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LETTER TO THE EDITOR

## Adsorption of branched polymers at surfaces: scaling and Monte Carlo analysis

P M Lam<sup>†‡</sup> and K Binder<sup>§</sup>

<sup>†</sup> Institut für Theoretische Physik, Universität zu Köln, 5000 Köln 41, Federal Republic of Germany

<sup>§</sup> Institut für Physik, Johannes Gutenberg Universität Mainz, 6500 Mainz 1, Federal Republic of Germany

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**Abstract.** Using Monte Carlo methods we calculate the specific heat of branched polymers near a hard wall in the presence of a short-range attractive force between monomers and the wall. The specific heat exhibits a peak at a temperature  $T_m(N)$  depending on the size of the polymer  $N$ . Both  $T_m(N)$  and the height of the peak increase monotonically with  $N$ . The result agrees very well with a scaling function for the specific heat derived from a scaling analysis in analogy with linear polymers. In addition, the scaling analysis yields the adsorption temperature  $T_a \approx 0.583$  and the crossover exponent  $\phi \approx 0.714$ .

The statistical mechanics of surface critical phenomena has been of interest for a long time. (For a detailed review see [1, 2].) In particular, the problem of adsorption of linear polymers at a wall had been analysed by Eisenriegler *et al* [3] using scaling arguments and Monte Carlo simulations. There, new critical exponents  $\gamma_1$  and  $\gamma_{11}$  at the 'ordinary' transition as well as at the adsorption multicritical point ('special transition') were estimated, as well as the so-called crossover exponent  $\phi$ . A similar problem in the case of branched polymers has not yet been studied at all, though it may have important and interesting physical applications. It possibly allows us to understand surface properties of such diverse materials as rubbers, solutions containing branched polymers, surface effects at the sol-gel transition, etc. Also introducing an attractive interaction between the surface and the branched polymers will allow us to address the problem of adsorption of branched polymers from the solution to the wall. In addition, a phase transition is expected (which has the properties of a multicritical point) where the polymer configuration changes from three dimensional to quasi-two dimensional.

We model branched polymers as site lattice animals on the simple cubic lattice. Between any two occupied sites of the animal a bond is assigned and if both these sites happen to be on the surface, this bond is assigned a negative interaction energy  $-\varepsilon$ . If we choose units such that  $\varepsilon/k_B = 1$ , where  $k_B$  is the Boltzmann constant, then the partition function for animals of size  $N$  is

$$Z_N = \sum_{n=1}^{M(N)} A_N(n) e^{n/T} \quad (1)$$

<sup>‡</sup> On leave from Institute of Theoretical Physics, Chinese Academy of Science, Beijing, China.

where  $A_N(n)$  is the number of  $N$ -site animals with  $n$  bonds on the surface and  $T$  is the absolute temperature.  $M(N)$  is the maximum possible number of surface bonds for animals of size  $N$  and for the simple cubic lattice,  $M(N) = [2(N - N^{1/2})]$ , where the square brackets denote the largest integer value of the argument. The lower limit in the summation is 1 since we require that there is at least one particle attached to the wall. A physical quantity easily derived from the partition function is the specific heat  $C(N)$ :

$$C = (\langle n^2 \rangle - \langle n \rangle^2) / (NT^2) \sim (T - T_a)^{-\alpha} \quad (2)$$

where

$$\langle n^p \rangle \equiv Z_N^{-1} \sum_{n=1}^{M(N)} n^p A_N(n) e^{n/T}. \quad (3)$$

