統計力学A VIII

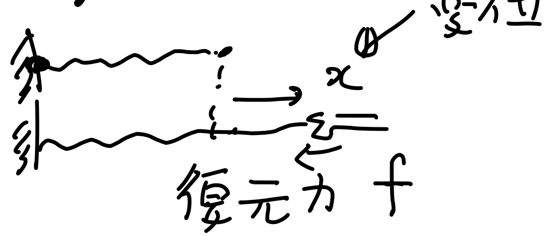
講義メモ

2022/12/06

§ 今日の目標

- ✓ ゴムの熱力学：エントロピー力
- ✓ 統計力学の設定
- ✓ エントロピー力の計算

§ 1次元ばねの熱力学



$$\begin{cases} f = -k(T)\,x \\ C = C_0 \end{cases}$$

$$F(T, x) - F(T, 0) = \frac{1}{2} k(T)\, x^2$$

$\Longrightarrow$ 熱力学 ; $k(T) = k_0 + k_1 T$

$k_0 \gg k_1 T$; エネルギー弾性 $\quad U(T, x) - U(T, 0) = \frac{1}{2} k_0 x^2$

$k_0 \ll k_1 T$; エントロピー弾性 $\quad S(T, x) - S(T, 0) = -\frac{1}{2} k_0 x^2$

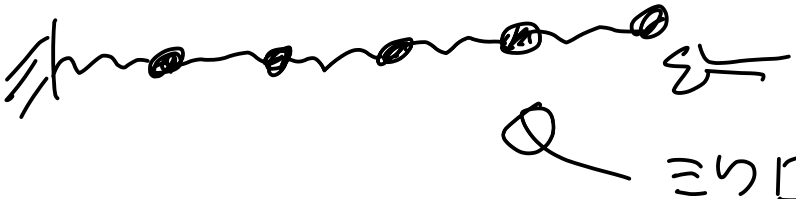
ゴム : エントロピー弾性

理想ゴム $k_0 = 0$

§ ゴムの特徴

・等温環境で引っ張っても内部にエネルギーが蓄えられない

・復元力が働く



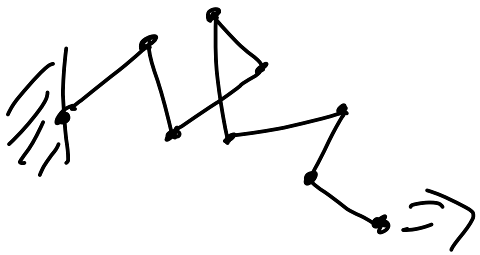
← こんな感じではない

ミクロなバネの集まりでマクロなバネができ

要素レベルにはない"復元力"が集団レベルで生じる

「力の創発」

§ ゴムの描像



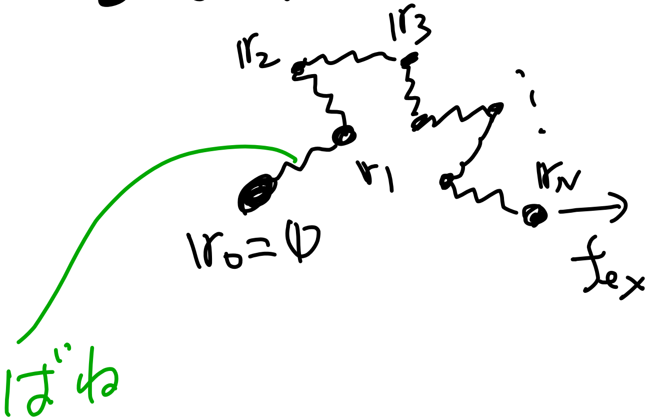
◎ 自由に回転できる"剛体"棒

⟶ 伸ばしても $\Delta U = 0$

◎ 復元力 ??

統計力学で具体的に計算する!!

