NOTE

Calculation of the integral

$$\boxed{\int_a^b x\, e^{-\alpha x^2} e^{\beta x}\, dx} \qquad (\alpha > 0)$$

We observe that

$$\frac{\partial}{\partial \beta}\int_a^b e^{-\alpha x^2} e^{\beta x}\, dx = \int_a^b x e^{-\alpha x^2} e^{\beta x}\, dx$$

and therefor we take into consideration the integral

$$\int_a^b e^{-\alpha x^2} e^{\beta x}\, dx =$$

$$= \int_a^b e^{-\alpha x^2 + \beta x}\, dx = \int_a^b e^{-\alpha\left(x^2 - \frac{\beta}{\alpha} x\right)} dx$$

$$(p-q)^2 = p^2 - 2pq + q^2$$

$$p = x$$

$$-2pq = -\frac{\beta}{\alpha} x \to 2q = \frac{\beta}{\alpha} \to q = \frac{\beta}{2\alpha}$$

$\int_0,$

$$\int_a^b e^{-\alpha x^2} e^{\beta x}\, dx =$$

$$= e^{\frac{\beta^2}{4\alpha}} \int_a^b e^{-\alpha\left(x^2 - \frac{\beta}{\alpha}x + \frac{\beta^2}{4\alpha^2}\right)} dx$$

$$= e^{\frac{\beta^2}{4\alpha}} \int_a^b e^{-\alpha\left(x - \frac{\beta}{2\alpha}\right)^2} dx$$

$$\xi = x - \frac{\beta}{2\alpha} \qquad d\xi = dx$$

$$\int_a^b e^{-\alpha x^2} e^{\beta x}\, dx = e^{\frac{\beta^2}{4\alpha}} \int_{a-\frac{\beta}{2\alpha}}^{b-\frac{\beta}{2\alpha}} e^{-\alpha \xi^2} d\xi$$

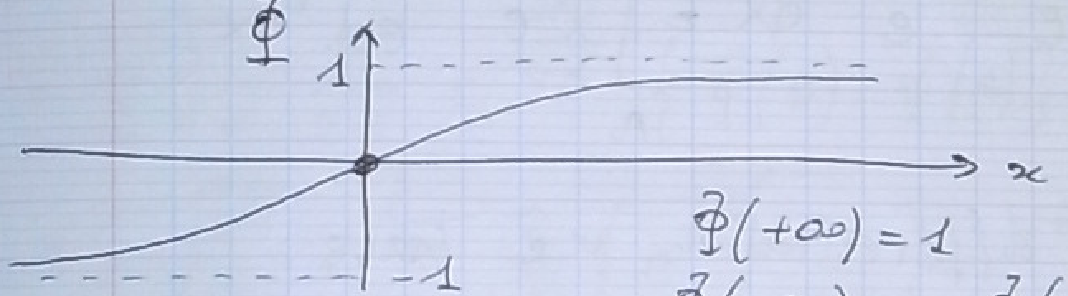
$$\alpha \xi^2 = t^2$$

$$\sqrt{\alpha}\, \xi = t \rightarrow d\xi = \frac{1}{\sqrt{\alpha}} dt$$

$$\int_a^b e^{-\alpha x^2} e^{\beta x}\, dx = \frac{e^{\frac{\beta^2}{4\alpha}}}{\sqrt{\alpha}} \int_{\sqrt{\alpha}\left(a-\frac{\beta}{2\alpha}\right)}^{\sqrt{\alpha}\left(b-\frac{\beta}{2\alpha}\right)} e^{-t^2} dt$$

Now, we use the definition

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \, dt$$



$$\Phi(+\infty) = 1$$
$$\Phi(-x) = -\Phi(x)$$

and, therefore:

$$\int_a^b e^{-\alpha x^2} e^{\beta x} \, dx = \frac{e^{\beta^2/4\alpha}}{\sqrt{\alpha}} \frac{\sqrt{\pi}}{2} \cdot \left[\Phi\left[\sqrt{\alpha}\left(b - \frac{\beta}{2\alpha}\right)\right] - \Phi\left[\sqrt{\alpha}\left(a - \frac{\beta}{2\alpha}\right)\right] \right]$$

So, the first result is:

$$\boxed{\int_a^b e^{-\alpha x^2} e^{\beta x} \, dx = \sqrt{\frac{\pi}{\alpha}} \, \frac{1}{2} \, e^{\beta^2/4\alpha} \cdot \left\{ \Phi\left[\sqrt{\alpha}\left(b - \frac{\beta}{2\alpha}\right)\right] - \Phi\left[\sqrt{\alpha}\left(a - \frac{\beta}{2\alpha}\right)\right] \right\}}$$

The second result can be obtained through the relation

$$\frac{\partial}{\partial \beta}\int_a^b e^{-\alpha x^2} e^{\beta x}\, dx = \int_a^b x\, e^{-\alpha x^2} e^{\beta x}\, dx$$

