R}_i$  ( $i = 1, 2, \dots, N$ ) of the units of a non-ideal polymer chain, in the presence of the interacting penetrable surface represented by the  $x, y$  plane, can be written as

$$P\{\mathbf{R}_i\} = P_0\{\mathbf{R}_i\} \exp\left(-u_a \sum_{i=1}^N \delta(z_i) - u_e \sum_{i=1}^N \sum_{j=1, j \neq i}^N \delta^3(\mathbf{R}_i - \mathbf{R}_j)\right). \quad (1.1)$$

$z_i$  is the distance of the  $i$ th unit from the surface and  $N$  is proportional to the length of the chain.  $P_0\{\mathbf{R}_i\}$  stands for the probability distribution of the ideal non-interacting

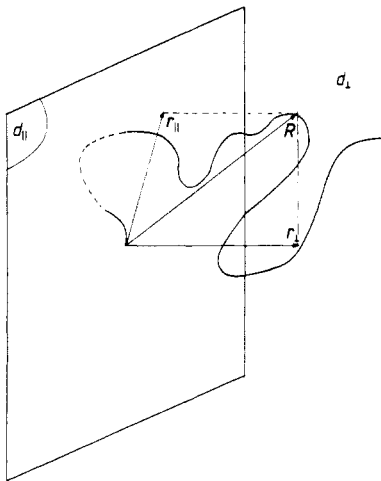


Figure 1. A polymer chain in the presence of an interacting penetrable plane.

chain while the two energy terms represent two different kinds of interaction: the interactions between the units and the surface (Kosmas 1981b) and the excluded volume interactions (Yamakawa 1971, Kosmas 1981a) respectively. The unit length of the polymer is taken equal to one for simplicity while the units of the adsorption parameter  $u_a$  and the excluded volume parameter  $u_e$  are chosen such that the exponential term is dimensionless.

The problem of adsorption from a penetrable surface (Hammersley *et al* 1982) is useful for two reasons.

(i) It is similar to the case of a polymer chain interacting with an impenetrable surface, which finds applications in the area of adsorption of polymers from liquid-solid interfaces (Kosmas 1981b, Freed 1983, Barber *et al* 1978) and in the area of semi-infinite systems (Bray and Moore 1977, Lubensky and Rubin 1975).

(ii) It is the simplest example of the coexistence of two different interaction parameters and its study will help in the understanding of the behaviour of systems with more than one kind of interaction.

The general features of the two cases in which the two interactions act independently are as follows. When the interacting surface is absent,  $u_a = 0$ , and one parameter remains in the problem, the excluded volume parameter  $u_e$ . In this case there is a critical dimensionality  $d = 4$  above which excluded volume effects are negligible. Two average quantities, the total number of configurations  $C$  and the number  $U$  of configurations returning to the origin have been found previously (Kosmas 1981a). At the dimensionality  $d = 4 - \varepsilon$  ( $\varepsilon$  small) and in the good solvent region where  $u_e > 0$  they are

$$C = \mu_0^N \exp(-2u_e N) [1 + 2u_e \ln N + (\frac{1}{2}u_e \varepsilon - 6u_e^2) \ln^2 N] \\ \sim [\mu_0 \exp(-2u_e)]^N N^{2u_e^*} = [\mu_0 \exp(-2u_e)]^N N^{\varepsilon/8}, \quad (1.2a)$$

$$U = [\mu_0^N \exp(-2u_e N) / N^{d/2}] [1 - 4u_e \ln N + (-u_e \varepsilon + 24u_e^2) \ln^2 N] \\ \sim \{[\mu_0 \exp(-2u_e)]^N / N^{d/2}\} N^{-4u_e^*} \\ = [\mu_0 \exp(-2u_e)]^N N^{-(d/2) - (\varepsilon/4)}, \quad u_a = 0, u_e^* = \varepsilon/16. \quad (1.2b)$$

The fixed point value  $u_e^* = \varepsilon/16$  describes the expanded state of the chain and it can be determined from second-order perturbation theory, equation (1.2a) or (1.2b); it is that value of  $u_e$  which exponentiates the series (Wilson and Kogut 1974, Kosmas 1981a, 1982). The exponents can then be determined to first order in  $\varepsilon$  from first-order perturbation theory as quoted in equations (1.2a) and (1.2b). Analogously, in the absence of excluded volume interactions ( $u_e = 0$ ) the parameter  $u_a$  remains to determine the conformational properties of the chain (DiMarzio and McCrackin 1965). For the adsorption problem the critical dimensionality above which the adsorption effects are negligible is 2 and the two average properties for  $d = 2 - \varepsilon$  are given by:  $C = \mu_0^N [1 + u_a(2/\varepsilon)(N^{\varepsilon/2} - 1)]^{-1}$  and  $U = (\mu_0^N / N^{d/2}) [1 + u_a(2/\varepsilon)(N^{\varepsilon/2} - 1)]^{-2}$  (Kosmas 1981b). Beyond the ideal behaviour taken from this solution for  $u_a = 0$ , a non-ideal behaviour is observed for  $u_a > 0$ , where the chain is desorbed and belongs mainly to the solution. Since  $N$  is a huge number, for  $u_a > 0$  the two properties behave as  $C \sim \mu_0^N N^{-\varepsilon/2}$  and  $U \sim \mu_0^N N^{-(d/2) - \varepsilon}$  and are characterised by the two critical exponents  $-\varepsilon/2$  and  $-(d/2) - \varepsilon$  respectively. The main features of the behaviour of the chain taken from the full solution can also be derived from second-order perturbation theory,

