

**1) (30p)** The surface tension  $\gamma(T, A)$  and heat capacity at constant area  $C_A(T)$  for a water surface of area  $A$  covered by a thin film containing  $N$  organic molecules are given by

$$\gamma(T, A) = \gamma_0 - \frac{Nk_B T}{A - bN} + \frac{aN^2}{A^2} \text{ and } C_A(T) = Nk_B + Nk_B \left(\frac{T}{T_0}\right)^2.$$

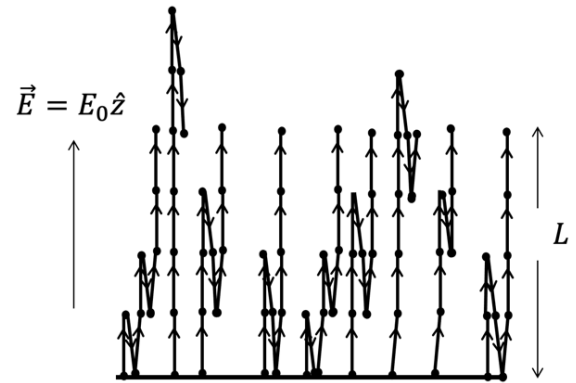
Where  $a$ ,  $b$ ,  $\gamma_0$  and  $T_0$  are constants and  $k_B$  is Boltzmann's constant. Expression for differential Helmholtz free energy is given by  $dF = -SdT + \gamma dA$ .

**a)** Find the entropy change  $\Delta S(T, A)$  of the surface film, from the state  $(T_0, A_0)$  to the state  $(T, A)$ .

**b)** The temperature of the surface increased from  $T_i = 300.0K$  to  $T_f = 300.1K$  keeping the surface area  $A$  constant. What is the probability of the surface returning back to its initial state due to the fluctuations in temperature?

Consider a surface that is covered by  $N$  dielectric polymer chains placed in a uniform electric field given by  $\vec{E} = E_0 \hat{z}$ . Each chain consists of  $n$  electric dipole monomer of which  $n_\uparrow$  dipole oriented along  $+z$  direction and  $n_\downarrow$  dipole oriented along  $-z$  direction. The energy of a dipole in an electric field is given by  $\varepsilon = -\vec{P} \cdot \vec{E}$ . Assume that all chains on the surface have the same extension  $L$  under constant and uniform electric field. The length of single dipole monomer is  $a$ . A model picture of this dielectric polymer surface in two dimensions is given.

$$\begin{array}{c} \uparrow \\ a \\ \downarrow \end{array} \vec{P} = q\vec{a}$$



**2) (30p)** In microcanonical ensemble, find the energy of the surface and the extension of dielectric polymers as a function of temperature,  $E_N(T)$  and  $L(T)$ .

Discuss the extension of dielectric polymers at the limits of  $T \rightarrow 0$ ,  $T \rightarrow \infty$ ,  $E_0 \rightarrow 0$  and  $E_0 \rightarrow \infty$  in the context of order-disorder and entropy.

**3) (20p)** In canonical ensemble, write the partition function for a single dipole monomer. Find the energy of the surface and the extension of dielectric polymers as a function of temperature,  $E_N(T)$  and  $L(T)$ .

**4) (30p)** Consider a gas consists of  $N$  non-interacting atoms in volume  $V$ . Each atom is formed by three fixed subatomic particles each with two possible energy state: spin up  $+\frac{1}{3}\varepsilon$  and spin down  $-\frac{1}{3}\varepsilon$ . One of the possible states of a single atom is given in the figure.

**a)** Write the number of quantum states in microcanonical ensemble for the gas. Give the reasoning to your answer.

**b)** Write the single particle partition function and find the probability of an atom being at the lowest energy state.

**c)** Find the average energy of an atom and the total energy of the gas as a function of temperature using Boltzmann probability function in canonical ensemble.