So, by differentiation we have:

$$\frac{\partial}{\partial \beta}\sqrt{\frac{\pi}{\alpha}}\,\frac{1}{2}\, e^{\frac{\beta^2}{4\alpha}} \cdot \left\{ \Phi(B) - \Phi(A) \right\} =$$

where
$$\boxed{\begin{array}{l} B = \sqrt{\alpha}\left(b - \frac{\beta}{2\alpha}\right) \\ A = \sqrt{\alpha}\left(a - \frac{\beta}{2\alpha}\right) \end{array}}
\begin{array}{l} \rightarrow \frac{\partial B}{\partial \beta} = -\frac{\sqrt{\alpha}}{2\alpha} = -\frac{1}{2\sqrt{\alpha}} \\ \rightarrow \frac{\partial A}{\partial \beta} = -\frac{\sqrt{\alpha}}{2\alpha} = -\frac{1}{2\sqrt{\alpha}} \end{array}$$

$$= \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\,\frac{2\beta}{4\alpha}\, e^{\frac{\beta^2}{4\alpha}} \left\{ \Phi(B) - \Phi(A) \right\} +$$

$$+ \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\, e^{\beta^2/4\alpha} \left\{ \Phi'(B)\frac{\partial B}{\partial \beta} - \Phi'(A)\frac{\partial A}{\partial \beta} \right\}$$

Now, $\Phi'(x) = \frac{2}{\sqrt{\pi}} e^{-x^2}$ and therefore:

$$\int_a^b x\, e^{-\alpha x^2} e^{\beta x}\, dx =$$

$$= \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \frac{\beta}{2\alpha} e^{\frac{\beta^2}{4\alpha}} \left\{ \Phi(B) - \Phi(A) \right\} +$$

$$+ \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\, e^{\frac{\beta^2}{4\alpha}} \frac{2}{\sqrt{\pi}} \left\{ e^{-B^2}\left(-\frac{1}{2\sqrt{\alpha}}\right) - e^{-A^2}\left(-\frac{1}{2\sqrt{\alpha}}\right) \right\}$$

$$= \sqrt{\frac{\pi}{\alpha}} \frac{\beta}{4\alpha} e^{\frac{\beta^2}{4\alpha}} \left\{ \Phi(B) - \Phi(A) \right\} +$$

$$- \frac{1}{2\alpha} e^{\frac{\beta^2}{4\alpha}} \left[e^{-B^2} - e^{-A^2} \right]$$

Finally:

$$\boxed{\begin{aligned} &\int_a^b x\, e^{-\alpha x^2} e^{\beta x}\, dx = \\ &\quad = \sqrt{\frac{\pi}{\alpha}} \frac{\beta}{4\alpha} e^{\frac{\beta^2}{4\alpha}} \left[\Phi(B) - \Phi(A) \right] + \\ &\quad\quad - \frac{1}{2\alpha} e^{\beta^2/4\alpha} \left[e^{-B^2} - e^{-A^2} \right] \end{aligned}}$$

where A and B have been previously defined.

Particular case: if $a=0$ and $b \to \infty$ we have:

$$a=0 \Rightarrow A = -\sqrt{\alpha}\,\frac{\beta}{2\alpha} = -\frac{\beta}{2\sqrt{\alpha}}$$

$$b \to \infty \Rightarrow B \to \infty \Rightarrow \Phi(B) = 1$$

and therefore:

$$\boxed{\int_0^{+\infty} x\, e^{-\alpha x^2} e^{\beta x}\, dx} =$$

$$= \sqrt{\frac{\pi}{\alpha}}\,\frac{\beta}{4\alpha}\, e^{\frac{\beta^2}{4\alpha}}\left[1-\Phi\left(-\frac{\beta}{2\sqrt{\alpha}}\right)\right] +$$

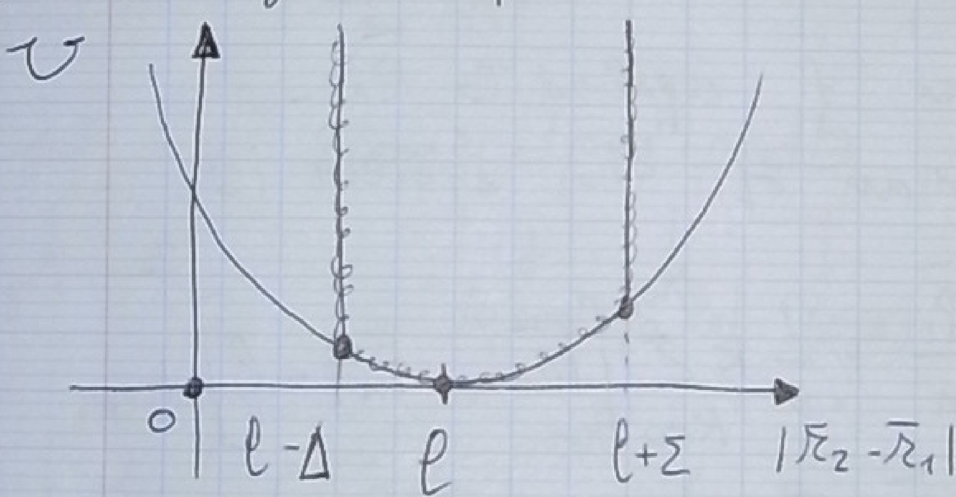
$$-\frac{1}{2\alpha}\, e^{\beta^2/4\alpha}\left[-e^{-\frac{\beta^2}{4\alpha}}\right] =$$

$$= \frac{1}{2\alpha} + \frac{\beta}{4\alpha}\sqrt{\frac{\pi}{\alpha}}\, e^{\frac{\beta^2}{4\alpha}}\left[1-\Phi\left(-\frac{\beta}{2\sqrt{\alpha}}\right)\right] =$$

$$= \boxed{\frac{1}{2\alpha} + \frac{\beta}{4\alpha}\sqrt{\frac{\pi}{\alpha}}\, e^{\frac{\beta^2}{4\alpha}}\left[1+\Phi\left(\frac{\beta}{2\sqrt{\alpha}}\right)\right]}$$

