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On the critical exponents of a non-ideal polymer chain interacting with an interface: from a penetrable to an impenetrable surface

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Abstract. The critical exponents of a non-ideal polymer chain attached by one of its ends to an impenetrable interacting surface are found to first order in the small parameter $\varepsilon = 4 - d$ where d is the dimensionality of the space. A comparison of the behaviour of a chain interacting with an impenetrable and a penetrable surface is given.

1. Introduction

In the Gaussian model (Yamakawa 1971) the probability $P_0(\mathbf{R}_i, \mathbf{R}_j; i, j)$ of the i th and j th units of an ideal polymer chain being found at the position vectors \mathbf{R}_i and \mathbf{R}_j is given by

$$P_0(\mathbf{R}_i, \mathbf{R}_j; i, j) = [d/2\pi l^2(j-i)]^{d/2} \exp[-d(\mathbf{R}_i - \mathbf{R}_j)^2/2(j-i)l^2] \quad j > i \quad (1.1)$$

where d is the dimensionality of the space and l is the length of the unit of the chain. The study of polymers at interfaces requires us to generalise (1.1) so that both the dimensionality of the surface and the dimensionality of its orthogonal complement be explicitly considered. Previously we have provided this generalisation (Kosmas 1985) for a penetrable surface as

$$P_0(\mathbf{R}_i, \mathbf{R}_j; i, j) = (d/2\pi l^2)^{d_{\parallel}/2} \exp[-d(\mathbf{R}_{\parallel,i} - \mathbf{R}_{\parallel,j})^2/2(j-i)l^2] \\ \times (d/2\pi l^2)^{d_{\perp}/2} \exp[-d(\mathbf{R}_{\perp,i} - \mathbf{R}_{\perp,j})^2/2(j-i)l^2] \quad (1.2)$$

where d_{\parallel} is the surface dimensionality and d_{\perp} is that of its orthogonal complement, $d = d_{\parallel} + d_{\perp}$, and \mathbf{R}_{\parallel} and \mathbf{R}_{\perp} are the component vectors of \mathbf{R} parallel and perpendicular to the surface. For a non-ideal chain, the excluded volume interactions between any pair (i, j) of units have to be included and they can be represented in a perturbation theory scheme by the d -dimensional delta function pseudopotential $u_e \delta^d(\mathbf{R}_i - \mathbf{R}_j)$ (Yamakawa 1971). In the d -dimensional space the presence of the surface of dimensionality $d_{\parallel} < d$ interacting with the polymeric units give rise to another potential of the form $u_a \delta^{d_{\perp}}(\mathbf{R}_{\perp,i})$ where the $\delta^{d_{\perp}}$ function obtains non-zero values only when the units are close to the surface. The interaction parameters u_e and u_a are proportional to the binary cluster integrals for the mean potentials between two units and a unit and the surface respectively and they are temperature dependent.

For the case of the penetrable surface (Hammersley *et al* 1982, Ishinabe 1984), we have shown that the study of the chain with both kinds of interactions corresponds to

a problem where both d and d_{\perp} have critical values (Kosmas 1985). Two combinations of the interaction parameters and the molecular weight govern the behaviour of the chain. One is $u_e N^{(4-d)/2}$ for the excluded volume interactions (Kosmas 1981a) and the other is $u_a N^{(2-d_{\perp})/2}$ for the interactions with the surface (Kosmas 1981b). From the first combination it is seen that for the dimensionality d , 4 is a critical value above which, in the limit $N \rightarrow \infty$, $u_e N^{(4-d)/2}$ and therefore excluded volume effects are negligible. From the second combination the critical value for d_{\perp} comes out to be 2. For $d_{\perp} > 2$, $u_a N^{(2-d_{\perp})/2}$ and the interactions between the surface and the polymer are negligible. The probability distribution $P\{\mathbf{R}_i\}$ for the N positions \mathbf{R}_i ($i = 1, 2, \dots, N$) of the polymeric units which incorporates both critical dimensionalities is

$$P\{\mathbf{R}_i\} = P_0\{\mathbf{R}_i\} \exp\left(-u_a \sum_{i=1}^N \delta^{2-\varepsilon}(\mathbf{r}_i) - u_e \sum_{i=1}^N \sum_{j=1}^N \delta^{4-\varepsilon}(\mathbf{R}_i - \mathbf{R}_j)\right). \quad (1.3)$$

