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## COMMENT

# Coil-globule transition temperature enhancement in a polymer molecule adsorbed to a wall

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**Abstract.** We present novel real-space renormalization results for a lattice model of the collapse (coil-globule) transition of a polymer molecule adsorbing to a wall. These results support the conjecture that adsorption stabilises the collapsed phase by enhancing the collapse transition temperature. The analysis is developed, in both two and three space dimensions, for a suitably modified version of a recently proposed geometrical self-attracting self-avoiding walk model of polymer collapse.

Recently, there has been considerable theoretical interest in the problem of polymer adsorption by a wall exhibiting a short-ranged attractive potential towards the macromolecule (see, e.g., Eisenriegler *et al* 1982, Kremer 1983, de Gennes 1987, Duplantier 1988, Burkhardt *et al* 1989, Guim and Burkhardt 1989 and references therein). It has been recognised that the problem is analogous to that of the critical behaviour of a magnetic system with modified couplings along the edge of the semi-infinite bulk, with the 'special' critical point (in magnetic language) corresponding to the adsorption transition for the macromolecule. At the same time, considerable efforts have been devoted to the understanding of the collapse (coil-globule, or  $\theta$ -point) transition of a macromolecule in a dilute solution, as induced by changes in the nature of the solvent (through, e.g., changes in temperature) (see, e.g., Baumgartner 1982, Duplantier 1982, 1986, Privman 1986, Saleur 1986, Jug 1987, Duplantier and Saleur 1987, 1988, Seno and Stella 1988 and references therein). The latter polymer transition also has a magnetic equivalent in the tricritical point of a (zero component) classical spin system.

Much of the current interest in the above polymer transition problems stems from the availability of recently developed conformal invariance methods of investigation (Cardy 1987) for two-dimensional lattice models of the transitions. However, particularly where three-dimensional systems are concerned, the transitions involved also have an intrinsic fundamental importance for the modelling of actual physical and biophysical processes. In particular, the  $\theta$ -point transition is an oversimplified but useful representation of protein folding induced by solvent changes (Volkenstein 1977). In this respect, little attention has been devoted to the situation in which both of the above transitions take place, possibly simultaneously, that is to the problem of the collapse of a polymer chain adsorbing to a rigid wall. New phenomena should take place in this situation, modelling what might happen, for example, to the folding of a protein molecule sitting at a fluid-solid interface (colloidal stabilisation by biopolymers) or on the surface of an impenetrable biological membrane.

In this comment we examine the problem of the collapse of an adsorbed macromolecule by means of simple real-space renormalisation methods applied to a suitable lattice model of the problem at hand. Our principal aim is to investigate the nature of the phase diagram for the macromolecule, as characterised by the fixed points and size exponents of the appropriate renormalisation group recursion relations. A key issue, beside the question of the existence of a multicritical point where collapse and adsorption coexist (a question to which preliminary affirmative answers have already been given by Bouchaud and Vannimenus (1989) and by Veal *et al* (1990) for less realistic polymer models), is whether or not the collapse temperature (or  $\theta$ -temperature) becomes modified by adsorption to a surface. Alternatively, the question might be whether or not the adsorption temperature is modified by collapse of the macromolecule. For the associated magnetic system no shift in the bulk tricritical temperature can be induced by the wall potential in the thermodynamic limit, as the fraction of modified bonds (those on the surface) always vanishes in that limit. However, for the polymer problem at hand the fraction of surface monomers becomes non-vanishing precisely upon adsorption, so that a macroscopic number of monomers becomes affected by the surface potential in the thermodynamic limit. Another possible reason for conjecturing a shift in the  $\theta$ -temperature lies in the entropy estimates of Dill and Alonso (1988) for a protein attached to a wall. These authors estimate the reduction of entropy for coil-like configurations with respect to that for globule-like ones when attachment to an (attractive) impenetrable wall takes place, ensuing in the stabilisation of the collapsed phase. In the following we give evidence for the first time that this stabilisation corresponds to an *enhancement* of the  $\theta$ -temperature induced by the attractive wall, as one might naively expect. Our results have been obtained through simple real-space renormalisation methods, but it is hoped that more powerful techniques (e.g. conformal invariance) can be employed to corroborate our findings.