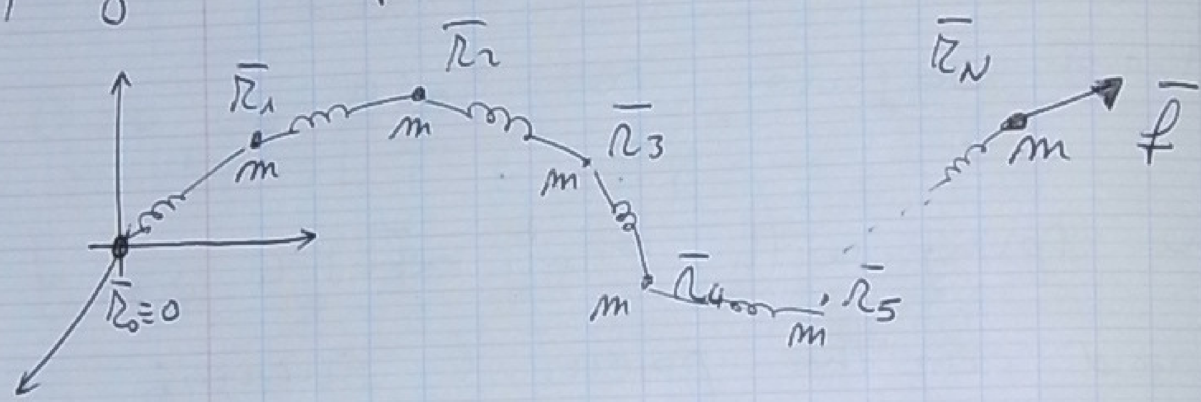
Polimer model with springs having finite extension and without angular potentials.

The spring with finite extension is defined by the potential energy:



where $\bar{r}_1$ and $\bar{r}_2$ are the points connected by the spring, l is its length at equilibrium. Two ideal walls at $l-\Delta$ and $l+\Sigma$ impose the finite extension of the spring both for expansion and compression.

We consider a chain of masses and springs as follow:



and a force $\bar{f}$ applied to $\bar{r}_N$ -
the Hamiltonian of the system is

$$H = \sum_{i=1}^{N} \frac{\bar{p}_i \cdot \bar{p}_i}{2m} + \frac{1}{2} k \sum_{k=0}^{N-1} \left[|\bar{r}_{k+1} - \bar{r}_k| - \ell \right]^2 + - \bar{f} \cdot \bar{r}_N$$

The partition function in the Gibbs ensemble is given by:

$$Z_f = \int_{\{p\}} \int_{\{q\}} e^{-H/k_B T} \, dq \, dp =$$

(k_B is the Boltzmann constant different from the spring constant k!)

$$= \Bigg\{ \underbrace{\int_{\mathbb{R}^3} \exp\left(-\frac{1}{2mKT}\,\bar{p}\cdot\bar{p}\right) d\bar{p}}_{1} \Bigg\}^N .$$

$$\cdot \int_{\mathbb{R}^3} \overset{N}{\cdots} \int_{\mathbb{R}^3} \exp\left(-\frac{k}{2k_BT}\sum_{k=0}^{N-1}\Big[\underbrace{|\bar{r}_{k+1}-\bar{r}_k|}_{\in(\ell-\Delta,\,\ell+\Sigma)}-\ell\Big]^2 + \frac{\bar{f}\cdot\bar{r}_N}{k_BT}\right) d\bar{r}_1 \cdots d\bar{r}_N$$

Calculation of 1:

$$d\bar{p} = p^2 \sin\theta \, dp \, d\varphi \, d\theta$$

$$\underset{\mathbb{R}^3}{\downarrow} \qquad \underset{(0,+\infty)}{\downarrow} \quad \underset{(0,2\pi)}{\downarrow} \quad \underset{(0,\pi)}{\downarrow}$$

$$1 = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta \, d\theta \int_0^{+\infty} \exp\left(-\frac{p^2}{2mk_BT}\right) p^2 \, dp$$

but, $\displaystyle\int_0^{+\infty} e^{-q^2x^2}\,dx = \frac{\sqrt{\pi}}{2q}$ or if

$q^2 = \alpha > 0$ we have:

$$\int_0^{+\infty} e^{-\alpha x^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

By differentiating:

$$\frac{\partial}{\partial\alpha}\int_0^{+\infty} e^{-\alpha x^2}dx = \frac{\partial}{\partial\alpha}\frac{\sqrt{\pi}}{2}\alpha^{-1/2} =$$

$$= \frac{\sqrt{\pi}}{2}\left(-\frac{1}{2}\right)\alpha^{-\frac{1}{2}-1}$$

So:

$$\int_0^{+\infty} -x^2 e^{-\alpha x^2}dx = -\frac{\sqrt{\pi}}{4}\alpha^{-3/2}$$

and finally:

$$\boxed{\int_0^{+\infty} x^2 e^{-\alpha x^2}dx = \frac{1}{4\alpha}\sqrt{\frac{\pi}{\alpha}}}$$