according to which

$$C = \mu_0^N [1 - u_a \ln N - (\frac{1}{4}\epsilon u_a - u_a^2) \ln^2 N] \\ \sim \mu_0^N N^{-u_a^*} = \mu_0^N N^{-\epsilon/2} \quad (1.3a)$$

and

$$U = (\mu_0^N / N^{d/2}) [1 - 2u_a \ln N + (-\frac{1}{2}\epsilon u_a + 3u_a^2) \ln^2 N] \\ \sim \mu_0^N N^{-(d/2)-2u_a^*} = \mu_0^N N^{-(d/2)-\epsilon}, \quad u_e = 0, u_a^* = \epsilon/2. \quad (1.3b)$$

The exponentiation of these series, that is the equation of the half of the square of the first-order term with the second-order term,  $\frac{1}{2}(-u_a^*)^2 = -\frac{1}{4}\epsilon u_a^* + u_a^{*2}$  which leads to the power-law dependence, determines two values of the adsorption parameter,  $u_a^* = 0$  and  $u_a^* = \epsilon/2$ . These two different fixed points represent the two different possible states of the chain: the ideal state with  $u_a^* = 0$  and the non-ideal desorbed state with  $u_a^* = \epsilon/2$ . The critical exponents can then be found as written in (1.3a) and (1.3b) and agree with the exponents taken from the full solution given above.

The question raised is what happens when both interactions are present and the purpose of the present work is to answer this problem. First of all we must find a formalism which can incorporate the two different critical dimensionalities 4 and 2. This is achieved by generalising the three-dimensional problem to a  $d$ -dimensional one with  $d = 4 - \epsilon$ . Two units of the chain at the position vectors  $\mathbf{R}_i$  and  $\mathbf{R}_j$  interact with a pseudopotential of the form  $u_e \delta^d(\mathbf{R}_i - \mathbf{R}_j)$ . At the same time the units interact with a generalised plane of dimensionality  $d_{\parallel} < d$  with a  $u_a \delta^{d_{\perp}}(\mathbf{r}_{i\perp})$  potential where  $d_{\perp} = d - d_{\parallel} = 2 - \epsilon$ , and  $\mathbf{r}_{i\perp}$  are the components of the position vectors  $\mathbf{R}_i$  in the subspace of dimensionality  $d_{\perp}$ . Of course the model has to give the real three-dimensional problem represented by equation (1.1), in the limit  $\epsilon \rightarrow 1$ . It is explained in detail in the next section. A solution up to second order in  $u_e$  and  $u_a$  will follow. Beyond the two solutions given in equations (1.2) and (1.3), representing the excluded volume and the adsorption problems respectively, new features due to the coexistence of the two phenomena are expected to come out of this solution.

## 2. Definitions

In many problems in statistical physics there are critical dimensionalities  $d_c$  above which the systems under study behave ideally. In such cases the analytic continuation of the dimensionality  $d$  to non-integer values is very helpful. The main reason for this is that the parameter  $\epsilon = d_c - d$  can be treated as a small continuous variable and the employment of perturbation theory for the study of the system at  $d$ 's where non-ideal behaviour occurs is possible. More than one generalisation of a three-dimensional problem to a  $d$ -dimensional one are possible, but all of them must yield the right three-dimensional problem in the limit  $d \rightarrow 3$ . The generalisation which we use here is represented in figure 1. Although the definitions are conceivable for integer values of dimensionalities, in the end we treat the dimensionalities as continuous variables so that an  $\epsilon$ -expansion is possible. The dimensionality of the full space where the  $\mathbf{R}_i$  vectors belong is  $d$ . Excluded volume interactions of the form  $u_e \delta^d(\mathbf{R}_i - \mathbf{R}_j)$  occur between all pairs of polymeric units and this is to imitate the  $u_e \delta^3(\mathbf{R}_i - \mathbf{R}_j)$  term of equation (1.1). Two subspaces of the full space are important. One is a generalised

plane created from the  $d_{\parallel} < d$  axis; this subspace goes to the  $x, y$  plane in the limit  $d \rightarrow 3$ . The second subspace is created from the rest  $d_{\perp} = d - d_{\parallel}$  axis not included in the generalised plane. All these  $d_{\perp}$  axes are perpendicular to the plane. In the limit  $d \rightarrow 3$  the second subspace goes to the  $z$  axis perpendicular to the  $x, y$  plane. A vector  $\mathbf{R}$  in the  $d$ -dimensional full space consists of two components, the component  $\mathbf{r}_{\parallel}$  parallel to the plane and the component  $\mathbf{r}_{\perp}$  perpendicular to the plane,  $\mathbf{R} = \mathbf{r}_{\parallel} + \mathbf{r}_{\perp}$ . The polymeric units at  $\mathbf{R}_i$  interact with the plane through a  $u_a \delta^{d_{\perp}}(\mathbf{r}_{i\perp})$  pseudopotential which is to imitate the  $u_a \delta(z_i)$  term of (1.1). In what follows the dimensionality of the full space will be taken equal to  $d = 4 - \varepsilon$  which in the limit  $\varepsilon \rightarrow 1$  goes to the dimensionality three of the real problem. The dimensionality of the generalised plane is kept constant and equal to  $d_{\parallel} = 2$ . In the limit  $d \rightarrow 3$  the generalised plane goes to the  $x, y$  plane. The dimensionality is  $d_{\perp} = 2 - \varepsilon$  and in the limit  $d \rightarrow 3$  ( $\varepsilon \rightarrow 1$ ) it goes to  $d_{\perp} \rightarrow 1$  and coincides with the dimensionality of the  $z$  axis. According to this generalisation the probability distribution can be written as