A convenient way to calculate  $C$  is to calculate the ratios

$$r_N(n) \equiv A_N(n) / A_N(n-1). \quad (4)$$

Then  $\langle n^p \rangle$  is given by

$$Z_N \langle n^p \rangle = A_N(1) \sum_{n=1}^{M(N)-1} n^p \prod_{j=1}^n [e^{1/T} / r_N(j)] \quad (5)$$

and

$$Z_N = A_N(1) \sum_{n=1}^{M(N)-1} \prod_{j=1}^n [e^{1/T} / r_N(j)]. \quad (6)$$

The Monte Carlo method we use to estimate the ratios  $r_N(n)$  is a straightforward modification of that due to Dickman and Schieve [4]. One starts with an animal in configuration  $\Gamma_n$  and numbers the occupied sites with the set  $\{1, 2, \dots, N\}$  with particle 1 at the origin which is always attached to the wall throughout the whole simulation. A trial configuration  $\Gamma'$  is generated in the following way. First, choose randomly a particle  $i$  from the set  $\{2, 3, \dots, N\}$  and denote its position by  $x_i$ . Now choose randomly a particle  $j$  from the set  $\{1, 2, \dots, N\}$ . The position  $x^*$  is a randomly chosen nearest neighbour of  $j$ . The trial configuration  $\Gamma'$  is the configuration in which particle  $i$  at position  $x_i$  is moved to position  $x^*$ . If  $x^*$  is occupied, if  $x^* = x_i$ , or if  $\Gamma'$  is disconnected, then the new animal configuration is  $\Gamma_{n+1} = \Gamma_n$ . Otherwise the new animal configuration  $\Gamma_{n+1}$  is taken as

$$\Gamma_{n+1} = \begin{cases} \Gamma' & \text{with probability } w = \min[v(x_i; \Gamma') / v(x^*; \Gamma_n), 1] \min[\exp(\Delta B_s / T), 1] \\ \Gamma_n & \text{with probability } (1 - w). \end{cases} \quad (7)$$

Here  $v(y; \Gamma)$  is the number of occupied nearest neighbours of  $y$  in the configuration  $\Gamma$  and  $\Delta B_s$  is the change in the number of surface bonds in going from  $\Gamma_n$  to  $\Gamma'$ . A convenient method for checking the connectivity of the cluster is the method of 'burning' [5]. Since the probability for choosing  $x_i$  is  $1/(N-1)$  and that for choosing  $x^*$  is  $v(x^*; \Gamma_n)/qN$ , where  $q$  is the coordination number of the lattice, the transition probability

$$p(\Gamma_n \rightarrow \Gamma') = [v(x^*; \Gamma_n) / qN(N+1)] \min(v(x_i; \Gamma') / v(x^*; \Gamma_n), 1) \min[\exp(\Delta B_s / T), 1] \quad (8)$$

satisfies detailed balance. Therefore the ratio  $r_N(n)$  defined in (4) is given by

$$r_N(n) \equiv A_N(n) / A_N(n-1) = e^{-1/T} N_n / N_{n-1} \quad (9)$$

where  $N_n$  is the number of realisations of animals with exactly  $n$  surface bonds at temperature  $T$ . Our method generates full lattice animals. For a method that generates loopless animals or lattice trees see [6].

Using the above Monte Carlo method we have calculated animal configurations with the number of surface bonds  $n$  ranging from  $n = 1$  to  $n = M(N)$ . Since at high temperatures most of the animals generated have very few surface bonds and at low temperatures only animals with very many surface bonds are generated, we have to use several (4–8) different temperatures for animals of large size  $N$ . For each temperature, 10–25 million trial configurations  $\Gamma'$  were generated. A successful trial is called an event. At high temperatures, up to 25% of the trials are successful, but at the lowest temperatures that we have used, only 2% of the trials are successful. The data for  $r_N(n)$  have statistical error of about 1%. The result for the specific heat  $C$  is shown in figure 1 for  $N = 30, 40, 50, 80$  and  $100$ . We see that the specific heat exhibits a peak at a temperature  $T_m(N)$  which increases monotonically with  $N$ . As  $N$  increases, the peak gets sharper and its height also increases. In table 1 we show the position of the peak  $T_m(N)$  and its height  $C_m(N)$  as a function of  $N$ .

