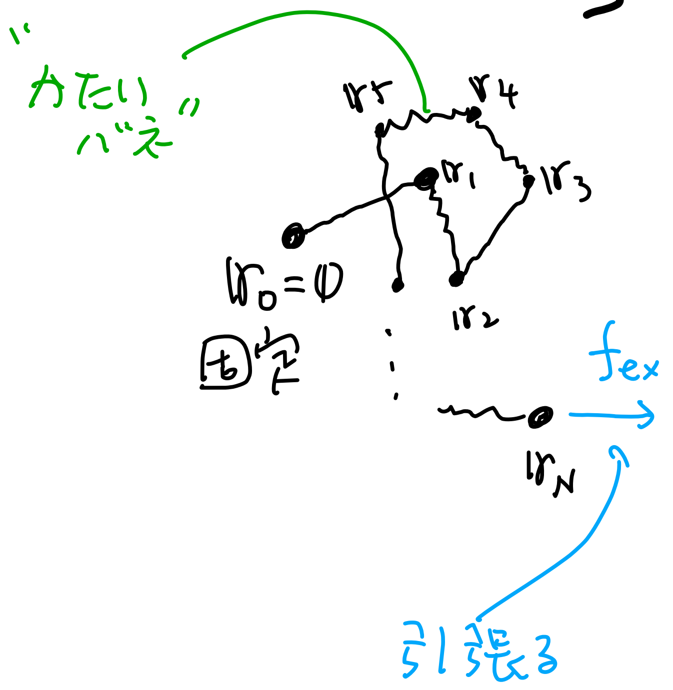
統計力学A Ⅸ

2020/12/08

§ 設定



$$\Gamma = (r_1, r_2, \cdots, r_N, p_1, \cdots, p_N)$$

$$H(\Gamma; f_{ex}, N) = \sum_{i=1}^{N} \frac{|p_i|^2}{2m} + \sum_{i=1}^{N} \frac{K}{2}\left(|r_i - r_{i-1}| - a\right)^2 - f_{ex} x_N$$

• $\beta K a^2 \gg 1 \quad ; \beta = \frac{1}{k_B T}$

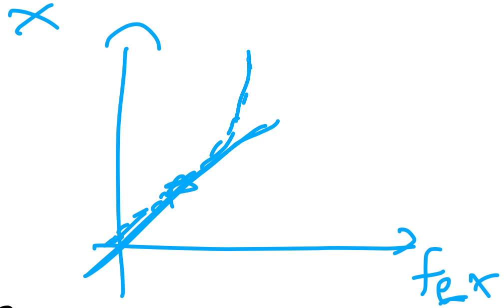
$r_i = (x_i, y_i, z_i)$

$$X \equiv \langle x_N \rangle^c_{\beta, f_{ex}} = \int d\Gamma \, x_N \, \rho^c_{\beta, f_{ex}}(\Gamma)$$

マクロな変位

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

§ 計算すべきこと

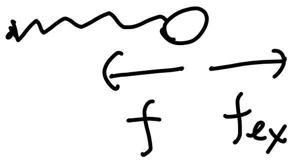


$$X = \frac{1}{k_{macro}} f_{ex} + o(f_{ex}\beta a)$$

マクロな バネ定数 k_{macro} を求める。

cf: 復元力 $f = -k_{macro} X$

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



結果　$k_{macro} = k_1 T$!!

→ 来週!

~Intermission~

§ 第一段階 — 配置にfocus —

$$\langle x \rangle = \int d\Gamma \frac{x_N}{Z(\beta, f_{ex}, N)} e^{-\beta\left[\sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \frac{K}{2}\sum_i (|\mathbf{r}_i - \mathbf{r}_{i-1}| - a)^2 - f_{ex} x_N\right]}$$

$$= \frac{\int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, x_N \, e^{-\beta\left[\frac{K}{2}\sum_i (|\mathbf{r}_i - \mathbf{r}_{i-1}| - a)^2 - f_{ex} x_N\right]}}{\underbrace{\int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, e^{-\beta\left[\frac{K}{2}\sum_i (|\mathbf{r}_i - \mathbf{r}_{i-1}| - a)^2 - f_{ex} x_N\right]}}_{\equiv Z_c(\beta, f_{ex}, N)}}$$

$$Z(\beta, f_{ex}, N) = \int d\mathbf{p}_1 \cdots d\mathbf{p}_N \, e^{-\beta \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m}} \times \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, e^{-\beta\left[\frac{K}{2}\sum_i (|\mathbf{r}_i - \mathbf{r}_{i-1}| - a)^2 - f_{ex} x_N\right]}$$