For $\varepsilon < 0$ both interactions yield negligible contributions, while in the limit $\varepsilon \rightarrow 1$ the three-dimensional chain interacting with the (x, y) plane is recovered. The solution of the problem to several orders in ε describes the chain properly at fictitious dimensionalities and helps in understanding the characteristics of the solution of the problem at the real dimensionalities $d = 3, 2$ or 1 (Kosmas 1982). The detection of new macroscopic states of the chain is possible, for example, in this way. These states are characterised by specific values (u_a^*, u_e^*) of the interaction parameters which can be determined from second-order perturbation theory (Kosmas 1985). The critical exponents of the macroscopic properties at the various states of the chain depend on u_a^* and u_e^* , and once u_a^* and u_e^* have been found, the exponents can be determined to first order in ε from first-order calculations. For the case of a chain fixed with one of its ends at a penetrable surface, the states and the corresponding values of (u_a^*, u_e^*) have been previously found and are quoted in table 1. In the table we also quote the values of the exponents of the following properties: the total number of configurations

$$C \sim N^{\gamma-1} \quad \gamma = 1 - u_a^* + 2u_e^* \quad (1.4a)$$

Table 1. The various states and the corresponding values of the interaction parameters and the critical exponents for the two cases of a chain interacting with a penetrable and an impenetrable surface.

	Interaction	Ideal	Desorption	Excluded volume	Desorption plus excluded volume
Penetrable surface	u_e^*	0	0	$\varepsilon/16$	$\varepsilon/16$
	u_a^*	0	$\varepsilon/2$	0	$3\varepsilon/8$
	γ	1	$1 - (\varepsilon/2)$	$1 + (\varepsilon/8)$	$1 - (\varepsilon/4)$
	β	$-2 + (\varepsilon/2)$	$-2 - (\varepsilon/2)$	$-2 + (\varepsilon/4)$	$-2 - (\varepsilon/2)$
	γ_{\parallel}	$\varepsilon/2$	$-\varepsilon/2$	$\varepsilon/2$	$-\varepsilon/4$
Impenetrable surface	γ_{\perp}	0	$-\varepsilon/2$	0	$-3\varepsilon/8$
	γ_{\parallel}	1	$1 - (\varepsilon/2)$	$1 + (3\varepsilon/16)$	$1 - (3\varepsilon/16)$
	β	$-2 + (\varepsilon/2)$	$-2 - (\varepsilon/2)$	$-2 + (\varepsilon/4)$	$-2 - (\varepsilon/2)$
	γ_{\parallel}	$\varepsilon/2$	$-\varepsilon/2$	$5\varepsilon/8$	$-\varepsilon/8$
	γ_{\perp}	0	$-\varepsilon/2$	$\varepsilon/16$	$-5\varepsilon/16$

the number of configurations of rings

$$U \sim N^\beta \quad \beta = -2 + (\varepsilon/2) - 2u_a^* - 4u_e^* \quad (1.4b)$$

the number of loops with both ends of the chain on the surface

$$C_{\parallel} \sim N^{\gamma_{\parallel}-1} \quad \gamma_{\parallel} = (\varepsilon/2) - 2u_a^* \quad (1.4c)$$

and the number of configurations with their second ends on the axis perpendicular to the surface

$$C_{\perp} \sim N^{\gamma_{\perp}-1} \quad \gamma_{\perp} = -u_a^*. \quad (1.4d)$$

2. Calculations of the critical exponents for a confined chain

In this work we generalise our previous treatment of the penetrable surface to an impenetrable surface. This is a non-trivial generalisation since the intuitive notion of the impenetrable surface can only be represented by a hyperplane of dimensionality $d - 1$ which divides the d -dimensional space into disjoint regions. We construct a model which incorporates both the impenetrable hyperplane and the interacting surface.

