1 January 2005, Thermodynamics, Problem 1

1.1 (a)

Since there is no preferred direction, and since the configurations all have equal energy, the average end-to-end distance must be zero. If, like me, you are not convinced by this, a more formal proof follows:

$$\boldsymbol{r_N} = \sum_{i=1}^{N} (acos\theta_i \hat{x} + asin\theta_i \hat{y})$$

Since all the angles are independent of each other, and since the average of cosine and sine over a full cycle is 0, the average end-to-end distance is 0. This implies, if the distribution of probabilities is Gaussian, that the actual form is:

$$P(\boldsymbol{r_N}) = e^{-ar_N^2} \tag{1}$$

But we only obtained the average end-to-end vector, not the average length. For that, we have to average r_N^2, and then take the square root.

$$r_N^2 = a^2 \left((\sum_{i=1}^{N} cos\theta_i)^2 + (\sum_{i=1}^{N} sin\theta_i)^2 \right)$$

When averaging this, all the cross terms from the squares will be 0, because the average of cosine and sine over a full cycle is 0. Thus, the average will just be:

$$r_N^2 = a^2 \left(\sum_{i=1}^{N} cos^2\theta_i + \sum_{i=1}^{N} sin^2\theta_i \right) = Na^2 \tag{2}$$

and the average end-to-end length is $\sqrt{N}a$. Thus, the full form of the probability is:

$$P(\boldsymbol{r_N}) = Ae^{-r_N^2/Na^2}$$

where A is a normalization constant, determined by the condition:

$$\int_0^{Na} \int_0^{2\pi} P(\boldsymbol{r}_N)\, d^2 r_N = 1$$

$$= 2\pi A \int_0^{Na} e^{-r_N^2/Na^2} r_N\, dr_N \approx 2\pi A \int_0^{\infty} e^{-r_N^2/Na^2} r_N\, dr_N = 2\pi A \frac{Na^2}{2}$$

$$P(\boldsymbol{r}_N) = \frac{1}{\pi N a^2} e^{-r_N^2/Na^2} \tag{3}$$

It can be checked that with this probability $< r_N^2 >= Na^2$, as expected.

1.2 (b)

The energy of a configuration is:

$$H = -\boldsymbol{F} \cdot \boldsymbol{r_N}$$

We are asked to calculate the Gibbs free energy. This is done by calculating a "partition function", where instead of varying F we vary r_N. This function has the form:

$$\mathcal{Z} = \int_0^{Na} \int_0^{2\pi} \frac{1}{N\pi a^2} e^{-r_N^2/Na^2} e^{\boldsymbol{F}\cdot\boldsymbol{r_N}/kT} r_N \, d\phi \, dr_N = \int_0^{Na} \int_0^{2\pi} \frac{1}{N\pi a^2} e^{-r_N^2/Na^2} e^{Fr_N cos\phi/kT} r_N \, d\phi \, dr_N$$

Apply the small-F approximation to the exponent to obtain:

$$\mathcal{Z} = \int_0^{Na} \int_0^{2\pi} \frac{1}{N\pi a^2} e^{-r_N^2/Na^2} \left(1 + \frac{Fr_N cos\phi}{kT} + \frac{F^2 r_N^2 cos^2\phi}{2k^2T^2}\right) r_N \, d\phi \, dr_N =$$

$$= 1 + \int_0^{Na} \int_0^{2\pi} \frac{1}{N\pi a^2} e^{-r_N^2/Na^2} \left(\frac{Fr_N cos\phi}{\sqrt{2}kT}\right)^2 r_N \, d\phi \, dr_N = 1 + \int_0^{Na} \frac{1}{Na^2} e^{-r_N^2/Na^2} \left(\frac{Fr_N}{\sqrt{2}kT}\right)^2 r_N \, dr_N =$$

$$\approx 1 + \frac{1}{Na^2} \left(\frac{F}{\sqrt{2}kT}\right)^2 \int_0^{\infty} e^{-r_N^2/Na^2} r_N^3 \, dr_N = 1 + \left(\frac{F}{2kT}\right)^2 Na^2$$

$$G = -kTln\mathcal{Z} \approx -\frac{F^2Na^2}{4kT} \tag{4}$$

1.3 (c)

We want to get the Legendre transform of the Gibbs free energy:

$$A(T, \boldsymbol{r_N}, N) = G(T, \boldsymbol{F}, N) - \boldsymbol{F} \cdot \boldsymbol{r_N}$$

and we have to obtain an expression for $\boldsymbol{F}$ that we can plug into this relation.

$$dG = -SdT + \boldsymbol{r_N} \cdot d\boldsymbol{F} + \mu dN$$

$$\boldsymbol{r}_N = \left(\frac{\partial G}{\partial \boldsymbol{F}}\right)_{T,N} = (\nabla_F G)_{T,N}$$

$$G = -\frac{(F_x^2 + F_y^2)Na^2}{4kT}$$

$$\frac{\partial G}{\partial F_x} = -\frac{F_x Na^2}{2kT}$$

$$(\nabla_F G)_{T,N} = -\frac{\boldsymbol{F}Na^2}{2kT} = \boldsymbol{r}_N \rightarrow \boldsymbol{F} = -\frac{2kT\boldsymbol{r}_N}{Na^2}$$

$$A(T, \boldsymbol{r}_N, N) = -\frac{Na^2}{4kT}\left(\frac{2kT}{Na^2}\right)^2 r_N^2 + \frac{2kTr_N^2}{Na^2} = \frac{kTr_N^2}{Na^2} \tag{5}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{F,N} = -\frac{F^2Na^2}{4kT^2} \tag{6}$$

$$U = A + TS = \frac{kTr^2}{Na^2} - \frac{F^2Na^2}{4kT} = \frac{kT}{Na^2}\left(\frac{FNa^2}{2kT}\right)^2 - \frac{F^2Na^2}{4kT} = 0 \tag{7}$$

1.4 (d)

As we said before, the energy of the configuration is:

$$H = -\boldsymbol{F} \cdot \boldsymbol{r}_N = \frac{2kTr_N^2}{Na^2}$$

which is exactly the potential energy for a Hooke's law spring.