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"Semiflexible Equilibrium Polymers: A Self-Assembling Molecular Model"

> R. PANDIT (Apratim Chatterji) Department of Physics IISc Bangalore, India

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strada costiera, 11 - 34014 trieste italy - tel. +39 0402240111 fax +39 040224163 - sci\_info@ictp.trieste.it - www.ictp.trieste.it

# Semiflexible Equilibrium Polymers: A Self-Assembling Molecular Model

Apratim Chatterji<sup>1</sup> and Rahul Pandit<sup>1,2</sup>

1 Centre for Condensed Matter Theory Department of Physics Indian Institute of Science Bangalore, India

#### and

2 Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore

Computational Facilities:

SERC, IISc, Bangalore

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# 1. Outline

- Motivation:
  - Experiments
  - Same Teffer These that Statios
- Our Model
- Results
- Monte Carlo Simulations
- Conclusions



## 2. Motivation

## • Equilibrium Polymers:

- The energy cost for scission and fusion of chains is comparable to  $k_BT$ .
- Thus the length distribution P(L) assumes an equilibrium form ( $\sim e^{(-L/\langle L \rangle)}$ ) which depends on the temperature T and the chemical potential  $\mu$ .
- Elving Protomar Vanamark galvi No. 400 Records (1997) (1997)
- Semiflexible Polymers: There is an energy cost for the bending of polymers. Polymer chains straighten at low T and nematic ordering or viscoelastic gels can form.



### • Experimental Motivation

- Rich Phase diagram of water- surfactant systems; include phases with long, wormlike micelles that are equilibrium polymers.
- Similar in some ways to conventional polymeric systems.
- Examples of equilibrium or living polymers: liquid sulphur, poly(α methylstyrene), protein filaments, and systems of long, worm-like micelles [in, say, ternary mixtures of water, cetyltrimethyl ammonium bromide (CTAB), and 3-hydroxy-naphthalene-2-carboxylate (SHNC)].

Schematic Phase Diagram for an Oil - Water Surfactant Mixture at fixed T.



Schematic Illustration of Threadlike Micelles.



1. INITIATION



Fig. 1. Reaction mechanism using an alkali metal naphthalide initiator to produce living poly( $\alpha$ -methylstyrene) with both ends active.





(8)

(A)

Fig. 3. Possible modes of Coulombic association for living polymers in solution: (a) intermolecular association; (b) intramolecular association. The solid lines represent the polymer chains, the circles with negative charges are the active anionic sites and  $t \in$  circles with positive charges are the countermient.



### • Some Earlier Theoretical Studies

Restrict ourselves to the lattice model of Menon, Barma, and Pandit which we will generalise below.

- First-Order transition from a high-T disordered phase to a low-T ordered phase.
   Order parameter jumps.
- Polymer length distribution is exponential.
- Rapid cooling yields a glass which can be studied by a Monte Carlo analogue of scanning calorimetry.

An **Off-Lattice Model** is required to remove the lattice artifacts above (e.g., orientational ordering and crystallisation are not easily distinguishable).

Other **Off-Lattice Models** for equilbrium polymers (e.g., Milchev, Landau, et al., or Kröger) either do not account for semiflexibility or have been studied in the dilute regime.

### II. Our Model.

- Occupied links are monomers (at most 1 per link).
- Have polydispersity, vacancies, and closed rings.
- Monomers fuse to form self-avoiding chains.
- Energies of various configurations:



#### **III. Principal Results.**

#### A. Equilibrium

• Disordered Phase at high T.

• Ordered Phase (all polymers aligned at low T).

#### 1. Two Dimensions.

- Continuous Ising-type transition.
- At low open-end density, equilibration slow.
- This is because of a "nearby" power-law phase.
- Exact solutions in certain limits.
- Length distributions are exponential, but can show deceptive power laws again because of a "nearby" power-law phase.
- 2. Three Dimensions.
- First-order transition; order parameters, etc. jump.

- Equilibration can be slow at low T.
- Length distributions are exponential.

The order parameter M and the susceptibility showing the first - order transition in dimension d = 3 (linear size L = 16).





