Ex2340: Tension of a chain molecule

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The problem:

A chain molecule consists of N units, each having a length a. The units are joined so as to permit free rotation about the joints. At a given temperature T, derive the relation between the tension f acting between both ends of the three-dimensional chain molecule and the distance L between the ends.

The solution:

Problematic solution: independence of x, y, z is questionable, and relation between $P(r)$ and F is not established.

In one-dimension, the average step length of the projection on the x-axis is $\langle a^2 cos^2\theta\rangle^{1/2} = a/\sqrt{3}$, which by using the "central limit theorem" for a long polymer ($N \gg 1$) leads to:

$$P(x, N) \propto e^{-3x^2/(2Na^2)} \tag{1}$$

with similar results for $P(y, N)$ and $P(z, N)$. Now, because each bond is oriented randomly, the x, y and z projections are independent of each other, and the probability density for the chain to end at $\vec{r}$ is, therefore, the product of independent factors:

$$P(\vec{r}, N) = P(x, N)P(y, N)P(z, N) \propto exp\left[-\frac{3}{2}\frac{r^2}{Na^2}\right] \tag{2}$$

In order to get the probability that the chain has a length L, one must multiply eqn.(2) by the surface of a sphere with radius L and get:

$$P(L, N) \propto 4\pi L^2 e^{-3L^2/(2Na^2)} \tag{3}$$

Finally, by using the entropy S, one can write the free energy as:

$$F = -TS = -Tln(P(L, N)) = \frac{3TL^2}{2Na^2} - 2Tln(L) + constant \tag{4}$$

and calculate the tension:

$$f = -\frac{\partial F}{\partial L} = \frac{2T}{L} - \frac{3TL}{Na^2} = \frac{2T}{L}\left(1 - \frac{3L^2}{2Na^2}\right) \tag{5}$$

It is also nice to see that we can find the relaxed length of the chain to be $L_0 = \sqrt{2Na^2/3}$.