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## COMMUNICATIONS

## Semiflexible self-avoiding polymers

R. G. Petschek

Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106

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The statistical behavior of long, semiflexible, self-avoiding chain polymers is a matter of controversy. On the basis of a mean-field type calculation Flory<sup>1</sup> has suggested there should be a first order transition with increasing stiffness. This has been disputed<sup>2,3</sup> on the basis of certain exactly soluble models for polymers which have continuous transitions but have certain artificial aspects. It has also been shown rigorously that certain aspects of the mean-field theory are incorrect.<sup>4,5</sup> Recently Baumgartner and Yoon (BY)<sup>6</sup> have performed Monte Carlo calculations for a model system on a finite lattice. They obtain discontinuities in the energy and other quantities (but not hysteresis) supporting the conclusion that this model has a first order transition.

In this paper exactly soluble models are used to give rigorous bounds for the free energy and average energy of a model. These bounds are used to demonstrate that the results of the Monte Carlo simulation are in serious conflict with those required in an infinite system of infinitely long polymers. Finally the magnitude of the finite size effects are estimated to be sufficiently large to cause this discrepancy.

Consider the following model of self-avoiding polymers on an infinite square lattice. The states consist of long polymer chains which do not end in the lattice. Exactly one monomer is on each site of the lattice. Each monomer is bonded to exactly two other monomers on nearest neighbor sites. The energy of each state is given by  $\epsilon N_g$ , where  $\epsilon$  is the (positive) energy cost per "gauche" bond and  $N_g$  is the number of gauche bonds; that is the number of monomers for which the two bonds to nearest neighbor monomers form a right angle rather than a straight line. The partition sum is given by

$$Z_p(\beta) = \sum \exp(-\beta N_g), \quad (1)$$

where the sum is over all states and the inverse temperature, i.e., (in units of  $\epsilon$ ) is  $\beta = \epsilon/k_B T$  where  $k_B T$  is Boltzmann's constant times the temperature. The free energy per particle is

$$f_p(\beta) = -(\ln Z_p)/\beta N, \quad (2)$$

where  $N$  is the number of sites on the lattice.

Nagle<sup>2</sup> has pointed out that the  $F$  model of ferroelectricity is related to this model of polymers. He demonstrates a

one to one correspondence between the states of the  $F$  model and states of a polymer system. The energies assigned to these  $F$  model states are proportional to the number of gauche bonds. The only difference is that the polymer model corresponding to the  $F$  model allows polymer rings in addition to polymer chains. Thus we may write the partition function for the  $F$  model as

$$Z_F = \sum \exp(-\beta N_g) + \sum' \exp(-\beta N_g) \quad (3a)$$

$$\geq Z_p, \quad (3b)$$

where  $\Sigma$  indicates a sum over those states of the  $F$  model which correspond to polymer configurations containing no rings and  $\Sigma'$  is the sum over other states. The inequality follows because the first sum is  $Z_p$  and the second sum is nonnegative. It follows that

$$f_p(\beta) \geq f_F(\beta), \quad (4)$$

where  $f_F(\beta) = -\ln Z_F/\beta N$  is a known function<sup>7</sup> in the limit of infinite volume.

It is well known that<sup>8</sup>

$$\beta f_p(\beta) \leq \beta' f_p(\beta') + E_p(\beta)(\beta - \beta'), \quad (5)$$

where  $\beta$  and  $\beta'$  are arbitrary and  $E_p(\beta) = d(\beta f_p)/d\beta$  is the average energy per site of the polymer system (in units of  $\epsilon$ ). This follows because  $d^2(\beta f_p)/d\beta^2 = -\beta^{-2}C \leq 0$  and  $C$ , the specific heat, is always nonnegative. It is clear that  $Z_p \geq 1$  so that<sup>9</sup>  $\beta' f_p(\beta') \leq 0$ . Combining this with Eqs. (4) and (5) we find that

$$\beta f_F(\beta) \leq E_p(\beta)(\beta - \beta') \quad (6)$$

for all  $\beta, \beta'$ . For any  $\beta < \beta'$  this yields an upper bound for  $E_p(\beta')$ . It is clear that the best such upper bound for  $E_p(\beta')$  is obtained by choosing  $\beta$  so that

$$\beta f_F(\beta)/(\beta - \beta') = d(\beta f_F)/d\beta = E_F(\beta). \quad (7)$$

Thus if  $\beta$  and  $\beta'$  are related by Eq. (7):  $E_F(\beta) \geq E_p(\beta')$ . As  $\beta f_F$  is convex there is at most one such  $\beta$ . Similar bounds based on the convexity of the free energy  $f$  as a function of temperature or on bounds on the entropy as a function of energy give identical results.

