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1988 J. Phys. A: Math. Gen. 21 L155

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LETTER TO THE EDITOR

Polymer chains with multiple interactions

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Received 21 October 1987

**Abstract.** The behaviour of a chain in a  $d$ -dimensional space interacting with a generalised surface (a plane, a rod or a point) of dimensionality  $d_{\parallel}$  (2, 1 or 0) is described. Fixed points of the system are calculated to first order in  $\varepsilon = (4-d)/2$  and  $\varepsilon_{\perp} = 2-d+d_{\parallel}$  using a multiple  $\varepsilon$  expansion procedure, and the relevance of the surface and the excluded volume interactions is discussed.

There are many interesting problems in polymer science where more than one interaction potential is present. Examples include the adsorption of non-ideal chains where excluded-volume interactions and interactions with a surface are present (Reeve and Guttmann 1980, 1981, Kosmas 1981, 1985, 1986, Diehl and Dietrich 1981a, b, 1983, Freed 1983, 1987, Eisenriegler 1985, Nemirovsky and Freed 1985a, b, 1986, Douglas *et al* 1986a, b, 1987, Nemirovsky *et al* 1986) or block copolymers where different interactions between the various blocks exist (Joanny *et al* 1984, Kosmas 1984, Douglas and Freed 1987, Sdranis and Kosmas 1987). There are also the important instances of binary and ternary interactions (Yamakawa 1966, Stephen and McCauley 1973, Stephen 1975, Bruns 1980, 1984, Duplantier 1982, 1987, Kholodenko and Freed 1984, Cherayil *et al* 1985) and the combination of hydrodynamic and excluded-volume interactions (Jasnow and Moore 1977, Al-Noaimi *et al* 1978, Shiwa and Kawasaki 1982, Oono and Kohmoto 1983, Allesandrini and Pesci 1984, Wang *et al* 1986). We can also take various permutations of these interactions to obtain a rather large class of multiple interaction problems. In this letter some thoughts on the specific example of adsorption of a non-ideal chain on a generalised (variable-dimension) surface (Kosmas 1981, 1985, 1986, Douglas *et al* 1986b, 1987) are presented as a representative example of a chain under the influence of more than one potential. This choice is also representative of the general case where the multiple interactions do not necessarily have the same critical dimension.

For the case of a chain with excluded volume, interacting with a generalised surface (a surface, a rod or a point) of dimensionality  $d_{\parallel}$ , the following probability distribution is suitable (Kosmas 1981, 1985, 1986, Douglas *et al* 1986a, b, 1987)

$$P(R(\tau)) = P_0(R(\tau)) \exp(-H_{\text{int}}/k_B T) \quad (1a)$$

with an interaction Hamiltonian

$$H_{\text{int}}/k_B T = u_s \int_0^N d\tau \delta^{d_{\perp}}(R(\tau)) + (u_2/2) \int_0^N \int_0^N d\tau d\tau' \delta^d(R(\tau) - R(\tau')) \quad (1b)$$

where  $P_0(R(\tau))$  is the probability distribution of the ideal chain,  $u_2$  is the excluded-volume parameter (defined to be double that used previously by Kosmas) and  $u_s$  is the interaction parameter between the  $N$  polymeric units and the surface.  $d_\perp = d - d_\parallel$  is the dimensionality of the space orthogonal to the surface of dimension  $d_\parallel$  such that the dimensionality of the space  $d$  equals  $d_\perp + d_\parallel$ . As has been discussed before (Kosmas 1981, 1985, 1986, Douglas *et al* 1986b, 1987), the critical values of  $d$  and  $d_\perp$  for the excluded-volume and surface-interaction theories are 4 and 2, respectively.

Two different  $\varepsilon$  parameters can be defined as  $\varepsilon = 4 - d$  and  $\varepsilon_\perp = 2 - d_\perp = 2 + d_\parallel - d$  expressing the deviation from the critical values of  $d$  and  $d_\perp$ . For  $\varepsilon = 1, 2$  or 3 we are at the three-dimensional, the two-dimensional (surface) and the one-dimensional (line) spaces, respectively, while for  $d_\parallel = 2, 1$  or 0 we have an interacting surface, an interacting rod or an interacting point, respectively. Here a multiple- $\varepsilon$  procedure is introduced involving an expansion in *both*  $\varepsilon$  and  $\varepsilon_\perp$  which recovers the theory with each  $\varepsilon$  alone and for the special case  $\varepsilon = \varepsilon_\perp (d_\parallel = 2)$  by construction.

The methods of Kosmas (Kosmas 1981, 1985, 1986, Freed 1987) based on exponentiation conditions and Freed and co-workers (Douglas *et al* 1986b, 1987, Freed 1987) using a direct renormalisation approach, when applied to the system of a non-ideal chain interacting with a surface ( $\varepsilon = \varepsilon_\perp = 1$ ) give the same equations (to be shown elsewhere) for the determination of the fixed points when there is only one  $\varepsilon$  ( $d_\parallel = 2$ ). Formally, the two methods can be extended to problems with more than one  $\varepsilon$  in leading order in perturbation theory. The equations determining the fixed points and the critical exponents, including both  $\varepsilon$  and  $\varepsilon_\perp$  parameters, are

$$8(u_2^*)^2 - u_2^* \varepsilon = 0 \quad (2a)$$

$$2u_s^* u_2^* + 2(u_s^*)^2 - u_s^* \varepsilon_\perp = 0 \quad (2b)$$

and determine the following fixed points of the system up to first order in  $\varepsilon$  and  $\varepsilon_\perp$ :

$$u_2^* = \varepsilon/8 \quad u_s^* = 0 \quad \text{expanded chain, no surface interactions}$$

$$u_2^* = 0 \quad u_s^* = \varepsilon_\perp/2 \quad \text{ideal, desorbed chain}$$

and the fixed point with both interactions non-zero:

$$u_2^* = \varepsilon/8 \quad u_s^* = (\varepsilon_\perp/2) - (\varepsilon/8) \quad \text{expanded, desorbed chain.}$$

No proof is given here that such a scheme holds in higher order and the authors recognise that until such a scheme is given the method must be considered tentative. We now explore the implications and consistency of the scheme at leading order.

