(a) A polymer chain consists of a large number $N \gg 1$ segments of length d each. The segments can freely rotate relative to each other. The temperature of the system is T. Find the mean displacement $\langle \mathbf{r}_{12} \rangle$ and the mean square distance $\langle \mathbf{r}_{12}^2 \rangle$ between the chain ends.

(b) For the chain of part (a) with a force applied at the ends, find the mean distance $\langle \mathbf{r}_{12} \rangle$ between the ends.

(c) Find the entropy of the chain of part (b).

(d) The chain of part (a) is suspended at one end in a gravitational field of strength g. The mass of each segment of the chain is m. What is the average length of this chain (i.e., $\langle \mathbf{r}_{12} \rangle$) as a function of temperature?

(a) By symmetry, $\langle \mathbf{r}_{12} \rangle = 0$ since there is no preferred direction. The squared distance represents a variance of the position of one end of the chain with the other held fixed. For a single-link chain, this is just the squared length of the chain d^2. Since all links rotate independently, variances add, so the variance for the whole chain is $\langle \mathbf{r}_{12}^2 \rangle = N d^2$. Alternatively, if the displacement of link i is $\mathbf{r}_i$, one can write

$$\begin{aligned}
\langle \mathbf{r}_{12}^2 \rangle &= \left\langle \left(\sum_{i=1}^{N} \mathbf{r}_i \right)^2 \right\rangle \\
&= \left\langle \sum_{i=1}^{N} \mathbf{r}_i^2 + \sum_{i \neq j} \mathbf{r}_i \cdot \mathbf{r}_j \right\rangle \\
&= N \langle \mathbf{r}_1^2 \rangle \\
&= N d^2
\end{aligned}$$

where the cross term vanishes since $\mathbf{r}_i$ and $\mathbf{r}_j$ are independent.

(b) If θ_i is the angle between link i and the applied force, then the potential energy of link i is

$$U_i = -f d \cos \theta_i$$

and so the Boltzmann factor for this link is

$$e^{-\beta U_i} = \exp\left(-\beta f d \cos \theta_i\right)$$

For a single link in 3-dimensional space, the states are all possible solid angles Ω, so the partition function for this link is

$$\begin{aligned}
Z_1 &= \int d\Omega\, e^{-\beta U} \\
&= \int_0^{2\pi} d\varphi \int_{-\pi}^{\pi} d(\cos\theta) \exp\left(-\beta f d \cos\theta\right) \\
&= 2\pi \frac{1}{\beta f d} \left(e^{\beta f d} - e^{-\beta f d}\right) \\
&= \frac{4\pi \sinh \beta f d}{\beta f d}
\end{aligned}$$

and the full partition function for N links is simply $Z = Z_1^N$.

The average energy can be found by differentiating the partition function:

$$\begin{aligned}
\langle U \rangle &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \\
&= -\frac{N}{Z_1} \frac{\partial \log Z_1}{\partial \beta} \\
&= -N \left(\frac{\beta f d}{4\pi \sinh \beta f d} \right) \left(\frac{4\pi f d \cosh \beta f d}{\beta f d} - \frac{4\pi \sinh \beta f d}{\beta^2 f d} \right) \\
&= -N f d \coth(\beta f d) + \frac{N}{\beta}
\end{aligned}$$

Since the energy is also equal to $-\mathbf{f} \cdot \mathbf{r}_{12}$, this also gives

$$|\langle \mathbf{r}_{12} \rangle| = -\frac{\langle U \rangle}{f} = N d \coth(\beta f d) - \frac{N}{\beta f}$$

(c) The entropy is given by

$$S = k_B \log Z + \frac{U}{T}$$

so we have

$$\begin{aligned}
S &= N k_B \log \left(\frac{4\pi \sinh \beta f d}{\beta f d} \right) - \frac{1}{T} \left(-N f d \coth(\beta f d) + \frac{N}{\beta} \right) \\
&= N k_B \left[\log \left(\frac{4\pi \sinh(\beta f d)}{\beta f d} \right) - \beta f d \coth(\beta f d) + 1 \right]
\end{aligned}$$

(d) Indexing segments in the chain from the bottom up, the force on segment i is img. (Technically, the force at the bottom of the segment is $(i-1)mg$, but for a chain with many links, the weight of a single link is negligible.) The average displacement of this segment is then

$$\langle \mathbf{r}_i \rangle = d \coth(imgd\beta) - \frac{1}{img\beta}$$

and then the length of the chain is

$$\langle \mathbf{r}_{12} \rangle = \sum_{i=1}^{N} \langle \mathbf{r}_i \rangle = \sum_{i=1}^{N} \left[d \coth(imgd\beta) - \frac{1}{img\beta} \right]$$

For $N \gg 1$, we can approximate the sum as an integral, so

$$\begin{aligned}
\langle \mathbf{r}_{12} \rangle &= \int_0^N d\lambda \, d \coth(\lambda mgd\beta) - \frac{1}{\lambda mg\beta} \\
&= d \frac{1}{mgd\beta} \left[\log \sinh(\lambda mgd\beta) \right]_0^N - \frac{1}{mg\beta} \left[\log \lambda \right]_0^N \\
&= \frac{1}{mg\beta} \left[\log \sinh(Nmgd\beta) - \log N - \lim_{\lambda \to 0} \left(\log \sinh(\lambda mgd\beta) - \log \lambda \right) \right]
\end{aligned}$$

Note that the $\lambda \to 0$ limit involves the cancellation of two terms that both diverge logarithmically. Their difference, however, is finite. Note that $\sinh x \sim x$ for small x, so $\sinh(\lambda mgd\beta) \sim \lambda mgd\beta$ and

$$\lim_{\lambda \to 0} \left(\log \sinh(\lambda mgd\beta) - \log \lambda \right) = \lim_{\lambda \to 0} \left(\log(\lambda mgd\beta) - \log \lambda \right) = \log(mgd\beta)$$

and thus

$$\langle \mathbf{r}_{12} \rangle = \frac{1}{mg\beta} \log \left(\frac{\sinh(Nmgd\beta)}{Nmgd\beta} \right)$$