$$P\{\mathbf{R}_i\} = P_0\{\mathbf{R}_i\} \exp\left(-u_a \sum_{i=1}^N \delta^{2-\varepsilon}(\mathbf{r}_{i\perp}) - u_e \sum_{i=1}^N \sum_{j=1, j \neq i}^N \delta^{4-\varepsilon}(\mathbf{R}_i - \mathbf{R}_j)\right). \quad (2.1)$$

This probability incorporates the two different critical dimensionalities 2 and 4 and yields the probability, equation (1.1), in the limit  $\varepsilon \rightarrow 1$ . We must mention through that equation (2.1) is not the only possible generalisation of (1.1). Another possibility for example is the generalisation to a  $d$ -dimensional problem in which the two subspaces are the  $(d-1)$ -dimensional subspace and the rest  $z$  axis. In this case the two potentials are  $u_e \delta^{4-\varepsilon}(\mathbf{R}_i - \mathbf{R}_j)$  and  $u_a \delta(z_i)$  respectively and again the problem is that represented by the probability distribution, equation (1.1), in the limit  $d \rightarrow 3$ . This picture has been used in previous studies (Bray and Moore 1977) but it cannot be of much help in our case because it cannot incorporate the two different critical dimensionalities 2 and 4 as equation (2.1) does.

In the following we will initially evaluate the following two quantities: the total number of walks

$$C = \int \prod_{i=1}^N d^d \mathbf{R}_i P\{\mathbf{R}_i\} \quad (2.2)$$

and the number of walks having their last unit at the origin

$$U = \int \prod_{i=1}^N d^d \mathbf{R}_i P\{\mathbf{R}_i\} \delta^d(\mathbf{R}_N). \quad (2.3)$$

Second-order calculations for the above two properties provide the values of the two parameters  $u_a$  and  $u_e$  at the fixed points, thus determining possible new fixed points for the problem. In order to check the theory, two more properties are evaluated up to second order. One is the number  $C_{\parallel}$  of walks having their second ends at the plane

$$C_{\parallel} = \mu_0^N \int \prod_{i=1}^N d^d \mathbf{R}_i P\{\mathbf{R}_i\} \delta^{d_{\perp}}(\mathbf{r}_{N\perp}), \quad (2.4)$$

and the other is the number  $C_{\perp}$  of walks with their ends on the axis perpendicular to the plane

$$C_{\perp} = \mu_0^N \int \prod_{i=1}^N d^d \mathbf{R}_i P\{\mathbf{R}_i\} \delta^{d_{\parallel}}(\mathbf{r}_{N\parallel}). \quad (2.5)$$

**3. Solution**

If we use for the ideal chain the Gaussian distribution

$$P_0\{\mathbf{R}_i\} = [d/(2\pi l^2)]^{dN/2} \exp\left(- (d/2l^2) \sum_{i=1}^N (\mathbf{R}_i - \mathbf{R}_{i+1})^2\right), \quad (3.1)$$

and absorb  $(d/2\pi l^2)^{d/2}$  factors in  $u$ 's, second-order perturbation theory gives for  $C$  the diagrammatic expansion (Kosmas 1981a)

$$C = \mu_0^N \left[ 1 - u_a \underline{\mathcal{O}}_C - 2u_e \overline{\mathcal{O}}_C + u_a^2 \underline{\mathcal{O}}_C + 4u_e^2 \left( \overline{\mathcal{O}}_C + \overline{\mathcal{O}}_C + \Theta_C \right) + 2u_a u_e \left( \underline{\mathcal{O}}_C + \underline{\mathcal{O}}_C + \Theta_C \right) \right]. \quad (3.2)$$

The first and second-order  $u_a$  diagrams come from one and two  $\delta^{d_\perp}(\mathbf{r}_\perp)$  functions respectively, while the first and second-order  $u_e$  diagrams come from one and two  $\delta^d(\mathbf{R})$  functions respectively. These diagrams correspond to the two independent cases (Kosmas 1981a, b); their expressions and values are given in tables 1 and 2 respectively. The diagrams of the cross  $u_a u_e$  term are new and come from the product of a  $\delta^{d_\perp}(\mathbf{r}_\perp)$  and a  $\delta^d(\mathbf{R})$  function. Their expressions and values are also given in the tables. In the appendix a demonstration is given of the evaluation of the new diagrams. By means of the values of table 2 we take that

$$C = \mu_0^N \exp(-2u_e N) \left[ 1 - u_a \ln N + 2u_e \ln N - (u_a \varepsilon / 4) \ln^2 N + (u_e \varepsilon / 2) \ln^2 N + u_a^2 \ln^2 N - 6u_e^2 \ln^2 N - u_a u_e \ln^2 N \right]. \quad (3.3)$$

