# Statistical Physics of Simple and Complex Fluids
## Soft Condensed Matter Theory

HOMEWORK #1

Corrections to Ex. 2

## Entropic elasticity of rubber: Freely Jointed Chain (FJC) chain model

1. Let $p_l$ be the probability distribution of any configuration $l$ of the polymer, satisfying or not the boundary conditions. The probability distribution for the configurations that satisfy the boundary conditions is:
$$p'_l = \frac{p_l}{\sum_{l \text{ satisfying b.c.}} p_l}.$$
It is then clear that if $p_l$ follows Gibbs statistics, so it is for $p'_l$.

2. The orientations of the monomers are not independent, as they must satisfy: $\sum_i a\cos\theta_i = X$.

3. The energy is:
$$E = E_{kinetic} + \frac{k}{2}\left(L - X - l_0\right)^2,$$
where $E_{kinetic}$ is the kinetic energy of the polymer.

4. If $|\delta X| \ll L - \langle X\rangle - l_0$:
$$E_{sp} = \frac{k}{2}\left(L - \langle X\rangle - \delta X - l_0\right)^2 \simeq \frac{k}{2}\left(L - \langle X\rangle - l_0\right)^2 - k\left(L - \langle X\rangle - l_0\right)\delta X.$$
Since $\delta X = X - \langle X\rangle$: $E_{sp} = E_0 - \tau X$ with $\tau = k\left(L - \langle X\rangle - l_0\right)$.
Physical meaning: the projected length of the polymer is free to fluctuate, but it experiences a **constant** tension $\tau$.

5. The condition $|\delta X| \ll L - \langle X\rangle - l_0$ is equivalent $k|\delta X| \ll \tau$. Therefore the approximation becomes increasingly accurate as $\tau$ increases.

6. Partition function:
$$Z = \sum_{configs\, l} e^{-\beta(E_l - \tau X_l)} = Z_{kin} \times \int \mathrm{d}^2\Omega_1 \ldots \mathrm{d}^2\Omega_N e^{\beta\tau a \sum_i \cos\theta_i}.$$
Introducing $z = \int \sin\theta \mathrm{d}\theta \mathrm{d}\varphi e^{\beta\tau a\cos\theta} = 4\pi\frac{\sinh(\beta\tau a)}{\beta\tau a}$, one gets $Z = Z_{kinetic} z^N$.
Note that we integrated over all possible angles, while we required small $\Delta X$. This is justified by the fact that the exponential term is sharply peaked around its max.

7. $F(T,\tau,N) = -k_B T\ln Z = F_0(T) - Nk_B T\ln\left(\frac{\sinh(\beta\tau a)}{\beta\tau a}\right)$.

8. $\langle X\rangle = -\frac{\partial F}{\partial\tau}$. Thus:
$$\langle X\rangle = Na\left(\coth(\beta\tau a) - \frac{1}{\beta\tau a}\right).$$
By definition $S = -k_B\sum_l p_l \ln p_l$, with here $p_l = e^{-\beta(E_l - \tau X_l)}/Z$. It comes: $-TS = -\langle E\rangle + \tau\langle X\rangle - k_B T\ln Z$, or equivalently, $F = \langle E\rangle - TS - \tau\langle X\rangle$.

9. Since $\coth \epsilon \simeq \epsilon^{-1} + \epsilon/3$, one gets:

$$\langle X \rangle = \frac{Na^2}{3k_B T}\tau.$$

The spring constant is $k = \frac{3k_B T}{Na^2}$.

10. When $\tau \to \infty$, $\langle X \rangle \to Na$. That is the maximal length of the chain.

11. When $T$ increases, the spring constant increases. For a given tension applied on the chain, the rubber contracts. (this is counter-intuitive: most materials dilate when heated).