Returning to 1 we obtain:

$$1 = 2\pi\cdot 2\cdot\int_0^{+\infty}\exp\left(-\frac{p^2}{2mk_BT}\right)p^2dp =$$

$$= 4\pi\frac{1}{4}2mk_BT\sqrt{\pi\, 2mk_BT} =$$

$$= \left(\sqrt{2\pi m k_B T}\right)^3$$

The partition function is:

$$Z_f = \left(\sqrt{2\pi m k_B T}\right)^{3N} \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} \exp\left(-\frac{K}{2k_B T}\sum_{k=0}^{N-1}\left[|\bar{r}_{k+1}-\bar{r}_k|-\ell\right]^2 + \frac{\bar{f}\cdot\bar{r}_N}{k_B T}\right) d\bar{r}_1 \cdots d\bar{r}_N$$

We let

$$\begin{cases} \bar{\xi}_1 = \bar{r}_1 - \bar{r}_0 \\ \vdots \\ \bar{\xi}_N = \bar{r}_N - \bar{r}_{N-1} \end{cases}$$

and then $\bar{\xi}_{k+1} = \bar{r}_{k+1} - \bar{r}_k$ -

Moreover, $\sum_{k=1}^{N} \bar{\xi}_k = \bar{r}_N - \bar{r}_0$ and

$\{d\bar{r}_i\} = \{d\bar{\xi}_i\}$ since the determinant of the transformation is unitary.

We have considered $\bar{r}_0 \equiv \bar{0}$ and therefore we obtain:

$$Z = \left(\sqrt{2\pi m k_B T}\right)^{3N} \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} \exp\left(-\frac{K}{2k_B T}\sum_{k=1}^{N}\left[|\bar{\xi}_k|-\ell\right]^2 + \frac{\bar{f}\cdot}{k_B T}\sum_{k=1}^{N}\bar{\xi}_k\right)\{d\bar{\xi}_i\}$$

$$= \left(\sqrt{2\pi m k_B T}\right)^{3N} \left[\int_{\mathbb{R}^3} \exp\left(-\frac{k}{2k_B T} \left[|\bar{\xi}| - \ell \right]^2 + \frac{\bar{f} \cdot \bar{\xi}}{k_B T} \right) d\bar{\xi} \right]^N \quad (*)$$

We let $\bar{f} = (0, 0, f)$

$$d\bar{\xi} = \xi^2 \sin\theta \, d\xi \, d\varphi \, d\theta$$

$$|\bar{\xi}| = \xi$$

$$\bar{f} \cdot \bar{\xi} = f \xi \cos\theta$$

Thus

$$Z_f = \left(\sqrt{2\pi m k_B T}\right)^{3N} \left[\int_{\ell-\Delta}^{\ell+\Sigma} \int_0^{2\pi} \int_0^{\pi} \cdot \right.$$

$$\exp\left(-\frac{k}{2k_B T} (\xi - \ell)^2 + \frac{f \xi \cos\theta}{k_B T} \right) \cdot$$

$$\left. \xi^2 \sin\theta \, d\xi \, \underbrace{d\varphi}_{2\pi} \, d\theta \right]^N =$$

$$= \left(\sqrt{2\pi m k_B T}\right)^{3N} \left[2\pi \int_{\ell-\Delta}^{\ell+\Sigma} \exp\left(-\frac{K}{2k_BT}(\xi-\ell)^2\right) \cdot \xi^2 \cdot \right.$$

$$\left. \cdot \underbrace{\int_0^{\pi} \sin\theta \exp\left(\frac{f\xi\cos\theta}{k_BT}\right) d\theta}_{\circledast}\ d\xi \right]^N =$$

$$\circledast = \int_0^{\pi} \sin\theta \exp\left(\frac{f\xi\cos\theta}{k_BT}\right) d\theta =$$

$$\cos\theta = \eta \rightarrow d\eta = -\sin\theta\, d\theta$$

$$= -\int_{+1}^{-1} \exp\left(\frac{f\xi\eta}{k_BT}\right) d\eta = \int_{-1}^{+1} \exp\left(\frac{f\xi\eta}{k_BT}\right) d\eta =$$

$$= \frac{k_BT}{f\xi} \exp\left(\frac{f\xi\eta}{k_BT}\right)\Bigg|_{-1}^{+1} =$$

$$= \frac{k_BT}{f\xi}\left[\exp\left(\frac{f\xi}{k_BT}\right) - \exp\left(-\frac{f\xi}{k_BT}\right)\right]$$

Therefore:

$$Z_f = \left(2\pi m k_BT\right)^{\frac{3N}{2}} (2\pi)^N \left[\int_{\ell-\Delta}^{\ell+\Sigma} \exp\left(-\frac{k}{2k_BT}(\xi-\ell)^2\right) \cdot \right.$$

$$\left. \cdot \left[\exp\left(\frac{f\xi}{k_BT}\right) - \exp\left(-\frac{f\xi}{k_BT}\right)\right] \frac{k_BT\xi}{f}\, d\xi \right]^N$$