The two independent cases, (1.2a) and (1.3a), can be recovered from this general solution by putting  $u_a = 0$  or  $u_e = 0$  respectively. A point to notice is that the cross  $u_a u_e$  term is different from the term which the product of the two independent cases would give, providing the first evidence that some new effects come from the coexistence of two interaction parameters. In the two independent cases the fixed point value and the critical exponents are calculable from second-order perturbation theory by means of an exponentiation condition (Kosmas 1981a). When two interactions are present, two routes are possible for the evaluation of the values of the interaction parameters at the fixed points; either to go to higher-order perturbation theory where more than one condition would be required for the exponentiation of the series, or to study other properties, the exponentiation condition of which bring further relations between the values of the interaction parameters at the fixed points. Here we choose the second route. We have two interaction parameters so that two properties are sufficient. One is the total number of walks  $C$  and as a second one we pick up the number  $U$  of the walks returning to the origin. From (2.3) we take that

$$U = \mu_0^N \left[ (1/N^{d/2}) - u_a \underline{\mathcal{O}}_U - 2u_e \overline{\mathcal{O}}_U + u_a^2 \underline{\mathcal{O}}_U + 4u_e^2 \left( \overline{\mathcal{O}}_U + \overline{\mathcal{O}}_U + \Theta_U \right) + 2u_a u_e \left( \underline{\mathcal{O}}_U + \underline{\mathcal{O}}_U + \Theta_U \right) \right]. \quad (3.4)$$

Table 1. Expressions of the diagrams.  $d = 4 - \epsilon$ ,  $d_{\perp} = 2 - \epsilon$ ,  $d_{\parallel} = 2$ .

Diagram	
Property	$\overline{\mathcal{O}} = \sum_{i=1}^N \sum_{j=i+1}^N$
C	$t^{-d/2}$
U	$[i(N-i)]^{-d/2} N^{-d/2}$
C <sub>  </sub>	$[(j-i)(N-j+i)]^{-d/2}$
C <sub>⊥</sub>	$(j-i)^{-d/2} N^{-d/2}$
Diagram	
Property	$\overline{\mathcal{O}} = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1}$
C	$[(j-i)(l-k)]^{-d/2}$
U	$[(j-i)(l-k)(N-l+k-j+i)]^{-d/2}$
C <sub>  </sub>	$[(j-i)(l-k)]^{-d/2} N^{-l+k-j+i}$
C <sub>⊥</sub>	$[(j-i)(l-k)]^{-d/2} N^{-j+i-l+k}$
Diagram	
Property	$\Theta = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1}$
C	$(j-i)^{-d/2}$
U	$[(j-i)(N-j+i)]^{-d/2}$
C <sub>  </sub>	$[(j-i)(N-j)]^{-d/2}$
C <sub>⊥</sub>	$(j-i)^{-d/2} N^{-j+i}$
Diagram	
Property	$\overline{\mathcal{O}} = \sum_{i=1}^{N-3} \sum_{j=i+1}^{N-2} \sum_{k=j+1}^{N-1} \sum_{l=k+1}^N$
C	$(l_1 l_2 + l_1 l_3 + l_2 l_3)^{-d/2}$
U	$[(l_1 l_2 l_3 + (N-l_1-l_2-l_3)(l_1 l_2 + l_1 l_3 + l_2 l_3))]^{-d/2}$
C <sub>  </sub>	$[(l_1 l_2 + l_1 l_3 + l_2 l_3)^{-d/2} (N-l_1-l_2-l_3)]^{-d/2}$
C <sub>⊥</sub>	$[(l_1 l_2 + l_1 l_3 + l_2 l_3)^{-d/2} (N-l_1-l_2-l_3+l)]^{-d/2}$
	$(l_l^{-1} = l_1^{-1} + l_2^{-1} + l_3^{-1})$
Diagram	
Property	$\Theta = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \sum_{k=i}^N$
C	$(j-i)^{-4q/2} [(k-j+i)(j-i)]^{-d/2}$
U	$[(j-i)(N-j+i)]^{-4q/2} [(k-j+i)(j-i)(N-k)]^{-d/2}$
C <sub>  </sub>	$(j-i)^{-4q/2} [(k-j+i)(N-k)]^{-d/2}$
C <sub>⊥</sub>	$(j-i)^{-4q/2} (k-j+i)^{-d/2} N^{-j+i}$
Diagram	
Property	$\overline{\mathcal{O}} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \sum_{k=i}^N$
C	$(j-i)^{-4q/2} [(k-j+i)(j-i)]^{-d/2}$
U	$[(j-i)(N-j+i)]^{-4q/2} [(k-j+i)(j-i)(N-k)]^{-d/2}$
C <sub>  </sub>	$(j-i)^{-4q/2} [(k-j+i)(N-k)]^{-d/2}$
C <sub>⊥</sub>	$(j-i)^{-4q/2} (k-j+i)^{-d/2} N^{-j+i}$

Table 2. Values of the diagrams.