When the two potentials act independently it is known that the values of the crossover exponents  $\phi_s^0 = (2 - d_\perp)/2$  for the surface interactions in the absence of excluded-volume interactions, and  $\phi_2 = (4 - d)/2$  for the binary excluded-volume interactions, must be positive for the interactions to be relevant. This can be seen from the known behaviour of the two independent cases. For example, the partition function at the critical dimension  $d_\perp = 2$  of a surface interacting chain without excluded-volume interactions ( $u_2 = 0$ ) is given by (Kosmas 1981)

$$C_s = C_0(1 - u_{s,0} \ln N + u_{s,0}^2 \ln N^2 - \dots) = C_0(1 + u_{s,0} \ln N)^{-1} = C_0(1 + \phi_s^0 \ln N)^{-1} \\ \Rightarrow \phi_s^0 = u_{s,0}^* = \varepsilon_\perp/2 = (2 - d_\perp)/2 \quad \text{surface interactions} \quad (3a)$$

where  $C_0$  is the Gaussian chain contribution in the limit of vanishing surface interaction. The partition function for the chains with only excluded volume at the critical dimension

$d = 4$  is similarly given by

$$\begin{aligned} C_2 &= C_0(1 + u_2 \ln N - \frac{3}{2}u_2^2 \ln N^2 + \dots) = C_0[1 + 4u_2 \ln N]^{1/4} \\ &= C_0[1 + \phi_2 \ln N]^{1/4} \end{aligned} \quad (3b)$$

where for variable dimension  $\phi_2$  is given by (Stephen 1975, Kosmas 1982, Douglas and Freed 1983, Duplantier 1986):

$$\phi_2 = 4u_2^* = \varepsilon/2 = (4-d)/2 \quad \text{excluded volume interactions.} \quad (3c)$$

For  $\phi_s^0, \phi_2 > 0$ ,  $\ln N^{\phi_s^0} \sim N^{\phi_s^0}$  and  $\ln N^{\phi_2} \sim N^{\phi_2}$  are dominant over the unity of the ideal problem and the corresponding interactions are relevant while for  $\phi_s^0, \phi_2 < 0$ ,  $N^{\phi_s^0}, N^{\phi_2}$  are negligible compared to unity and the interactions are irrelevant.

For example, for an ideal chain ( $u_2 = 0$ ) in a three-dimensional space, interacting with a point, where  $d = 3$  and  $d_{\parallel} = 0$  we have  $\varepsilon_{\perp} = 2 - d_{\perp} = -1$ . The adsorption crossover exponent  $\phi_s^0$  of (3a) then becomes negative,  $\phi_s^0 = u_{s,0}^* = \varepsilon_{\perp}/2 = -\frac{1}{2} < 0$ , and the interactions with the point are irrelevant and can be neglected in the long-chain limit. For the case of a rod interacting with a Gaussian chain  $u_2 = 0$  and  $\varepsilon_{\perp} = 0$  so that  $\phi_s^0 = 0$ . In this case we have marginality and the various properties involve log corrections (Kosmas 1981, 1985, 1986, Douglas *et al* 1986b, 1987) and can be summed up.

The presence of the excluded-volume interactions modify  $\phi_s^0$  of (3a) to  $\phi_s$  according to the new value of  $u_s^*$ . For the case of  $d_{\parallel} = 2$ , for example,  $\varepsilon_{\perp} = \varepsilon = 4 - d$  and a modified value of  $\phi_s = u_s^* = 3\varepsilon/8$  from the third fixed point of (2a) and (2b) is taken in agreement with the exact  $\varepsilon$ -expansion results of Douglas *et al* (1986b, 1987). Of interest is the study of the non-trivial fixed point  $u_s^* = (\varepsilon_{\perp}/2) - (\varepsilon/8) + O(\varepsilon_{\perp}\varepsilon, \varepsilon^2)$  taken when both interactions are turned on. For a three-dimensional chain,  $\varepsilon = 4 - d = 1$  so that  $u_s^*$  becomes  $-\frac{5}{8}$  for the case of an interacting point ( $d_{\parallel} = 0$ ),  $-\frac{1}{8}$  for the interacting rod ( $d_{\parallel} = 1$ ) and  $\frac{3}{8}$  for the interacting plane ( $d_{\parallel} = 2$ ). What we see is that there is a lowering of the values of  $u_s^*$  of an expanded chain from those of the ideal chain being  $-\frac{1}{2}$  for the point, 0 for the rod and  $\frac{1}{2}$  for the plane, which reflects the chain swelling and the reduced probability of surface contacts.

Similar phenomena are expected to occur when applying the method to polymers with excluded volume of both ternary and binary types (Yamakawa 1966, Stephen and McCauley 1973, Stephen 1975, Lawrie 1979, 1984, Duplantier 1982, 1987, Bruns 1980, 1984, Kholodenko and Freed 1984, Cherayil *et al* 1985). Again two different critical values of the dimensionality exist for the two kinds of interactions, 4 for the binary and 3 for the ternary interactions, and again as the chain swells the three-body interactions should become irrelevant. We hope to apply the method to this important problem once the method has been further studied using the relatively simple example of surface-interacting polymers with excluded volume.

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