Our model is the surface adsorption version of a self-attracting self-avoiding walk (SASAW) lattice model proposed by one of the present authors to study the bulk  $\theta$ -point via real-space renormalisation methods (Jug 1987). In the original model, the macromolecule is represented by a random walk on a suitably chosen lattice where sites can be visited twice at the most, provided a probability  $f$  is assigned to each chain self-contact. The  $f$ -factor can represent temperature changes in the solvent via the plausible functional dependence  $f = 1 - \exp(E/kT)$ ,  $E < 0$  representing the effective solvent-mediated monomer-monomer attraction energy. The lattice structure is chosen so as to disallow more than single contacts amongst the chain monomers, a geometrical way of taking into account three- and higher-body repulsions which are believed to be always present when collapse takes place. In two dimensions, this is accomplished by making use of a triangular lattice, which then forms the basis for the three-dimensional lattice structure we use in this work. Real-space renormalisation methods can then be implemented by enumerating random walks in the appropriate cell and weighting each chain link by a bond fugacity  $k_b$  and each contact by a probability factor  $f$ . A recursion relation is set up for the pair  $(k_b, f)$ , yielding the correct phase diagram with a SAW (self-avoiding walk, or coil phase), a G (globular, or collapsed phase) and  $\theta$ -point fixed point structure characterised by reasonable values for the related exponents (Jug 1987).

Following the approach by Kremer (1983), the short-ranged potential on the surface is then introduced by modifying the bond fugacities along the edge of the surface from  $k_b$  to  $k_s$ . Figure 1 gives a schematic representation of the geometrical nature of the resulting lattice model. Recursion relations for  $k_b$  and  $k_s$  are then derived by equating

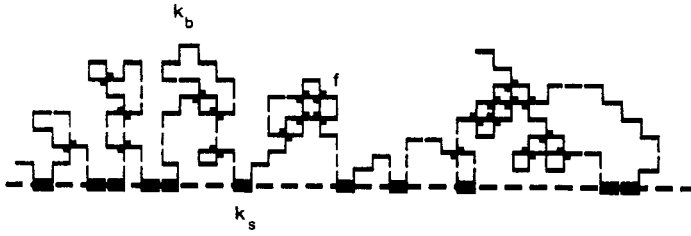


Figure 1. Schematic representation of the SASAW model of adsorption of a collapsing macromolecule ( $d = 2$  space dimensions).

bare and renormalised cell partition functions for the SASAW model with and without the surface added:

$$Z'_\theta{}^{s(x)}(k'_b, k'_s, f') = Z_\theta{}^{s(x)}(k_b, k_s, f) \quad (1)$$

$$Z'_\theta{}^b(k'_b, f') = Z_\theta{}^b(k_b, f). \quad (2)$$

Here, the cell partition functions are given by (Jug 1987)

$$Z_\theta{}^b(k_b, f) = (1-f)^{n_{\max}} Z_{\text{SAW}}^b(k_b) + \sum_{m=1}^{n_{\max}} f^m Z_{Gm}^b(k_b) \quad (3)$$

$$Z_\theta{}^{s(x)}(k_b, k_s, f) = (1-f)^{n_{\max}} Z_{\text{SAW}}^{s(x)}(k_b, k_s) + \sum_{m=1}^{n_{\max}} f^m Z_{Gm}^{s(x)}(k_b, k_s) \quad (4)$$

where  $Z_{\text{SAW}}$  and  $Z_{Gm}$  enumerate the walks with no ( $m=0$ ) or  $m$  contacts in the cell, respectively. Using a generic notation:

$$Z_\alpha = \sum_{\text{spanning walks}} c_\alpha(n_b, n_s) k_b^{n_b} k_s^{n_s} \quad (5)$$