Property	Diagram	$\Omega$	$\sigma$	$\omega$	$\omega\omega$	$\delta$	$\phi$
C		$\ln N + \frac{1}{4}\epsilon \ln^2 N$	$N - \ln N - \frac{1}{4}\epsilon \ln^2 N$	$\ln^2 N$	$\frac{1}{2}N^2 - 2N \ln N + \ln^2 N$	$N \ln N - \ln^2 N$	$-\frac{1}{2} \ln^2 N$
U		$(2/N^2)(\ln N + \frac{3}{4}\epsilon \ln^2 N)$	$(1/N^2)[N + 2 \ln N + \frac{1}{2}\epsilon(N \ln N + 3 \ln^2 N)]$	$(3/N^2) \ln^2 N$	$(1/N^2)(\frac{1}{2}N^2)$	$(1/N^2)(2N \ln N + 3 \ln^2 N)$	$(3/N^2) \ln^2 N$
C <sub>  </sub>		$(2/N)(\ln N + \frac{1}{2}\epsilon \ln^2 N)$	$(1/N)(N + \frac{1}{2}\epsilon N \ln N)$	$(3/N) \ln^2 N$	$(1/2N)(N^2 - 2N \ln N)$	$(1/N)(N \ln N)$	$O(\ln^2 N)$
C <sub>⊥</sub>		$(1/N)(\ln N + \frac{1}{4}\epsilon \ln^2 N)$	$(1/N)(N)$	$(1/N) \ln^2 N$	$(1/2N)(N^2 - 2N \ln N)$	$(1/N)(N \ln N)$	$O(\ln^2 N)$

Property	Diagram	$\omega\omega$	$\delta$	$\phi$
C		$N \ln N - \ln^2 N$	no second order terms	$\frac{1}{2} \ln^2 N$
U		$(1/N^2)(N \ln N + \frac{1}{2} \ln^2 N)$	$(1/N^2)(N \ln N + \frac{1}{2} \ln^2 N)$	$(2/N^2) \ln^2 N$
C <sub>  </sub>		$(1/N)(N \ln N)$	$(1/N)(N \ln N)$	$(1/N) \ln^2 N$
C <sub>⊥</sub>		$(1/N)(N \ln N)$	$O(\ln N)$	$(1/2N) \ln^2 N$



Using the values of the diagrams we take that

$$U = [\mu_0^N \exp(-2u_e N) / N^2] [1 + (\varepsilon/2) \ln N - 2u_a \ln N - 4u_e \ln N + (\varepsilon^2/8) \ln^2 N - (3/2)u_a \varepsilon \ln^2 N - 3u_e \varepsilon \ln^2 N + 3u_a^2 \ln^2 N + 24u_e^2 \ln^2 N + 10u_a u_e \ln^2 N]. \quad (3.5)$$

When  $u_a = 0$  or  $u_e = 0$  the two independent cases are recovered and again the cross  $u_a u_e$  term is different from the term which the product of the two independent cases would give, indicating cross effects.

Results from the studies of problems of a single parameter show that various perturbation order terms yield the corresponding powers of  $\ln N$ , and that the expansion series sum up to exponential functions of the form  $e^{a \ln N} = N^a$  at the fixed points. The critical exponents  $a$  can be determined from the value of the interaction parameter at the fixed points and characterise the several states at which the chain can exist. For problems of two parameters the existence of series of  $\ln N$ 's again presages power laws. The various states of the chain are defined in terms of the values of two parameters and are characterised by different critical exponents. Varying the values of the interaction parameters the chain can go from one state to another. This picture is in accord with the Monte Carlo results of Eisenriegler *et al* (1982) who determined different critical exponents for different values of the two interaction parameters. In the case of the present problem of two parameters, in order to determine the fixed points and the values  $(u_a^*, u_e^*)$  of the interaction parameters at these points, as well as for the evaluation of the critical exponents, an analysis similar to that of the single parameter problems can be followed. The series in  $\ln N$ 's in equations (3.3) and (3.5) sum up to exponentials of the form  $e^{a \ln N} = N^a$  for the specific values  $(u_a^*, u_e^*)$  of the interaction parameters at the fixed points. In order for a series to fit into an exponential form, half of the square of the first-order term must be equal to the second-order term. Two such exponentiation conditions are possible for the above two series which determine pairs of values  $(u_a^*, u_e^*)$  of the two interaction parameters at the fixed points. They can be written in the following manner

$$\left. \begin{aligned} \frac{1}{2}(-u_a^* + 2u_e^*)^2 &= -\frac{1}{4}u_a^* \varepsilon + \frac{1}{2}u_e^* \varepsilon + u_a^{*2} - 6u_e^{*2} - u_a^* u_e^* \\ \frac{1}{2}[(\varepsilon/2) - 2u_a^* - 4u_e^*]^2 &= (\varepsilon^2/8) - \frac{3}{2}u_a^* \varepsilon - 3u_e^* \varepsilon + 3u_a^{*2} + 24u_e^{*2} + 10u_a^* u_e^* \end{aligned} \right\} \Rightarrow$$

$$(32u_e^{*2} - 2u_e^* \varepsilon) - (4u_a^* u_e^* + 2u_a^{*2} - u_a^* \varepsilon) = 0$$

$$(32u_e^{*2} - 2u_e^* \varepsilon) + (4u_a^* u_e^* + 2u_a^{*2} - u_a^* \varepsilon) = 0. \quad (3.6)$$