Or:

$$Z_f = \left(2\pi m K_B T\right)^{\frac{3N}{2}} \left(\frac{2\pi K_B T}{f}\right)^N \cdot$$

$$\cdot \left[\int_{\ell-\Delta}^{\ell+\Sigma} \exp\left(-\frac{k}{2K_B T}(\xi-\ell)^2\right) \left[\exp\left(\frac{f\xi}{K_B T}\right) - \exp\left(-\frac{f\xi}{K_B T}\right)\right] \xi \, d\xi \right]^N$$

This is the partition function integral and it can be solved through the result found at page 5:

$$\int_a^b x e^{-\alpha x^2} e^{\beta x} dx =$$

$$= \sqrt{\frac{\pi}{\alpha}} \frac{\beta}{4\alpha} e^{\frac{\beta^2}{4\alpha}} \left[\Phi(B) - \Phi(A)\right] +$$

$$- \frac{1}{2\alpha} e^{\beta^2/4\alpha} \left[e^{-B^2} - e^{-A^2}\right]$$

where
$$A = \sqrt{\alpha}\left(a - \frac{\beta}{2\alpha}\right)$$
$$B = \sqrt{\alpha}\left(b - \frac{\beta}{2\alpha}\right)$$

Now we observe that

$$\exp\left(-\frac{k}{2k_BT}(\xi-\ell)^2\right) =$$

$$= \exp\left(-\frac{k}{2k_BT}\xi^2 + \frac{k}{2k_BT}2\xi\ell - \frac{k}{2k_BT}\ell^2\right)$$

and then:

$$\# = \int_{\ell-\Delta}^{\ell+\Sigma} \exp\left(-\frac{k}{2k_BT}\xi^2\right)\exp\left(-\frac{k}{2k_BT}\ell^2\right)\cdot$$

$$\cdot \exp\left(\frac{k}{2k_BT}2\xi\ell\right)\left[\exp\left(\frac{f\xi}{k_BT}\right)-\exp\left(-\frac{f\xi}{k_BT}\right)\right]\xi\, d\xi$$

$$= \exp\left(-\frac{k\ell^2}{2k_BT}\right)\int_{\ell-\Delta}^{\ell+\Sigma}\exp\left(-\frac{k\xi^2}{2k_BT}\right)\cdot$$

$$\cdot\left[\exp\left(\frac{(k\ell+f)\xi}{k_BT}\right)-\exp\left(\frac{(k\ell-f)\xi}{k_BT}\right)\right]\xi\, d\xi$$

So we let $\alpha = \dfrac{k}{2k_BT}$ $\qquad a = \ell-\Delta$

$\qquad b = \ell+\Sigma$

$$\beta^{\pm} = \frac{k\ell \pm f}{k_BT}$$

$$\boxed{A^{\pm}} = \sqrt{\alpha}\left(a - \frac{\beta^{\pm}}{2\alpha}\right) =$$

$$= \sqrt{\frac{K}{2K_BT}}\left(\ell - \Delta - \frac{\frac{K\ell \pm f}{\cancel{K_BT}}}{\frac{K}{\cancel{K_BT}}}\right) =$$

$$= \sqrt{\frac{K}{2K_BT}}\left(\cancel{\ell} - \Delta - \cancel{\ell} \mp \frac{f}{K}\right) =$$

$$= \sqrt{\frac{K}{2K_BT}}\left(-\Delta \mp \frac{f}{K}\right) = \boxed{-\sqrt{\frac{K}{2K_BT}}\left(\Delta \pm \frac{f}{K}\right)}$$

$$\boxed{B^{\pm}} = \sqrt{\alpha}\left(b - \frac{\beta^{\pm}}{2\alpha}\right) =$$

$$= \sqrt{\frac{K}{2K_BT}}\left(\ell + \Sigma - \frac{\frac{K\ell \pm f}{K_BT}}{\frac{K}{K_BT}}\right) =$$

$$= \sqrt{\frac{K}{2K_BT}}\left(\cancel{\ell} + \Sigma - \cancel{\ell} \mp \frac{f}{K}\right) =$$

$$= \sqrt{\frac{K}{2K_BT}}\left(\Sigma \mp \frac{f}{K}\right) = \boxed{-\sqrt{\frac{K}{2K_BT}}\left(-\Sigma \pm \frac{f}{K}\right)}$$

$$\sqrt{\frac{\pi}{\alpha}} = \sqrt{\frac{\pi}{\frac{k}{2K_BT}}} = \sqrt{\frac{2\pi K_B T}{K}}$$

$$\frac{\beta^{\pm}}{\alpha} = \frac{Kl \pm f}{\cancel{K_BT}} \frac{2\cancel{K_BT}}{K} =$$

$$= 2\left(l \pm \frac{f}{K}\right)$$

$$\frac{\beta^2}{4\alpha} = \left(\frac{Kl \pm f}{K_BT}\right)^2 \frac{2K_BT}{4K} =$$

$$= \frac{(Kl \pm f)^2}{2K K_B T}$$

(check: $[Kl] = [f] = N$

$[K] = N/m$

$[K_BT] = J = N \cdot m$

$$\left[\frac{(Kl \pm f)^2}{2K K_BT}\right] = \frac{N^2}{\frac{N}{m} \cdot N \cdot m} = \text{adimensional}$$)