$n_b$  and  $n_s$  being the number of random walk steps in the bulk and on the surface (if present), respectively, and  $c_\alpha(n_b, n_s)$  the number of SASAW with  $(n_b, n_s)$  steps and having the property  $\alpha$ .  $n_{\max}$  is the maximum number of contact sites available in the chosen lattice cell and  $x$  represents the minimum allowed fraction of surface bonds in a partition sum like (5) (that is, we sum only over walks spanning in the direction of the surface and having  $n_s/(n_b + n_s) \geq x$  if the surface is present). For the renormalised cell partition function we have used the modified construction

$$Z'_\theta = \sum_{m=0}^{n_{\max}} f'^m Z'_{Gm} \quad (6)$$

where  $Z'_{G0} \equiv Z'_{\text{SAW}}$ , since we must allow for the possibility of globule-like walks to be renormalised into coil-like walks when  $f = f' = 1$ . The recursion relation for the contact probability  $f'$  is given as in Jug (1987), in terms of the fraction of weighted walks containing at least one contact in the bare cell:

$$f' = \frac{\sum_{m=1}^{n_{\max}} f^m (1-f)^{n_{\max}-m} Z_{Gm}^{s(x_{\min})}}{(1-f)^{n_{\max}} Z_{\text{SAW}}^{s(x_{\min})} + \sum_{m=1}^{n_{\max}} f^m (1-f)^{n_{\max}-m} Z_{Gm}^{s(x_{\min})}} \quad (7)$$

where the partition functions refer to the minimum allowed adsorbed fraction in order to take as many configurations as possible into account.

We have determined the phase behaviour of our SASAW model through the study of the fixed-point structure of the recursion relations (1), (2) and (7) thus defined. In

**Table 1.** Fixed point characterisation for the recursion relation in  $d = 2$ . Reported are the SAW,  $\theta$  and G fixed point values both with and without surface interactions to support our main claim in the paper. Results refer to  $2 \times 2 \Rightarrow 1 \times 1$ ,  $3 \times 3 \Rightarrow 1 \times 1$  and  $3 \times 3 \Rightarrow 2 \times 2$  cell renormalisations. A study as a function of the minimum adsorbed fraction  $x$  is reported in one case. Stars denote complex eigenvalues; in brackets are the expected exponent values, when known.