When  $u_a^* = 0$  the excluded volume problem fixed points are obtained with  $u_e^* = 0$ ,  $\varepsilon/16$ ; when  $u_e^* = 0$  the adsorption problem fixed points are obtained with  $u_a^* = 0$ ,  $\varepsilon/2$ . The simultaneous solution of the two equations (3.6) yields further fixed points. From (3.6) we obtain the relations

$$32u_e^{*2} - 2u_e^* \varepsilon = 0, \quad 4u_a^* u_e^* + 2u_a^{*2} - u_a^* \varepsilon = 0. \quad (3.7a, b)$$

The first equation is identical to the equation of the excluded volume problem without the presence of the plane, which means that the adsorption interactions do not influence the fixed point values 0 and  $\varepsilon/16$  of the excluded volume parameter  $u_e^*$ . The same is not true for the values of  $u_a$  at the fixed points. The second equation reveals that the values of  $u_a^*$  depend on the excluded volume interactions. For  $u_e^* = 0$  the two values  $u_a^* = 0$ ,  $\varepsilon/2$  of the adsorption problem are obtained but for  $u_e^* = \varepsilon/16$  a new value of

$u_a^*$  is taken. All the possible fixed points are quoted in table 3. The critical exponents of  $C$  and  $U$  at the fixed points can be found from the expressions

$$C \sim \mu_0^N \exp(-2u_e N) N^{-u_a^* + 2u_e^*} \sim N^{\gamma-1}, \quad \gamma = 1 - u_a^* + 2u_e^*, \quad (3.8a)$$

$$U \sim \mu_0^N \exp(-2u_e N) N^{-2 + (\epsilon/2) - 2u_a^* - 4u_e^*} \sim N^\beta, \quad \beta = -2 + (\epsilon/2) - 2u_a^* - 4u_e^*, \quad (3.8b)$$

and they are also given in table 3.

**Table 3.** Values of the interaction parameters at the fixed points and critical exponents.

Interaction	Ideal	Adsorption	Excluded volume	Adsorption + excluded volume
$u_e^*$	0	0	$\epsilon/16$	$\epsilon/16$
$u_a^*$	0	$\epsilon/2$	0	$3\epsilon/8$
$\gamma$	1	$1 - (\epsilon/2)$	$1 + (\epsilon/8)$	$1 - (\epsilon/4)$
$\gamma_{\parallel}$	$\epsilon/2$	$-\epsilon/2$	$\epsilon/2$	$-\epsilon/4$
$\gamma_{\perp}$	0	$-\epsilon/2$	0	$-3\epsilon/8$
$\beta$	$-2 + (\epsilon/2)$	$-2 - (\epsilon/2)$	$-2 + (\epsilon/4)$	$-2 - (\epsilon/2)$

A check on the theory will be provided from the evaluation of more properties.  $C_{\parallel}$  and  $C_{\perp}$  have been chosen for his pupose. Their evaluation goes in a similar way. Starting from their definitions, (2.4) and (2.5), we take

$$C_{\parallel} = \mu_0^N \left[ 1/N^{d_{\perp}/2} - u_a \Omega_{C_{\parallel}} - 2u_e \overline{\sigma}_{C_{\parallel}} + u_a^2 \underline{\omega}_{C_{\parallel}} + 4u_e^2 \left( \overline{\sigma\sigma}_{C_{\parallel}} + \overline{\delta}_{C_{\parallel}} + \Theta_{C_{\parallel}} \right) + 2u_a u_e \left( \underline{\omega\omega}_{C_{\parallel}} + \underline{\delta}_{C_{\parallel}} + \Theta_{C_{\parallel}} \right) \right] \quad (3.9a)$$

and

$$C_{\perp} = \mu_0^N \left[ 1/N^{d_{\parallel}/2} - u_a \Omega_{C_{\perp}} - 2u_e \overline{\sigma}_{C_{\perp}} + u_a^2 \underline{\omega}_{C_{\perp}} + 4u_e^2 \left( \overline{\sigma\sigma}_{C_{\perp}} + \overline{\delta}_{C_{\perp}} + \Theta_{C_{\perp}} \right) + 2u_a u_e \left( \underline{\omega\omega}_{C_{\perp}} + \underline{\delta}_{C_{\perp}} + \Theta_{C_{\perp}} \right) \right]. \quad (3.9b)$$

By means of the values of the diagrams of table 2 we take that

$$C_{\parallel} = \mu_0^N \exp(-2u_e N) (1/N) [1 + (\epsilon/2) \ln N - 2u_a \ln N + (\epsilon^2/8) \ln^2 N - (3/2)u_a \epsilon \ln^2 N + 3u_a^2 \ln^2 N + 2u_a u_e \ln^2 N] \quad (3.10a)$$

$$C_{\perp} = \mu_0^N \exp(-2u_e N) (1/N) [1 - u_a \ln N - (1/4)u_a \epsilon \ln^2 N + u_a^2 \ln^2 N + u_a u_e \ln^2 N]. \quad (3.10b)$$