The probability distribution P_0 , equation (1.1), for a free chain is a product of d one-dimensional probabilities along the d perpendicular directions, so that each one of them can be separated as

$$P_0(\mathbf{R}_i, \mathbf{R}_j; i, j) = [d/2\pi l^2(j-i)]^{(d-1)/2} \exp[-d(\mathbf{R}'_i - \mathbf{R}'_j)^2/2(j-i)l^2] \\ \times [d/2\pi l^2(j-i)]^{1/2} \exp[-d(Z_i - Z_j)^2/2(j-i)l^2]. \quad (2.1)$$

Z_i are the components of the position vectors \mathbf{R}_i along the specific Z axis while \mathbf{R}'_i represent the rest components of \mathbf{R}_i . In the d -dimensional space the equation $Z = 0$ represents the $(d - 1)$ -dimensional hyperplane which separates the d -dimensional space into two halves, one with $Z \geq 0$ and the other with $Z < 0$. For a confined chain belonging to the half-space $Z \geq 0$ and for the absorption boundary conditions according to which the derivative of the probability with respect to Z vanishes on the plane $Z = 0$ (Chandrasekhar 1943, Simha *et al.* 1953, Kosmas 1981b), an image term has to be added so that the corresponding probability becomes

$$P_{co}(\mathbf{R}_i, \mathbf{R}_j; i, j) = [d/2\pi l^2(j-i)]^{(d-1)/2} \exp[-d(\mathbf{R}'_i - \mathbf{R}'_j)^2/2(j-i)l^2] \\ \times [d/2\pi l^2(j-i)]^{1/2} \{ \exp[-d(Z_i - Z_j)^2/2(j-i)l^2] \\ + \exp[-d(Z_i + Z_j)^2/2(j-i)l^2] \}. \quad (2.2)$$

This probability distribution can describe properly the fact that all polymeric units lie in the positive $Z \geq 0$ half-space, and in order to study a chain in the presence of an impenetrable surface the probability P_{co} , equation (2.2), of the confined chain, instead of the probability P_0 , equation (1.1), of the free chain has to be employed. For $d \geq 3$, the interacting surface is a subset of the impenetrable hyperplane, $d_{\parallel} \leq d - 1$, but in the limit of $d \rightarrow 3$ ($\varepsilon \rightarrow 1$) the impenetrable hyperplane of dimensionality $d - 1 \rightarrow 2$ and the interacting surface of $d_{\parallel} = 2$ coincide and both go to the (x, y) plane. The real three-dimensional space with a confined chain interacting with the (x, y) plane is recovered in this way. The present model differs from that of Bray and Moore on semi-infinite systems where the one-dimensional Z potential is used to describe the

interactions with the surface. Though both models can describe properly three-dimensional systems of interest the model of Bray and Moore does not incorporate the adsorption critical dimensionality $d_c = 2$. Of course the same results have to come out from the two models for the case $u_a = 0$ (special transition of Bray and Moore), where a confined non-ideal chain without interactions with the impenetrable surface is described.

Second-order calculations for the case of impenetrable surface show that the presence of the surface does not change the universal character of the fixed points. The values u_a^* and u_e^* (table 1) are the same for the two cases of the penetrable and the impenetrable surfaces. This permits the determination of the critical exponents of the macroscopic properties of the confined chain to first order in ϵ from first-order calculations. The following diagrammatic expressions are taken for the properties under study:

$$C = \mu_0^N (1 - u_a \text{---} \bigcirc_c - 2u_e \text{---} \bigcirc_c) \tag{2.3a}$$

$$U = \mu_0^N ((2/N^{d/2}) - u_a \text{---} \bigcirc_v - 2u_e \text{---} \bigcirc_v) \tag{2.3b}$$

$$C_{\parallel} = \mu_0^N ((2/N^{d_{\parallel}/2}) - u_a \text{---} \bigcirc_{c_{\parallel}} - 2u_e \text{---} \bigcirc_{c_{\parallel}}) \tag{2.3c}$$

$$C_{\perp} = \mu_0^N ((1/N^{d_{\perp}/2}) - u_a \text{---} \bigcirc_{c_{\perp}} - 2u_e \text{---} \bigcirc_{c_{\perp}}). \tag{2.3d}$$