	SAW		$\theta$		Globule	
$2 \times 2$ Bulk $1 \times 1$	$k_b = 0.316$ $f = 0$	$\nu_b = 0.782 (\frac{3}{4})$	$k_b = 0.498$ $f = 0.663$	$\nu_b = 0.542 (\frac{4}{7})$ $\nu_f = 1.945$	$k_b = 0.451$ $f = 1$	$\nu_b = 0.560 (\frac{1}{2})$
Surface $x = \frac{1}{4}$	$k_b = 0.316$ $k_s = 0.432$ $f = 0$	$\nu_b = 0.782 (\frac{3}{4})$ $\nu_s = 1.465 (\frac{3}{2})$	$k_b = 0.518$ $k_s = 1.005$ $f = 0.480$	$\nu_b = 0.580$ $\nu_s = 1.060$ $\nu_f = 2.466$	$k_b = 0.451$ $k_s = 0.862$ $f = 1$	$\nu_b = 0.560 (\frac{1}{2})$ $\nu_s = 1.000 (1)$
Surface $x = \frac{1}{3}$	$k_b = 0.316$ $k_s = 0.384$ $f = 0$	$\nu_b = 0.782 (\frac{3}{4})$ $\nu_s = 1.613 (\frac{3}{2})$	$k_b = 0.516$ $k_s = 0.795$ $f = 0.510$	$\nu_b = 0.572$ $\nu_s = 1.241$ $\nu_f = 2.521$	$k_b = 0.451$ $k_s = 0.687$ $f = 1$	$\nu_b = 0.560 (\frac{1}{2})$ $\nu_s = 1.155 (1)$
Surface $x = \frac{1}{6}$	$k_b = 0.316$ $k_s = 0.377$ $f = 0$	$\nu_b = 0.782 (\frac{3}{4})$ $\nu_s = 1.630 (\frac{3}{2})$	$k_b = 0.514$ $k_s = 0.615$ $f = 0.534$	$\nu_b = 0.564$ $\nu_s = 1.507$ $\nu_f = 2.563$	$k_b = 0.451$ $k_s = 0.553$ $f = 1$	$\nu_b = 0.560 (\frac{1}{2})$ $\nu_s = 1.365 (1)$
$3 \times 3$ Bulk $1 \times 1$	$k_b = 0.298$ $f = 0$	$\nu_b = 0.772 (\frac{3}{4})$	$k_b = 0.376$ $f = 0.535$	$\nu_b = 0.615 (\frac{4}{7})$ $\nu_f = 3.056$	$k_b = 0.338$ $f = 1$	$\nu_b = 0.632 (\frac{1}{2})$
Surface $x = \frac{1}{6}$	$k_b = 0.298$ $k_s = 0.413$ $f = 0$	$\nu_b = 0.772 (\frac{3}{4})$ $\nu_s = 1.547 (\frac{3}{2})$	$k_b = 0.392$ $k_s = 0.617$ $f = 0.404$	$\nu_b = 0.618$ $\nu_s = 1.271$ $\nu_f = 6.063$	$k_b = 0.338$ $k_s = 0.529$ $f = 1$	$\nu_b = 0.632 (\frac{1}{2})$ $\nu_s = 1.241 (1)$
$3 \times 3$ Bulk $2 \times 2$	$k_b = 0.284$ $f = 0$	$\nu_b = 0.757 (\frac{3}{4})$	$k_b = 0.449$ $f = 0.256$	$\nu_b = 0.552 (\frac{4}{7})$ $\nu_f = 1.622$	$k_b = 0.356$ $f = 1$	$\nu_b = 0.487 (\frac{1}{2})$
Surface $x = \frac{1}{6}$	$k_b = 0.284$ $k_s = 0.453$ $f = 0$	$\nu_b = 0.757 (\frac{3}{4})$ $\nu_s = 1.490 (\frac{3}{2})$	$k_b = 0.435$ $k_s = 0.847$ $f = 0.180$	$\nu_b = * * *$ $\nu_s = 1.109$ $\nu_f = * * *$	$k_b = 0.356$ $k_s = 0.675$ $f = 1$	$\nu_b = 0.487 (\frac{1}{2})$ $\nu_s = 0.999 (1)$

**Table 2.** As in table 1, but for  $d = 3$   $2 \times 2 \times 2 \Rightarrow 1 \times 1 \times 1$  cell renormalisation.

	SAW		$\theta$		Globule	
$2 \times 2 \times 2$ Bulk $1 \times 1 \times 1$	$k_b = 0.222$ $f = 0$	$\nu_b = 0.635 (0.588)$	$k_b = 0.319$ $f = 0.524$	$\nu_b = 0.410 (\frac{1}{2})$ $\nu_f = 2.383$	$k_b = 0.281$ $f = 1$	$\nu_b = 0.425 (\frac{1}{2})$
Surface $x = \frac{1}{4}$	$k_b = 0.222$ $k_s = 0.256$ $f = 0$	$\nu_b = 0.633 (0.588)$ $\nu_s = 0.911$	$k_b = 0.341$ $k_s = 0.379$ $f = 0.268$	$\nu_b = 0.454$ $\nu_s = 0.688$ $\nu_f = 3.616$	$k_b = 0.281$ $k_s = 0.306$ $f = 1$	$\nu_b = 0.425 (\frac{1}{2})$ $\nu_s = 0.643$
Surface $x = \frac{1}{8}$	$k_b = 0.222$ $k_s = 0.245$ $f = 0$	$\nu_b = 0.635 (0.588)$ $\nu_s = 0.972$	$k_b = 0.335$ $k_s = 0.348$ $f = 0.372$	$\nu_b = 0.418$ $\nu_s = 0.741$ $\nu_f = 6.173$	$k_b = 0.281$ $k_s = 0.291$ $f = 1$	$\nu_b = 0.426 (\frac{1}{2})$ $\nu_s = 0.711$
Surface $x = \frac{1}{12}$	$k_b = 0.222$ $k_s = 0.245$ $f = 0$	$\nu_b = 0.635 (0.588)$ $\nu_s = 0.972$	$k_b = 0.333$ $k_s = 0.342$ $f = 0.394$	$\nu_b = 0.415$ $\nu_s = 0.753$ $\nu_f = 5.894$	$k_b = 0.281$ $k_s = 0.288$ $f = 1$	$\nu_b = 0.425 (\frac{1}{2})$ $\nu_s = 0.733$