The following interesting points come out of the analysis of (3.10). First, the exponentiation conditions for the two different properties  $C_{\parallel}$  and  $C_{\perp}$  give the same equation, (3.7b), yielding the same fixed points and providing in this way a positive check on the present theory. The meaning of the fixed points expressed by pairs of values ( $u_a^*$ ,  $u_e^*$ ) does not depend on the specific property. This helps in the determination of the structure and the critical exponents of the macroscopic properties to order  $\epsilon$  from first-order perturbation theory once the fixed points have been found. The exponents

for example of  $C_{\parallel}$  and  $C_{\perp}$  can be determined from the relations

$$C_{\parallel} \sim \mu_0^N \exp(-2u_e N) N^{\gamma_{\parallel}-1} = [\mu_0 \exp(-2u_e)]^N N^{(\varepsilon/2)-2u_a^*-1}, \quad \gamma_{\parallel} = (\varepsilon/2) - 2u_a^* \quad (3.11a)$$

$$C_{\perp} \sim \mu_0^N \exp(-2u_e N) N^{\gamma_{\perp}-1} = [\mu_0 \exp(-2u_e)]^N N^{-u_a^*-1}, \quad \gamma_{\perp} = -u_a^*, \quad (3.11b)$$

and are given in table 3.

#### 4. Conclusions

Variation of the parameters of the physical problem such as temperature, solvent, polymer or substrate makes  $u_a$  and  $u_e$  vary. In this way they can reach the neighbourhoods of the fixed points of table 3, where the corresponding macroscopic behaviour occurs. According to the classical description, the free energy of the system comes from the sum of the free energies of the two independent phenomena and this does not seem to be true for the present case. The existence of the new fixed point makes the behaviour of the system with two kinds of interactions different from the simple classical picture. The properties coming from the probability  $P\{\mathbf{R}_i\}$ , (2.1), which include to first order a  $u_a \ln N$  term but not a  $u_e \ln N$  term like  $C_{\parallel}$  and  $C_{\perp}$  have critical exponents which though independent of  $u_e^*$  do depend on the excluded volume interactions. Their dependence comes through the creation of the new fixed point  $(u_a^*, u_e^*) = (3\varepsilon/8, \varepsilon/16)$ , which alters the value  $u_a^*$  from that of the case of a chain without excluded volume interactions. The exponents for example of  $C_{\parallel}$  and  $C_{\perp}$  take the values  $(\gamma_{\parallel}, \gamma_{\perp}) = (\varepsilon/2, 0)$  for the ideal chain, the values  $(\gamma_{\parallel}, \gamma_{\perp}) = (-\varepsilon/2, -\varepsilon/2)$  for the desorbed chain without excluded volume interactions but the values  $(\gamma_{\parallel}, \gamma_{\perp}) = (-\varepsilon/4, -3\varepsilon/8)$  for a desorbed chain with excluded volume interactions. In the case of properties which have a first order  $u_e \ln N$  but not a  $u_a \ln N$  term like the moments of the end-to-end probability distribution, the critical exponents depend only on  $u_e^*$  which means that adsorption effects do not influence the exponents of such properties.

We are now going to compare where possible the results of the present work with those from other methods. The critical exponents of  $C \sim N^{\gamma-1}$  and  $U \sim N^{\beta}$ :  $\gamma = 1 - u_a^* + 2u_e^*$  and  $\beta = -2 + (\varepsilon/2) - 2u_a^* - 4u_e^*$  (see (3.8)) are functions of both the excluded volume and the adsorption interaction parameters. The case with  $u_e = 0$ ,  $u_a > 0$  corresponds to an exactly soluble problem. It is also described by means of the state with  $u_e^* = 0$  and  $u_a^* = \varepsilon/2$  of table 3. For an ideal chain ( $u_e = 0$ ) in a three-dimensional space, with a  $u_a \delta(z_i)$  interaction, the exact solution yields on the one hand that  $C \sim N^{-1/2}$  so that  $\gamma_3 = \frac{1}{2}$  and that  $U \sim N^{-(d/2)-1}$  so that  $\beta_3 = -\frac{5}{2}$ . On the other hand the values of the two exponents from table 3 are  $\gamma = 1 - (\varepsilon/2)$  so that for  $d = 3$  ( $\varepsilon = 1$ )  $\gamma_3 = \frac{1}{2}$  and  $\beta = -2 - (\varepsilon/2)$  so that  $\beta_3 = -\frac{5}{2}$ . The two results coincide showing that, as far as the states with  $u_e = 0$  are concerned, the  $\varepsilon$ -expansion predicts correctly the values of the critical exponents even for  $\varepsilon = 1$ . The states with  $u_a = 0$  refer to the excluded volume problem of a polymer chain and they have been studied and compared with the results from other methods previously (Kosmas 1981a). Of interest, for example, is that the exponent  $\beta$  agrees with what simple scaling predicts. The simple relation between the number  $U$  of the walks returning to the origin and the radius  $\langle R^2 \rangle$  of the chain  $U \sim \langle R^2 \rangle^{-d/2}$  (de Gennes 1979), permits the writing of the exponent  $\beta$  in terms of the exponent  $\nu = (\frac{1}{2}) + (\varepsilon/16)$  of the radius as  $\beta = -d\nu$ . This relation can easily be checked from table 3 to be true for the states with  $u_a = 0$ . For the states where both the interaction parameters are significant this simple scaling picture cannot be of much help. The results regarding these states can be compared with the results from