The diagrams in equations (2.3) represent configurations of the chain with a knot coming from the action of the delta functions. The u_a diagrams have a knot between the polymer and the surface while the u_e diagrams have a knot between two polymeric units. The subscripts on the diagrams denote the corresponding properties. The forms and the finite values of the diagrams are written in table 2. An extra factor of 2 produced for each u_a term in all orders comes from the different normalisation factors for the confined and the unconfined chains. It is irrelevant for the determination of the values u_a^* and u_e^* and the critical exponents, so it can be absorbed with the rest ($d/2\pi l^2$) constants in u . Using the values of the diagrams in equations (2.3) we take

$$C \sim [1 + (-u_a + 3u_e) \ln N] = N^{\gamma_1 - 1} \quad \gamma_1 = 1 - u_a^* + 3u_e^* \tag{2.4a}$$

Table 2. Forms and values for the first-order diagrams for $d = 4$ and $d_{\perp} = 2$.

$\bigcirc_c = 2 \int_0^N di(1/i) = 2 \ln N$	$\bigcirc_v = (2^2/N) \int_0^N di 1/[i(N-i)] = (8/N^2) \ln N$
$\bigcirc_{c_{\parallel}} = 2^2 \int_0^N di 1/[i(N-i)] = (8/N) \ln N$	$\bigcirc_{c_{\perp}} = (2/N) \int_0^N di(1/i) = (2/N) \ln N$
$\bigcirc_c = \int_0^N dl \int_0^{N-l} di [l^{-2} + l^{-3/2}(1+4i)^{-1/2}] = -\frac{3}{2} \ln N$	
$\bigcirc_v = 2 \int_0^N dl \int_0^{N-l} di [l^{-2}(N-l)^{-2} + [-4i^2 + 4(N-l)i + l(N-l)]^{-1/2} l^{-3/2}(N-l)^{-3/2}]$ $= (4/N^2) \ln N$	
$\bigcirc_{c_{\parallel}} = 2 \int_0^N dl \int_0^{N-l} di [l^{-2}(N-l)^{-1} + [-4i^2 + 4(N-l)i + l(N-l)]^{-1/2} l^{-3/2}(N-l)^{-1/2}]$ $= -(2/N) \ln N$	
$\bigcirc_{c_{\perp}} = \int_0^N dl \int_0^{N-l} di [l^{-2}(N-l)^{-1} + (l+4i)^{-1/2} l^{-3/2}(N-l)^{-1}] = -(1/2N) \ln N$	

$$U \sim 2[(1/N^{(4-\epsilon)/2}) + (-2u_a - 4u_e) \ln N/N^2] = 2N^\beta \quad \beta = -2 + (\epsilon/2) - 2u_a^* - 4u_e^* \tag{2.4b}$$

$$C_{\parallel} \sim 2[(1/N^{(2-\epsilon)/2}) + (-2u_a + 2u_e) \ln N/N] = 2N^{\gamma_{\parallel}-1} \quad \gamma_{\parallel} = (\epsilon/2) - 2u_a^* + 2u_e^* \tag{2.4c}$$

$$C_{\perp} \sim [(1/N) + (-u_a + u_e) \ln N/N] = N^{\gamma_{\perp}-1} \quad \gamma_{\perp} = -u_a^* + u_e^* \tag{2.4d}$$

thus obtaining the values of the corresponding exponents which we quote in table 1 for the various states of the confined chain.

3. Conclusions

The present results, though first order in the small parameter ϵ , can reproduce the general characteristics of the behaviour of the chain also taken from other methods. It was found that on increasing the attraction between the chain and the interface a transition takes place from a three-dimensional behaviour where the chain mainly belongs to the solution to a two-dimensional behaviour where the chain is adsorbed on the interface (Lax 1974, Mark and Windwer 1974, Whittington 1975). The results of the present work lead to similar conclusions. The values of the critical exponents for the states with $u_a = 0$, where there are no interactions between the impenetrable surface and chain, decrease on increasing the dimensionality of the system (decreasing ϵ). This means that the two-dimensional behaviour is characterised by larger values of exponents than the three-dimensional one. The same trend comes from the dependence on the interaction parameter u_a which expresses the interactions between the polymer and the surface. Larger values of u_a mean greater repulsion between the monomers and the interface. The exponents become smaller as u_a^* increases which again means that on increasing the repulsions between the surface and the monomers a change from a two-dimensional-like behaviour with larger exponents to a three-dimensional one with smaller exponents takes place.