Thus:

$$Z_f = \left(2\pi m k_B T\right)^{\frac{3N}{2}} \left(\frac{2\pi k_B T}{f}\right)^N \exp\left(-\frac{kN\ell^2}{2k_B T}\right) \cdot$$

$$\cdot \left\{ \sqrt{\frac{2\pi k_B T}{k}}\, \frac{1}{2}\left(\ell + \frac{f}{k}\right) \exp\left(\frac{(k\ell + f)^2}{2k k_B T}\right) \cdot \right.$$

$$\cdot \left[\Phi(B^+) - \Phi(A^+)\right] - \frac{k_B T}{k} \exp\left(\frac{(k\ell + f)^2}{2k k_B T}\right) \cdot$$

$$\cdot \left[e^{-(B^+)^2} - e^{-(A^+)^2}\right] +$$

$$\sqrt{\frac{2\pi k_B T}{k}}\, \frac{1}{2}\left(\ell - \frac{f}{k}\right) \exp\left(\frac{(k\ell - f)^2}{2k k_B T}\right) \cdot$$

$$\cdot \left[\Phi(B^-) - \Phi(A^-)\right] + \frac{k_B T}{k} \exp\left(\frac{(k\ell - f)^2}{2k k_B T}\right) \cdot$$

$$\left. \cdot \left[e^{-(B^-)^2} - e^{-(A^-)^2}\right] \right\}^N$$

where:

$$\boxed{\begin{aligned} B^{+} &= -\sqrt{\frac{k}{2k_BT}}\left(-\Sigma+\frac{f}{k}\right) \\ A^{+} &= -\sqrt{\frac{k}{2k_BT}}\left(\Delta+\frac{f}{k}\right) \\ B^{-} &= -\sqrt{\frac{k}{2k_BT}}\left(-\Sigma-\frac{f}{k}\right) \\ A^{-} &= -\sqrt{\frac{k}{2k_BT}}\left(\Delta-\frac{f}{k}\right) \end{aligned}}$$

A particular case is given by a series of springs without limitations on the extension. In this case we have $\Delta = \ell$ and $\Sigma \to \infty$ (see Fig. pag. 7 for details). Thus, we have $U_{ij} = \frac{1}{2}k(|\bar{r}_i - \bar{r}_j| - \ell)^2$ where $0 < |\bar{r}_i - \bar{r}_j| < +\infty$, as usual.

The coefficients $B^{\pm}$ and $A^{\pm}$ assume the values:

$$B^{+} \rightarrow +\infty$$

$$B^{-} \rightarrow +\infty$$

$$A^{+} = -\sqrt{\frac{K}{2K_BT}}\left(\ell + \frac{f}{K}\right)$$

$$A^{-} = -\sqrt{\frac{K}{2K_BT}}\left(\ell - \frac{f}{K}\right)$$

$$\Phi(B^{+}) = \Phi(B^{-}) \rightarrow 1$$

$$e^{-(B^{\pm})^2} \rightarrow 0$$

$$(A^{\pm})^2 = \frac{K}{2K_BT}\left(\ell \pm \frac{f}{K}\right)^2 =$$

$$= \frac{(K\ell \pm f)^2}{2KK_BT}$$

So, when $\Delta \to \ell$ and $\Sigma \to 0$ we obtain:

$$Z_f = \left(2\pi m k_B T\right)^{\frac{3N}{2}} \left(\frac{2\pi k_B T}{f}\right)^N \cancel{\exp\left(-\frac{\kappa N \ell^2}{2k_B T}\right)} \cdot$$

$$\cdot \left\{ \frac{1}{2}\sqrt{\frac{2\pi k_B T}{\kappa}} \left(\ell + \frac{f}{\kappa}\right) \cancel{\exp\left(\frac{\kappa^2 \ell^2}{2\kappa k_B T}\right)} \exp\left(\frac{2\kappa \ell f}{2\kappa k_B T}\right) \right.$$

$$\exp\left(\frac{f^2}{2\kappa k_B T}\right) \left[1 - \Phi(A^+)\right] + \cancel{\frac{k_B T}{\kappa}} +$$

$$- \frac{1}{2}\sqrt{\frac{2\pi k_B T}{\kappa}} \left(\ell - \frac{f}{\kappa}\right) \cancel{\exp\left(\frac{\kappa^2 \ell^2}{2\kappa k_B T}\right)} \exp\left(\frac{-2\kappa \ell f}{2\kappa k_B T}\right)$$

$$\left. \cdot \exp\left(\frac{f^2}{2\kappa k_B T}\right) \left[1 - \Phi(A^-)\right] - \cancel{\frac{k_B T}{\kappa}} \right\}^N =$$

$$= \left(2\pi m k_B T\right)^{3N/2} \left(\frac{2\pi k_B T}{f}\right)^N \frac{1}{2^N} \left(\frac{2\pi k_B T}{\kappa}\right)^{N/2} \cdot \exp\left(\frac{N f^2}{2\kappa k_B T}\right)$$

$$\cdot \left\{ \left(\ell + \frac{f}{\kappa}\right) \exp\left(\frac{\ell f}{k_B T}\right) \left[1 - \Phi(A^+)\right] + \right.$$

$$\left. - \left(\ell - \frac{f}{\kappa}\right) \exp\left(-\frac{\ell f}{k_B T}\right) \left[1 - \Phi(A^-)\right] \right\}^N$$