theories which study the effect of the adsorption parameter on the behaviour of non-ideal adsorbed chains. Previous methods studying a chain attached to an impenetrable surface find that the change of  $u_a$  from negative to positive values changes the state of the chain from an adsorbed two-dimensional chain to a desorbed three-dimensional chain (Whittington 1975). The critical exponent  $\gamma$  in the absence of adsorption effects ( $u_a = 0$ ) decreases going from the two-dimensional chain with  $\gamma_2|_{u_a=0} = 1 + (\frac{1}{4})$  to a three-dimensional chain with  $\gamma_3|_{u_a=0} = 1 + (\frac{1}{8}) < \gamma_2|_{u_a=0}$ . Similar conclusions can be derived from the full dependence  $\gamma = 1 + 2u_e^* - u_a^*$  of the present work regarding a penetrable surface. We see that on increasing  $u_a^*$ ,  $\gamma$  goes from large to small values like going from two-dimensional to three-dimensional behaviour. Similar conclusions can be derived from the study of the exponent  $\beta = -(d/2) - 4u_e^* - 2u_a^*$ , which again decreases both on increasing  $u_a^*$  as well as on increasing the dimensionality of the system; for  $u_a^* = 0$ , it takes the value  $b_2|_{u_a=0} = -\frac{6}{4}$  for the two-dimensional chain and the value  $b_3|_{u_a=0} = -\frac{7}{4}$  for the three-dimensional chain. Of much interest also is the comparison of the present results with the results from the Monte Carlo analysis of Eisenriegler *et al.* The value of the exponent  $\gamma$  from Monte Carlo calculations is found to be equal to  $\gamma = 1.44 > 1$  for  $u_a = 0$  and  $\gamma = 0.69 < 1$  for  $u_a > 0$ . These values compare well with the values taken from  $\gamma = 1 + 2u_e^* - u_a^*$ , being  $\gamma = 1 + (\frac{1}{8}) > 1$  for  $u_a^* = 0$  and  $u_e^* = \epsilon/16$  (non-interacting expanded chain); and  $\gamma = 1 - (\frac{1}{4}) < 1$  for  $u_a^* = 3\epsilon/8$  and  $u_e^* = \epsilon/16$  (desorbed expanded chain).

**Appendix**

We will demonstrate the evaluation of diagrams by describing the evaluation of the following new diagrams:  $\mathcal{Q}_{C_1}$ ,  $\mathcal{T}_{C_2}$ ,  $\mathcal{TT}_{C_3}$  and  $\mathcal{W}_{C_4}$ . First-order diagrams are evaluated up to  $\epsilon^1$  and second-order diagrams up to  $\epsilon^0$ . The summations in these evaluations are approximated with integrations, so we take from table 1 in the limit of large  $N$  that

$$\begin{aligned} \mathcal{Q}_{C_1} &= \int_1^{N-1} di \, 1/[i(N-i)]^{(2-\epsilon)/2} = \int_1^{N-1} di \{ [1/i(N-i)] [1 + (\epsilon/2) \ln[i(N-i)]] \} \\ &= (2/N) [\ln N + (\frac{3}{4})\epsilon \ln^2 N], \end{aligned} \tag{A1}$$

a result quoted in table 2.

$$\begin{aligned} \mathcal{T}_{C_2} &= \int_1^{N-1} di \int_{i+1}^N dj \, 1/(j-i)^{(4-\epsilon)/2} (N-j+i) \\ &= \int_1^{N-1} dl \int_1^{N-l} di \{ [1/l^2(N-l)] [1 + (\epsilon/2) \ln l] \} \\ &= \int_1^{N-1} dl (1/l^2) [1 + (\epsilon/2) \ln l] = (1/N) [N + O(N, \ln N)] \end{aligned} \tag{A2}$$

$$\begin{aligned} \mathcal{TT}_{C_3} &= \int_1^{N-3} di \int_{i+1}^{N-2} dj \int_{j+1}^{N-1} dk \int_{k+1}^N dl \, 1/(j-i)^2 (l-k)^2 (N-l+k-j+i) \\ &= \int_1^N dl_1 \int_1^{N-l_1} dl_2 (N-l_1-l_2) / 2l_1^2 l_2^2 \\ &= \frac{1}{2} \int_1^N dl_1 [ (N/l_1^2) - (2/l_1) ] = \frac{1}{2} (N - 2 \ln N) \end{aligned} \tag{A3}$$

$$\begin{aligned}
 \Omega_{C_2} &= \int_1^{N-1} di \int_{i+1}^N dj \int_1^i dk \frac{1}{(j-i)^2 k(N-j+i)} = \int_1^{N-1} dl \int_1^{N-l} di \ln i/l^2(N-l) \\
 &= \int_1^{N-1} dl \ln(N-l)/l^2 = \ln N.
 \end{aligned}
 \tag{A4}$$

The rest diagrams can be evaluated similarly and their values can be found in table 2.

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