The distribution of polymer lengths is exponential. Data are shown just below and just above the first - order transition (L = 16 and d = 3).





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#### **B.** Nonequilibrium

- 1. Glasses in Three Dimensions.
- Quenches to low T yield disordered metastable states or glasses.
- Glasses of two types: completely disordered (for a low density of open ends) or "lamellar".
- Relaxation out of these glasses can be logarithmically slow.
- The system falls out of equilibrium if cooled at a finite rate.
- Study via a Monte Carlo analogue of scanning calorimetry.
- Behaviour akin to real polymeric glasses.
- Autocorrelation functions are slowly decaying exponentials for shallow quenches, but for deeper ones these decays are too slow to obtain reliable fits.
- Lowering h facilitates local rearrangements, thus easing the frustration in the disordered network obtaine

Evolution of the energy E with time t after the quench for disordered (large h) and lamellar (low h) glasses in our model (d = 3 and L = 16).





The system falls out of equilibrium when cooled at a finite rate to yield a disordered glass at large h. The Monte Carlo analogue of scanning calorimetry is also shown for the disordered glass; note glass crystal and crystal - liquid transitions (d = 3 and L = 16).



Instantaneous snapshots of disordered (large h) and lamellar (low h) glasses obtained on quenching from high- to low-T phases in our model (d = 3 and L = 16).







- 1. Two Dimensions.
- Square Lattices of side L with L from 4 80; for long runs use L = 20.
- Periodic Boundary Conditions.
- Upto 1 million MCS per link. Discard first 0.1 million MCS.
- Average every 50 MCS.
- 2. Three Dimensions.
- As in d = 2 for equilibration but with a simple cubic lattice with L = 16.
- Similar updates for glasses (no conservation).
- For quenches we start with short chains (length roughly 4), obtained by equilibration at T = 10 and h=1.2, and reduce T in one step.
- We compute E, etc., at a time t (in MCS) by averaging over 20 measurements, centered at t; each measurement is made every 10 MCS.
- We follow the time evolution for roughly 0.5 million MCS.
- Different initial conditions yield qualitatively similar results.

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### 3. Our Model

- Interacting spherical monomers.
- Aggregate, at low enough T, to form equilibrium polymers.
- Interactions such that polymers, once formed, are *semiflexible*.
- Energy penalties enforce self-avoidance and suppress branching.
- Interaction potential: sum of a two-body part  $V_2(r)$  and a three-body part  $V_3(r_{ij}, r_{ik}, \theta)$ .
- Two-body potential:

$$V_{2}(r) = \epsilon [(\sigma/r)^{12} - (\sigma/r)^{6}] + \epsilon_{1} e^{-a(r/\sigma)} - V_{0}; \quad (1)$$

r: separation between two monomers.

- We use:  $\epsilon_1/\epsilon = 1.34, \ \sigma = 1, \ a = 1.72;$ 
  - $V_0/\epsilon = 0.0142$



- We choose  $V_0$  such that our potential is continuous at  $r = r_{max}$  beyond which we set  $V_2(r) = 0$ . We set  $r_{max} = 5\sigma$
- Three-body potential: IF  $r_{ij} < \sigma_3$  AND  $r_{ik} < \sigma_3$   $V_3(r_{ij}, r_{ik}, \theta) = \epsilon_3(\frac{\sigma_3}{r_{ij}} - 1)(\frac{\sigma_3}{r_{ik}} - 1)\tan^2\theta$ ;(2)  $r_{ij} \equiv |\vec{r}_{ij}|$  and  $r_{ik} \equiv |\vec{r}_{ik}|$ : separations of particles j and k from particle i;  $\theta$ : angle between  $\vec{r}_{ij}$  and  $\vec{r}_{ik}$ .
- We set  $\sigma_3/\sigma = 3$  and  $\epsilon/\epsilon_3 = 4.66$ .
- The  $\tan^2 \theta$  part of  $V_3$  leads to semiflexible polymer chains.
- $V_3$  suppresses branches with  $\theta \simeq \pi/2$  and the hard-sphere part of  $V_2$  suppresses smallangle branches.