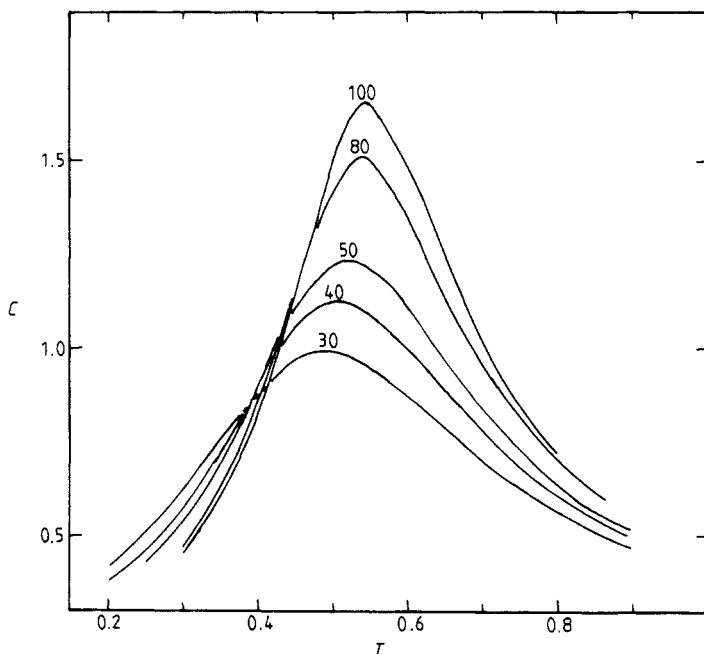


Figure 1. Specific heat  $C$  plotted against temperature  $T$  for various animal sizes  $N$ .

For linear polymers, it is known that the partition function has the scaling form [3], for  $N \rightarrow \infty$  and  $t \equiv (T - T_a)/T_a \rightarrow 0$ ,

$$Z_N = N^{\gamma-1} \psi(tN^\phi) \quad (10)$$

(the  $\gamma$  exponent here is actually  $\gamma_{SB}$  in the notation of [3] because it is required that at least one end of the polymer touches the surface, and we consider the vicinity of the surface-bulk multicritical point), where  $T$  is the adsorption temperature,  $\phi$  is a

**Table 1.** Position  $T_m(N)$  and height  $C_m(N)$  of the specific heat peak as a function of the animal size  $N$ .

$N$	$T_m(N)$	$C_m(N)$
30	0.4940	0.9898
40	0.5055	1.1205
50	0.5215	1.2302
80	0.5390	1.5074
100	0.5440	1.6555

crossover exponent and  $\psi$  is a universal scaling function. From (10) and the relation  $\alpha = 2 - 1/\phi$  one obtains the scaling form for the specific heat, for  $N \rightarrow \infty$  and  $t \rightarrow 0$ ,

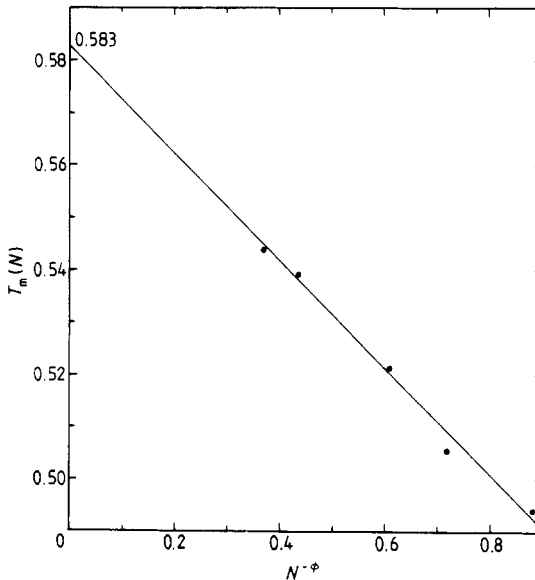
$$C \sim N^{2\phi-1} g(tN^\phi). \quad (11)$$