Higher-order calculations in the small parameter ϵ would yield better estimates for the critical exponents at the dimensionality $d = 3$ where ϵ is extrapolated to the value 1. Though the exponents taken from the present first-order calculations can be paralleled with the values taken from other methods, these exponents characterise the various states of the chain and they do not depend explicitly on the temperature T or the nature of the solvent, the polymer and the substrate. This permits a comparison with the results from other techniques even if they refer to extreme temperature values like $T = \infty$ (Eisenriegler *et al* 1982). The value, for example, of the exponent γ_{\perp} for the three-dimensional problem ($\epsilon = 1$) at the expanded-desorbed state is estimated from relation (2.4a) to be $\gamma_{\perp} = 0.81$ and it is in accord with the values of γ_{\perp} found to be in the range 0.68-0.71 (Lax 1974, Barber *et al* 1978, Eisenriegler *et al* 1982). Similarly from relation (2.4c) γ_{\parallel} is found to take the negative value $\gamma_{\parallel} = -0.125$ and compares with the value of γ_{\parallel} in the range from -0.56 to -0.39 found before.

The presence of the impenetrable plane, even for the case of $u_a = 0$ (no interactions with the surface), changes the exponent γ of the case of a penetrable surface to the exponent γ_{\perp} . The latter is taken from (2.4a) to be $\gamma_{\perp} = 1 + 3u_e^*$ ($u_a = 0$) and it agrees with the value found by Bray and Moore by means of the n -vector model ($n \rightarrow 0$) and by Freed by means of direct renormalisation group theory. Other symbols used before for the special case $u_a = 0$ are γ_{\perp}^{sp} and γ_{\parallel}^{sp} (Bray and Moore 1977) and $\gamma_{s\beta}^{\perp}$ and $\gamma_{s\beta}^{\parallel}$ (Eisenriegler *et al* 1982). The comparison of the two values $\gamma_{\perp} = 1 + 3u_e^*$ and $\gamma = 1 + 2u_e^*$

is of some interest because it expresses the influence of impermeability. We see that $\gamma_1 > \gamma$ and this agrees with the inequality taken from the generally accepted values $\gamma_1 = 1.44 > \gamma = 1.17$ (Eisenriegler *et al* 1982, Domb 1969). In the present model the two values $\gamma_1 = 1 + 3u_e^*$ and $\gamma = 1 + 2u_e^*$ correspond to the region of the adsorption-desorption phase change where u_a becomes negligible. This change has been reported to occur at different temperatures for the cases of impenetrable and penetrable surfaces (Hammersley *et al* 1982).

The comparison of the values of γ_1 for the various states is also in accord with the results of Eisenriegler *et al* who find that $\gamma_1 = 1.44 > 1$ for $u_a = 0$ and $\gamma_1 = 0.69 < 1$ for $u_a > 0$. These values compare well with the values taken from $\gamma_1 = 1 + 3u_e^* - u_a^*$, being $\gamma_1 = 1 + \frac{3}{16} > 1$ for $u_a^* = 0$ and $u_e^* = \varepsilon/16$ (non-interacting expanded chain) and $\gamma_1 = 1 - \frac{3}{16} < 1$ for $u_a^* = 3\varepsilon/8$ and $u_e^* = \varepsilon/16$ (desorbed expanded chain).

The knowledge of the behaviour of a single chain is the initial step towards studying more complicated problems related to polymers at interfaces, like adsorption isotherms or the stability of colloids (Theodoor and Overbeek 1982). The dependence given in the above analysis on both solvent quality (u_e) and the intensity of surface interactions (u_a) as well as the comparison between penetrable and impenetrable surfaces provide the bases for a detailed analysis and a better understanding of the role of the solvent and the substrate in such phenomena.

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