Given the known exact solution of the  $F$  model Eq. (7)

can be solved numerically. For  $\beta' = 1.07$ , where BY see a discontinuity in the Monte Carlo value for  $E_p$ , an upper bound for  $E_p$  of 0.225... is obtained. This is substantially less than the value  $E_p = 0.3$  obtained by Baumgartner and Yoon in a Monte Carlo simulation for a finite size realization of this model. It follows that finite size effects or other errors in the calculation lead to  $> 30\%$  errors in this energy. Thus there is substantial question whether the results of this Monte Carlo simulation have direct relevance to the behavior of the model polymer system in the infinite volume limit.

It is reasonable that finite size effects should be important to the BY calculation in this range. BY use a model of chain polymers as discussed above except that instead of infinite polymer chains on an infinite lattice they use 21 polymers 20 monomers long on a  $21 \times 21$  square lattice. In the totally ordered state in which the polymer chains are straight and parallel the ends of each polymer can be at any one of 21 sites leading to the finite size free energy  $\beta f_p = -\ln(21)/21 \sim -0.14$  for  $\beta = 0$ . On an infinite lattice with infinitely long polymers  $\beta f_p$  is zero for  $\beta = 0$ . On the other hand we know that in the infinite system  $\beta f_p \gg \beta f_F \sim -0.0175$  for  $\beta = 1.07$ . Thus the error in the free energy due to finite size effects is large in comparison to the contribution to the free

energy from thermal fluctuations at the temperature of interest. If this finite size contribution to the free energy differs by as little as 14% between "ordered" and "disordered" states it could lead to the observed effects. In fact an examination of the low energy excited states of the system shows that they constrain the ends of two polymers to be close to each other, substantially changing this contribution. Note in addition that the effect of this constraint is to decrease the number of states with low energies relative to the number at zero energy. This could very well lead to a first order transition which is an artifact of the finite size of the system.

<sup>1</sup>P. J. Flory, Proc. R. Soc. London Ser. A **234**, 60 (1956); Proc. Natl. Acad. Sci. **79**, 4510 (1982).

<sup>2</sup>J. F. Nagle, Proc. R. Soc. London Ser. A **337**, 569 (1974).

<sup>3</sup>A. Malakis, J. Phys. A **13**, 651 (1980).

<sup>4</sup>P. D. Gajrati, J. Phys. A **13**, L437 (1980); J. Stat. Phys. **28**, 441 (1982).

<sup>5</sup>P. D. Gujrati and M. Goldstein, J. Chem. Phys. **74**, 25, 96 (1981).

<sup>6</sup>A. Baumgartner and D. Y. Yoon, J. Chem. Phys. **79**, 521 (1983).

<sup>7</sup>See, e.g., E. H. Lieb and F. Y. Wu, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1972), Vol. 1, p. 332.

<sup>8</sup>See, e.g., R. P. Feynman, *Statistical Mechanics* (Benjamin, Reading, Mass., 1972), p. 67.

<sup>9</sup>A somewhat better bound can be obtained by using the upper bound for  $\beta f_p$  obtained in Ref. 5.

## NOTES

# Substrate signal suppression in Raman spectra of sputter deposited TiO<sub>2</sub> films

G. J. Exarhos<sup>a)</sup>

Pacific Northwest Laboratory,<sup>b)</sup> Richland, Washington 99352

(Received 25 June 1984; accepted 31 July 1984)

Recent work<sup>1</sup> has demonstrated that thin film TiO<sub>2</sub> optical coatings can be characterized rapidly and unambiguously by the nonintrusive technique of vibrational Raman spectroscopy. Raman spectra of sputter deposited TiO<sub>2</sub> have been measured for anatase and rutile phases of single layer optical coatings to thicknesses greater than 0.8  $\mu$  with little interference from Raman scattering attributed to the fused silica substrate.<sup>1</sup> For thinner coatings, the weak substrate scattering is appreciable relative to the thin film and can obscure Raman lines attributed to the coating and significantly modulate band intensities. To minimize this problem, interference enhancement methods may be used,<sup>1</sup> the Raman scattering geometry can be altered or a substrate subtraction routine can be attempted. These procedures may not be entirely satisfactory requiring sample modification,

significant alteration of scattering geometry, or in the final case, producing artifacts and decreasing the signal/noise ratio.

A simple technique is available for minimizing substrate interference and takes advantage of the contrasting polarization properties of Raman scattering from the vitreous silica substrate and the fine grained sputter deposited coating. Inherent molecular disorder present in vitreous silica substrates results in marked polarization anisotropy for Raman scattered light. Raman scattering from a fine grained TiO<sub>2</sub> film does not exhibit polarization anisotropy since the individual randomly oriented grains act to scramble the polarization information carried in the scattered radiation. Therefore, substrate interference effects in Raman spectra of polycrystalline sputtered films on vitreous silica can be mini-