§ 設定



$$\Gamma = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)$$

かたいバネ
$\beta K a^2 \gg 1$

$$H(\Gamma; f_{ex}, N)$$
$$= \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \sum_{i=1}^{N} \frac{K}{2}\left(|\mathbf{r}_i - \mathbf{r}_{i-1}| - a\right)^2 \underline{- f_{ex} x_N}$$

自然長

$$\rho^{c}_{\beta, f_{ex}}(\Gamma) = \frac{1}{Z(\beta, f_{ex}, N)} e^{-\beta H(\Gamma; f_{ex}, N)}$$

$$X = \langle x_N \rangle^{c}_{\beta, f_{ex}} = \int d\Gamma \, x_N \frac{1}{Z(\beta, f_{ex}, N)} e^{-\beta H(\Gamma; f_{ex}, N)}$$

$$= \frac{k_B T}{Z(\beta, f_{ex}, N)} \frac{\partial}{\partial f_{ex}} Z(\beta, f_{ex}, N) = k_B T \frac{\partial}{\partial f_{ex}} \log Z(\beta, f_{ex}, N) \quad //$$

$$\boxed{\begin{aligned} &Z(\beta, f_{ex}, N) \\ &= \int d\Gamma \, e^{-\beta H(\Gamma; f_{ex}, N)} \end{aligned}}$$

§ 計算 - $\mathbf{r} \to \mathbf{q}$ -

$$Z(\beta, f_{ex}, N) = \int d\mathbf{p}_1 \cdots d\mathbf{p}_N \, e^{-\frac{\beta}{2m}\sum_{i=1}^{N}|\mathbf{p}_i|^2} \to Z_K(\beta, N)$$

$$\times \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, e^{-\frac{\beta}{2}K\sum_{i=1}^{N}(|\mathbf{r}_i - \mathbf{r}_{i-1}| - a)^2 + \beta f_{ex} x_N} \to Z_C(\beta, f_{ex}, N)$$

$$\frac{\partial}{\partial f_{ex}} \log Z(\beta, f_{ex}, N) = \frac{\partial}{\partial f_{ex}}\left(\log Z_K(\beta, N) + \log Z_C(\beta, f_{ex}, N)\right)$$

$$= \frac{\partial}{\partial f_{ex}} \log Z_C(\beta, f_{ex}, N)$$

$\Rightarrow$ $Z_C(\beta, f_{ex}, N)$ を計算すればよい.

$$\begin{cases} \mathbf{q}_1 = \mathbf{r}_1 - \mathbf{r}_0 \\ \mathbf{q}_2 = \mathbf{r}_2 - \mathbf{r}_1 \\ \vdots \\ \mathbf{q}_N = \mathbf{r}_N - \mathbf{r}_{N-1} \end{cases}$$

$\mathbf{q}_i = (\xi_i, \eta_i, \zeta_i)$

$$\mathbf{r}_N = \sum_{i=1}^{N} \mathbf{q}_i$$

$$Z(\beta, f_{ex}, N) = \int d\mathbf{q}_1 \cdots d\mathbf{q}_N \, e^{-\frac{\beta}{2}K\sum_{i=1}^{N}(|\mathbf{q}_i| - a)^2 + \beta f_{ex}\sum_{i=1}^{N}\xi_i}$$

$$= \Big[\underbrace{\int d\mathbf{q} \, e^{-\frac{\beta}{2}K(|\mathbf{q}| - a)^2 + \beta f_{ex}\xi_i}}_{= Z_C^{(1)}(\beta, f_{ex})}\Big]^N$$