- and finally, if $\Delta = \ell$ and $\varepsilon \to \infty$ we have the partition function:

$$\boxed{\begin{aligned} Z_f &= \frac{(2\pi k_B T)^{3N} \, m^{\frac{3N}{2}}}{(2f)^N \, k^{N/2}} \exp\left(\frac{N f^2}{2 k k_B T}\right) \cdot \\ &\cdot \left\{ \left(\ell + \frac{f}{k}\right) \exp\left(\frac{\ell f}{k_B T}\right) \left[1 - \Phi(A^+)\right] + \right. \\ &\left. - \left(\ell - \frac{f}{k}\right) \exp\left(-\frac{\ell f}{k_B T}\right) \left[1 - \Phi(A^-)\right] \right\}^N \end{aligned}}$$

<u>where</u>:

$$\boxed{\begin{aligned} A^+ &= -\sqrt{\frac{k}{2 k_B T}} \left(\ell + \frac{f}{k}\right) \\ A^- &= -\sqrt{\frac{k}{2 k_B T}} \left(\ell - \frac{f}{k}\right) \end{aligned}}$$

Turning back to the general case we can write the partition function in a more convenient way by considering that:

$$\exp\left(\frac{(\kappa\ell \pm f)^2}{2\kappa k_B T}\right) =$$

$$= \exp\left(\frac{\kappa^2\ell^2}{2\kappa k_B T}\right)\exp\left(\pm\frac{2\kappa\ell f}{2\kappa k_B T}\right)\exp\left(\frac{f^2}{2\kappa k_B T}\right) =$$

$$= \exp\left(\frac{\kappa\ell^2}{2k_B T}\right)\exp\left(\pm\frac{\ell f}{k_B T}\right)\exp\left(\frac{f^2}{2\kappa k_B T}\right)$$

In fact, the expression of pag. 18 assumes the form:

$$Z_f = \left(2\pi m K_B T\right)^{\frac{3N}{2}} \left(\frac{2\pi K_B T}{f}\right)^{N} \exp\left(\frac{N f^2}{2 K K_B T}\right) \cdot$$

$$\cdot \left\{ \frac{1}{2}\sqrt{\frac{2\pi K_B T}{K}} \left(\ell + \frac{f}{K}\right) e^{+\frac{\ell f}{K_B T}} \left[\Phi(B^+) - \Phi(A^+)\right] + \right.$$

$$- \frac{K_B T}{K} e^{+\frac{\ell f}{K_B T}} \left[e^{-(B^+)^2} - e^{-(A^+)^2}\right] +$$

$$- \frac{1}{2}\sqrt{\frac{2\pi K_B T}{K}} \left(\ell - \frac{f}{K}\right) e^{-\frac{\ell f}{K_B T}} \left[\Phi(B^-) - \Phi(A^-)\right]$$

$$\left. + \frac{K_B T}{K} e^{-\frac{\ell f}{K_B T}} \left[e^{-(B^-)^2} - e^{-(A^-)^2}\right] \right\}^{N}$$

Where $A^\pm$ and $B^\pm$ are defined at page 19.

Some comments about the use of the partition function (in the different versions):

the eq. (*), pag. 12, shows, inside the brackets, a 3D Fourier Transform of the function $\exp\left(-\frac{k}{2K_BT}[|\bar{\xi}|-e]^2\right)$ since the term $\exp\left(\frac{\bar{f}\cdot\bar{\xi}}{K_BT}\right)d\bar{\xi}$ completes the integral. It means that we are performing a Fourier transform of a function having spherical symmetry (i.e. depending only on $|\bar{\xi}|$) and, therefore, the partition function also depends directly on the value of $|\bar{f}|$.

For this reason we have adopted the hypothesis $\bar{f}=(0,0,f)$ at pag. 12

So, in order to have $Z_f(\bar{f})$,
it is sufficient to make the substitution $f \to |\bar{f}|$ inside the previous expressions.
Since we are working within the Gibbs ensemble, the partition function must be used in the following way in order to obtain the force-elongation curve:

$$\bar{r} = kT \frac{\partial}{\partial \bar{f}} \ln Z_f(\bar{f})$$

So, we can write

$$\bar{r} = kT \frac{\partial}{\partial \bar{f}} \ln Z_f(|\bar{f}|) =$$

$$= kT \frac{1}{Z_f} \frac{\partial Z_f}{\partial \bar{f}} =$$

$$= kT \frac{1}{Z_f} \frac{\partial Z_f}{\partial f} \frac{\partial f}{\partial \bar{f}} =$$

$$= KT \frac{1}{Z_f} \frac{\partial Z_f}{\partial f} \frac{\bar{f}}{f}$$

in fact $\dfrac{\partial f}{\partial \bar{f}} = \dfrac{\bar{f}}{f}$

(proof: $\dfrac{\partial f}{\partial \bar{f}} = \left(\dfrac{\partial f}{\partial f_1}, \dfrac{\partial f}{\partial f_2}, \dfrac{\partial f}{\partial f_3} \right)$

$$\frac{\partial f}{\partial f_i} = \frac{\partial \sqrt{f_1^2 + f_2^2 + f_3^2}}{\partial f_i} = \frac{1}{2f} \cdot 2 f_i = \frac{f_i}{f}$$

i.e. $\dfrac{\partial f}{\partial \bar{f}} = \left(\dfrac{f_1}{f}, \dfrac{f_2}{f}, \dfrac{f_3}{f} \right) = \dfrac{\bar{f}}{f}$)

but $\bar{f}/f$ is the unit vector along which the force is applied and therefor we may consider the scalar constitutive equation:

$$\boxed{\Gamma = KT \frac{1}{Z_f} \frac{\partial Z_f}{\partial f} \quad \text{with } Z_f = Z_f(f)} \tag{a}$$

and $\Gamma = |F|$.