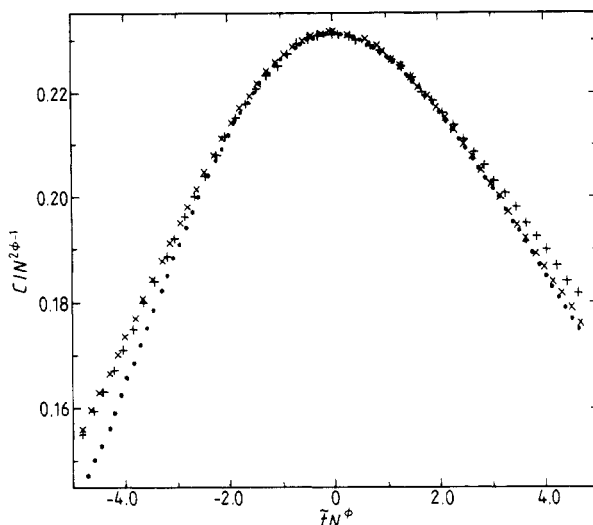
Although the scaling form (11) was derived only for linear polymers, we feel that the scaling structure carries over straightforwardly into the case of branched polymers. Only the critical exponents, upper critical dimension, scaling functions such as  $\psi$  and  $g$  change.

The crossover exponent  $\phi$  is obtained by fitting the values  $C_m(N)$  in table 1 to the form  $C_m(N) \sim N^{2\phi-1}$ . This procedure relies on the tentative assumption that the data in figure 1 are already close enough to the asymptotic region where (11) holds. We obtain  $\phi \approx 0.714$ . Using this value of  $\phi$  in the finite-size scaling relation

$$T_m(N) = T_a - aN^{-\phi} \quad (12)$$

and fitting the value of  $T_m(N)$  in table 1 we find  $T_a \approx 0.583$ . In figure 2 we plot  $T_m(N)$  against  $N^{-\phi}$  with  $\phi = 0.714$ . The points lie more or less on a straight line with intercept at  $T_a$  and thus are consistent with finite-size scaling.

**Figure 2.** Positions of the specific heat peaks  $T_m(N)$  plotted against  $N^{-\phi}$ , with  $\phi = 0.714$ .



**Figure 3.** Scaled specific heat  $C/N^{2\phi-1}$  plotted against scaling variable  $\tilde{t}N^\phi$ , with  $\tilde{t} \equiv (T - T_m(N))/T_m(N)$  and  $\phi = 0.714$ , for various  $N$ :  $\bullet$ ,  $N = 50$ ;  $\times$ ,  $N = 80$ ;  $+$ ,  $N = 100$ .

To test the scaling form (11), we plot in figure 3 the quantity  $C/N^{2\phi-1}$  against the scaling variable  $\tilde{t}N^\phi$ , where here we have taken  $\tilde{t} \equiv (T - T_m(N))/T_m(N)$ . Since  $T_m(N)$  approach  $T_a$  for large  $N$ ,  $\tilde{t}$  and  $t$  are equivalent for large  $N$ . From figure 3 we see that all the data for various  $N$  fall more or less on the same curve, which is the scaling function  $g$ . This confirms the scaling form (11). The increasing deviations in the wings of the scaling function are interpreted as corrections to scaling. Our data do not cover a wide enough range of  $N$  to allow a systematic analysis of these corrections, however.

We have calculated the specific heat of branched polymers interacting with a hard wall. In the vicinity of the adsorption multicritical point, the data confirm rather well a scaling form derived for the specific heat of linear polymers, yielding the tentative estimates  $T_a \approx 0.583$  and  $\phi \approx 0.714$  for the adsorption temperature and the crossover exponent. This yields a specific heat exponent  $\alpha = 2 - 1/\phi \approx 0.6$ . We plan to extend this investigation to other quantities, e.g. the squared gyration radii as considered in [3], in later work.

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