$d = 2$  space dimensions we have considered triangular lattice cells of three sizes:  $3 \times 3$  ( $n_{\max} = 9$ ),  $2 \times 2$  ( $n_{\max} = 4$ ) and  $1 \times 1$  ( $n_{\max} = 1$ ), with the adsorbing line along the base of the cell. In  $d = 3$  we have considered triangular lattice based cells of two sizes:  $2 \times 2 \times 2$  ( $n_{\max} = 8$ ) and  $1 \times 1 \times 1$  ( $n_{\max} = 1$ ), with the adsorbing surface on the triangular base. Details of the walks' enumeration algorithm employed and of the respective partition functions will be given elsewhere. Here we discuss the overall physical picture emerging from the fixed point structure. Needless to say, for  $f' = f = 0$  we recover the SAW adsorption phase diagram of Kremer (1983), with differences allowing for the different lattice structure. A completely analogous phase structure applies for  $f' = f = 1$  for the adsorption of a collapsed globule. The decrease of the  $\nu_s$  exponent (expected for a more compact globular structure) should be noted. For  $k'_s = k_s = 0$  we recover the bulk  $d$ -dimensional collapse phase diagram (Jug 1987, though novel results for  $d = 3$  are presented in this work), whilst for  $k'_b = k_b = 0$  we obtain the bulk  $(d - 1)$ -dimensional collapse phase diagram (non-trivial only for  $d = 3$ ).

As anticipated, a novel fixed point ( $\theta_s$ , or  $S_\theta$ ) where collapse and adsorption coexist is also found in all cases. The feature we want to stress in this comment is that we have always found the value of  $f_{\theta_s}^*$  to be significantly *depressed* by the presence of the attracting surface, corresponding to an *enhancement* of the  $\theta$ -point transition temperature. Tables 1 and 2 present the fixed point characterisation for the various renormalisation schemes adopted, with the exponents  $\nu_b$  and  $\nu_s$  characterising the size of the SASAW in the directions parallel and perpendicular to the surface, respectively, whilst  $\nu_f$  characterises the size of the incipient collapsed cluster on approach to the  $\theta$ -point. It can be seen that exponents appear to be close to the expected values, when known. The cell renormalisation method employed, however, does not allow us to make a particular claim on any new exponent. A finite size analysis is also beyond the capabilities of the method; however, we do believe that even within our relatively small cell calculations the shift in the  $\theta$ -point temperature induced by adsorption is a genuine effect not induced by finite size circumstances.

In conclusion, we have presented results from a cell renormalisation study of a SASAW model of collapsing polymer adsorption to a wall. There is strong evidence for both  $d = 2$  and  $d = 3$  that adsorption induces an enhancement of the collapse temperature, owing to a stabilisation of the collapsed phase by the wall, as conjectured by Dill and Alonso (1988). Clearly, owing to the short range of the surface attractive potential, the shift should be considered as a novel collective effect within the polymer molecule as a whole. In view of the quality of the results obtained and of its simplicity and adaptability, the SASAW model now appears as an ideal candidate for extensions to the study of more realistic models of protein molecule conformation, both in bulk and at interfaces or membranes.

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