When we want To consider the Helmoltz ensemble we need To apply the Laplace integral in the well-known form

$$Z_r(r) = \frac{1}{(2\pi kT)^{7/2} \, m^{9/2}} \int_{-\infty}^{+\infty} Z_f(i\eta) \frac{\eta}{r} \sin \frac{\eta r}{kT} \, d\eta$$

and we obtain the constitutive equation in the form

$$\boxed{f = -kT \frac{\partial}{\partial r} \ln Z_r \quad \text{with } Z_r = Z_r(r)}$$

(b)

It is important To draw a comparison between (a) and (b) for several values of N in order to understand the validity of the thermodynamic limit.

The limit for high values of K and the Freely-Jointed Chain model

When $K \to \infty$ the springs becomes completely rigid and they assume the behavior of segments of fixed length ℓ. Each segment is freely moving remaining attached to the previous and the following link.

In order to evaluate the limit for $K \to \infty$ of the previous theory we must pay attention since we have to evaluate the limit of the overall density distribution and not of the sole partition function.

So, to do this, we consider the Hamiltonian of pag. 8 and the density

$$\rho(q,p) = \frac{e^{-H/k_B T}}{Z_f}$$

where

$$H = \sum_{i=1}^{N} \frac{\bar{p}_i \cdot \bar{p}_i}{2m} + \frac{1}{2} k \sum_{k=0}^{N-1} \left[|\bar{r}_{k+1} - \bar{r}_k| - \ell \right]^2 - \bar{f} \cdot \bar{r}_n$$

Now, to solve the problem, we take into consideration a particular representation of the delta-function: at page 9 we have proved that

$$\int_0^{+\infty} e^{-\alpha x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$$

and, therefore:

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

or, equivalently:

$$\sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = 1$$

It means that

$$\boxed{\sqrt{\frac{\alpha}{\pi}} e^{-\alpha x^2} \xrightarrow[\alpha \to +\infty]{} \delta(x)}$$

At the end we must consider

$$\lim_{K\to\infty} \rho = \lim_{K\to\infty} \frac{K^{N/2}\, e^{-H/k_B T}}{K^{N/2}\int e^{-H/k_B T}\, dq\,dp}$$

in order to have finite limits both in numerator and denominator.
So, the new partition function is

$$Z_{f\,FJC} = \lim_{K\to\infty} K^{N/2} Z_f$$

From eq. at page 19 we have

$$\left.\begin{aligned} B^+ &= B^- \to +\infty \\ A^+ &= A^- \to -\infty \end{aligned}\right\} \text{ if } K \to +\infty$$

then, $\Phi(B^+) - \Phi(A^+) = \Phi(B^-) - \Phi(A^-) =$

$$= +1 - (-1) = 2$$

So, we can use the general expression of page 23 and we simply obtain:

$$\mathcal{Z}_{f\,FJC} = \lim_{k\to\infty} k^{N/2} Z_f =$$

$$= (2\pi m k_B T)^{3N/2} \left(\frac{2\pi k_B T}{f}\right)^N e^N (2\pi k_B T)^{N/2} \cdot$$

$$\cdot \left\{ e^{\frac{\ell f}{k_B T}} - e^{-\frac{\ell f}{k_B T}} \right\}^N =$$

$$= \text{costante} \times \left(\frac{\sinh \frac{\ell f}{k_B T}}{\frac{\ell f}{k_B T}} \right)^N$$

finally neglecting the constant:

$$\boxed{\mathcal{Z}_{FJC} = \left(\frac{\sinh \frac{\ell f}{k_B T}}{\frac{\ell f}{k_B T}} \right)^N}$$

From this equation we have

$$\Gamma = KT \frac{\partial \ln}{\partial f} Z_{FJC} = \qquad x = \frac{\ell f}{K_B T}$$

$$= KT \frac{\partial}{\partial x}\{\ln Z_{FJC}\} \cdot \frac{\partial x}{\partial f} =$$

$$= \ell \frac{\partial}{\partial x}\{\ln Z_{FJC}\} =$$

$$= \ell \frac{\partial}{\partial x}\left\{\ln\left[\frac{\sinh x}{x}\right]^N\right\} =$$

$$= N\ell \frac{\partial}{\partial x}\left\{\ln \frac{\sinh x}{x}\right\} =$$

$$= N\ell \frac{\partial}{\partial x}\{\ln \sinh x - \ln x\} =$$

$$= N\ell \left\{\frac{\cosh x}{\sinh x} - \frac{1}{x}\right\} =$$

$$= N\ell \left\{\coth\left(\frac{f\ell}{K_B T}\right) - \frac{K_B T}{f\ell}\right\}$$

At the end we have

$$\boxed{r = N\ell \, \mathcal{L}\left(\frac{f\ell}{k_B T}\right)}$$

where $\mathcal{L}(x)$ is the Langevin function:

$$\boxed{\mathcal{L}(x) = \coth(x) - \frac{1}{x}}$$