- Convention: Two monomers are part of the same chain if the distance between them is  $\leq 1.5\sigma$ .
- Our qualitative results do not depend upon this convention nor on the details of the parametrization of  $V_2$  and  $V_3$ .

•  $H_n$ : field conjugate to the order parameter  $s = \langle P_2(cos\theta) \rangle$ ; energy  $= -H_n^2 cos^2 \phi$ 

for a segment of polymer chain connecting nearest neighbours with  $\phi$  the angle between the vector connecting two monomers and the z axis.





Representative plot of the potential  $[V_2(r) + V_3(r_{12}, r_{13}, \theta)]/\epsilon$  for  $\theta = 0$  (full line), and  $\theta = 45^\circ$  (line with \*)  $r_{12} = 2.5\sigma$  and  $r_{13} = r$ .  $V_3(r_{12}, r, \theta) = 0$  for  $r > 3\sigma$ ; and  $V_2(r) = 0$  for  $r > 5\sigma$  (we use units with  $\sigma = 1$ ).



### 4. Results

- Instantaneous snapshots: for  $\mu = 0.020$  and  $H_n/\sqrt{\epsilon} = -.0293$ .
  - HIGH T: Disordered phase at  $T/\epsilon = 0.00757$ .



- LOW T : Nematically ordered phase at  $T/\epsilon = 0.00707$ .





The length distribution P(L) of polymers of length L above and below the  $\mathcal{I}$ - $\mathcal{N}$ transition (semilog plot) can be fit to an exponential form for  $2L\sigma < \ell$ , where  $\ell$  is the length of the box, for  $\mu/\epsilon = -0.020$  and nematic-ordering field  $H_n/\sqrt{\epsilon} = 0.0293$  for T = 0.00757(5) and T = 0.00707.



Hysteresis plots of (*i*) the internal energy  $U/\epsilon$ , (*ii*) the nematic order parameter  $s = \langle P_2(cos\theta) \rangle$ , (*iii*) the mean polymer length  $\langle L \rangle$  and number of particles N versus  $T/\epsilon$  for the nematic ordering field  $H_n/\sqrt{\epsilon} = -0.0293$  and for  $\mu/\epsilon = 0.02$ . Cooling runs are shown by dots (·) and heating runs by open circles (*o*).  $\ell = 60\sigma$ ;  $\Delta T/\epsilon = 0.0000714$ 



Hysteresis plots of (*i*) the internal energy  $U/\epsilon$ , (*ii*) the nematic order parameter  $s = \langle P_2(cos\theta) \rangle$ , (*iii*) the mean polymer length  $\langle L \rangle$  and number of particles N versus  $T/\epsilon$  for the nematic ordering field  $H_n/\sqrt{\epsilon} = -0.0293$  and for  $\mu/\epsilon = 0.0171$ . Cooling runs are shown by dots (·) and heating runs by open circles (*o*).

 $\ell = 60\sigma; \ \Delta T/\epsilon = 0.0000714$ 



Hysteresis plots of (*i*) the internal energy  $U/\epsilon$ , (*ii*) the nematic order parameter  $s = \langle P_2(cos\theta) \rangle$ , (*iii*) the mean polymer length  $\langle L \rangle$  and number of particles N versus  $T/\epsilon$  for the nematic ordering field  $H_n/\sqrt{\epsilon} = -0.0293$  and for  $\mu/\epsilon = 0.0229$ . Cooling runs are shown by dots (·) and heating runs by open circles (*o*).  $\ell = 78\sigma$ ;  $\Delta T/\epsilon = 0.0000714$ 



Hysteresis plots of (*i*) the internal energy  $U/\epsilon$ , (*ii*) the nematic order parameter  $s = \langle P_2(cos\theta) \rangle$ , (*iii*) the mean polymer length  $\langle L \rangle$  and number of particles N versus  $T/\epsilon$  for the nematic ordering field  $H_n/\sqrt{\epsilon} = -0.0293$  and for  $\mu/\epsilon = 0.0229$ . Cooling runs are shown by dots (·) and heating runs by open circles (*o*).  $\ell = 60\sigma$ ;  $\Delta T/\epsilon = 0.0000357$ 



### • Scanning Calorimetry

 Glass formation on cooling followed by the reappearance of a nematic in a scanning calorimetry heating run.