§ 計算 − 極座標へ −

$$Z_c^{(1)}(\beta, f_{ex}) = 2\pi \int_0^\infty dq\, q^2\, e^{-\frac{\beta K}{2}(q-a)^2} \underbrace{\int_0^\pi d\theta \sin\theta\, e^{\beta f_{ex} q \cos\theta}}$$

$$t = \cos\theta$$

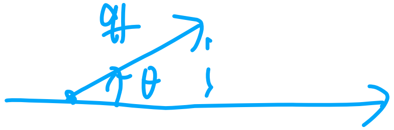
$$dt = -\sin\theta\, d\theta$$

$$\int_{-1}^{1} dt\, e^{\beta f_{ex} q t}$$

$$= \frac{1}{\beta f_{ex} q}\left(e^{\beta f_{ex} q} - e^{-\beta f_{ex} q}\right)$$

$$= \frac{2}{\beta f_{ex} q} \sinh \beta f_{ex} q$$

$$d\mathbf{q} = 2\pi q^2 \sin\theta\, dq\, d\theta$$



$$\xi = q\cos\theta$$

$$\therefore\ Z_c^{(1)}(\beta, f_{ex}) = \frac{4\pi}{\beta f_{ex}} \int_0^\infty dq\, q\, e^{-\frac{\beta K}{2}(q-a)^2} \times \sinh(\beta f_{ex} q)$$

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§ 漸近形

$\beta K a^2 \gg 1$ （かたいばね）

$$Z_c^{(1)}(\beta, f_{ex}) = \frac{4\pi a^2}{\beta f_{ex}} \int_{-1}^{\infty} d\tilde{q}\,(1+\tilde{q})\, e^{-\beta \frac{K}{2} a^2 \tilde{q}^2} \sinh\left[\beta f_{ex}\, a(1+\tilde{q})\right]$$

$q = a + \tilde{q} a$

$dq = a\, d\tilde{q}$

$\tilde{q} \simeq 0$ の周りの寄与が dominant

$$= \frac{4\pi a^2}{\beta f_{ex}} \left[\int_{-1 \to -\infty}^{\infty} d\tilde{q}\, e^{-\beta \frac{K}{2} a^2 \tilde{q}^2} \sinh \beta f_{ex} a + \underbrace{O\left(\sqrt{\frac{1}{\beta K a^2}}\right)}_{\to 0} \right]$$

むし

$$= \frac{4\pi a^2}{\beta f_{ex}} \sinh \beta f_{ex} a \cdot \sqrt{\frac{2\pi}{\beta K a^2}}$$

§ 線形化

$$X = k_B T \frac{\partial}{\partial f_{ex}} \log Z_c^{(1)}(\beta, f_{ex})^N$$

$$= N k_B T \frac{\partial}{\partial f_{ex}} \left[\log \sinh(\beta f_{ex} a) - \log f_{ex} \right]$$

$$= N k_B T \left[\underbrace{\frac{\cosh(\beta f_{ex} a)}{\sinh(\beta f_{ex} a)} \beta a}_{} - \frac{1}{f_{ex}} \right]$$

$$\beta a \frac{1 + \frac{1}{2}(\beta f_{ex} a)^2 + \cdots}{\beta f_{ex} a + \frac{1}{6}(\beta f_{ex} a)^3 + \cdots} = \beta a \frac{1 + \frac{1}{2}(\beta f_{ex} a)^2 - \frac{1}{6}(\beta f_{ex} a)^3 + \cdots}{\beta f_{ex} a}$$

$$= \frac{1}{f_{ex}} + \frac{1}{3}(\beta a)^2 f_{ex}$$

$\beta f_{ex} a \to 0$

$$\therefore \quad X = N k_B T \frac{1}{3}(\beta a)^2 f_{ex} + o(\beta f_{ex} a) \cdot aN$$

$$= Na \cdot \frac{\beta a f_{ex}}{3} + o(\beta f_{ex} a)\, aN$$

§まとめ

$$X = Na \frac{\beta f_{ex} a}{3}$$

$$= \frac{Na^2}{3k_BT} f_{ex}$$

$$\fallingdotseq \frac{1}{k_{macro}} f_{ex}$$

$$k_{macro} = \frac{3k_BT}{Na^2}$$

$$(Na)^2 k_{macro} \sim N k_B T$$

f：復元力

$$f + f_{ex} = 0$$

$$\Rightarrow f = -k_{macro} X$$

マクロなバネ定数があらわれた!!