(a) $U/\epsilon$  versus  $T/\epsilon$  for  $\mu/\epsilon = -0.0214$  and  $H_n/\sqrt{\epsilon} = 0.0293$  in our MC analogue of scanning calorimetry. The rapid-cooling run is denoted by \*'s and the slow-heating run by •'s.

(b) s versus  $T/\epsilon$  for the heating run showing increase in nematic ordering on heating; at sufficiently high  $T/\epsilon$  this nematic order is lost and the isotropic phase obtains.



(c) The configuration at T = 0.00686 for the heating run for  $\mu/\epsilon = -0.0214$  and  $H_n/\sqrt{\epsilon} = 0.0293$ .



### • Shear of Equilibrium Polymers

 Shear promotes ordering by aligning polymers; but it also tears these polymers apart and so, eventually, suppresses nematic ordering.



The variation of s with  $T/\epsilon$  for  $\mu/\epsilon = -0.0214$ , and  $H_n/\sqrt{\epsilon} = 0.0$  in the presence of shear (a)B = 0.00007 and (b)B = 0.00018. Cooling runs are indicated by  $(\cdot)$  and heating runs by  $(\circ)$ .





The variation of the mean length of polymers  $\langle L \rangle$  with  $T/\epsilon$  for  $\mu/\epsilon = -0.0214$ ,  $H_n/\sqrt{\epsilon} = 0.0$  and with shear; for B = 0.00018, cooling runs are indicated by (+) and heating runs by  $\oplus$ ; and for B = 0.00007, cooling runs are indicated by  $\cdot$  and heating runs by open circles ( $\circ$ ).

High shear produces shorter chains.



### 5. Monte Carlo Simuations

- Cubical box, side  $L = 60\sigma$  (or  $78\sigma$ ).
- Periodic boundary conditions and the nearestimage convention for calculating energies.
- Metropolis algorithm.
- value of  $\Delta T/\epsilon = 0.0000714$  (or  $\Delta T/\epsilon = 0.0000357$ )
- Grand-canonical ensemble for equilibrium studies and the canonical ensemble while shearing the system.
- At each temperature data is averaged over 60000 MCS being collected every 15 MCS after thowing away 3000MCS at each temperature (90000 for large system after throwing away 45000 iterations).
- We attempt to introduce 500 particles every 15 MCS



- Calculation of  $\langle P_2(\cos\theta) \rangle$  for a chain.
  - Calculate centre of gravity for a chain
  - Calculate moment of Inertia Tensor for a chain
  - Diagonalise moment of Inertia Tensor
  - The angle of the major axis with the z direction is the angle  $\theta$
  - Ratio of major axis and minor axis gives the aspect ratio of the chain.
- Shear is applied by the Dynamic Monte Carlo technique in a canonical ensemble of 2700 particles.
- To study the effect of shear, we impose rigid walls perpendicular to the x direction and PBC in the y and z directions.





• We introduce the shear via an external field  $\vec{F}$  whose only non-vanishing component is directed along the z axis and changes linearly along the x direction, i.e.,

$$F_z(x) = \mathcal{B} (x/\ell - 1/2),$$
 (3)

• The energy change and the work done by the shear in an MC move is

$$\delta E = \delta z \ \mathcal{B} \ (\frac{x_1 + x_2}{2\ell} - \frac{1}{2}) + \delta E_1, \quad (4)$$



## 6. Conclusions

We propose a molecular model for equilibrium polymers which has the following properties.

- Monomers self assemble into equilibrium polymers as T is lowered.
- At even lower temperatures they straighten out to form a nematically ordered state.
- Rapid cooling leads to glassy, entangled states which, when heated steadily, develop nematic ordering that is eventually lost at sufficiently high T.
- Shear initially promotes nematic ordering but, if large, tears apart our equilibrium polymers and thus decreases the nematic ordering.