分母と分子で打ち消す

$$k_B T \frac{\partial}{\partial f_{ex}} Z_c(\beta, f_{ex}, N)$$

§第2段階 — 公式 —

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

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

公式I

$$\therefore \quad Z_c(\beta, f_{ex}, N) = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, e^{-\beta\left[\sum_i \frac{k}{2}(|\mathbf{r}_i - \mathbf{r}_{i-1}| - a)^2 - f_{ex} x_N\right]}$$

を計算すればよい。

§ 第3段階 — 変数変換 —

$$Z_c(\beta, f_{ex}, N) = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \, e^{-\beta\left[\sum_i \frac{K}{2}(|\mathbf{r}_i-\mathbf{r}_{i-1}|-a)^2 - f_{ex} x_N\right]}$$

$\mathbf{r}_0 = \mathbf{0}$

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

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

$$= \left[\int d\mathbf{q} \, e^{-\beta \frac{K}{2}(|\mathbf{q}|-a)^2 + \beta f_{ex} \xi}\right]^N$$

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

$$x_N = \sum_{i=1}^{N} \xi_i$$

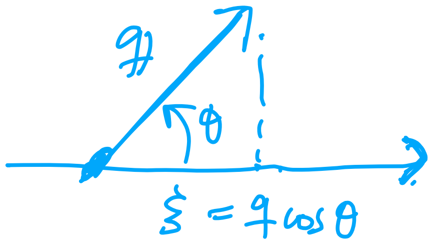
$$= \left[Z_c^{(1)}(\beta, f_{ex})\right]^N$$

$$e^{x+y} = e^x \cdot e^y$$

$$\therefore \; Z_c^{(1)}(\beta, f_{ex}) = \int d\mathbf{q} \, e^{-\beta \frac{K}{2}(|\mathbf{q}|-a)^2 + \beta f_{ex} \xi}$$

を計算すればよい。

§第4段階 — 積分 —



$$Z_c^{(1)}(\beta, f_{ex}) = \int d\mathbf{q}\, e^{-\beta\frac{k}{2}(|\mathbf{q}|-a)^2 + \beta f_{ex}\xi}$$

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

$t = \cos\theta$

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

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

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

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

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

$\therefore$

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

§第5段階 —漸近形—

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

$\beta\kappa a^2 \gg 1$

かたいバネ

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

$$= \frac{4\pi a^2}{\beta f_{ex}} \int_{-1}^{\infty} d\tilde{q}\,(1+\tilde{q})\, e^{-\overbrace{\beta\frac{\kappa}{2}a^2}^{\gg 1}\tilde{q}^2} \sinh(\beta f_{ex}(a+\tilde{q}a))$$

$$= \frac{4\pi a^3}{\beta f_{ex}} \left[\sinh\beta f_{ex} a \int_{-\infty}^{\infty} d\tilde{q}\, e^{-\beta\frac{\kappa}{2}a^2\tilde{q}^2} + O\left(\sqrt{\frac{1}{\beta\kappa a^2}}\right) \right]$$

−1 を置換えてよい

主要項はzero

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

§ 第6段階 — 線形化 —

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

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

$$= k_B T N \left[\underbrace{\frac{\cosh(\beta f_{ex} a)}{\sinh(\beta f_{ex} a)} \beta a}_{\beta a \frac{1 + \frac{1}{2}(\beta f_{ex} a)^2 + \cdots}{\beta f_{ex} a + \frac{1}{6}(\beta f_{ex} a)^3 + \cdots}} - \frac{1}{f_{ex}} \right]$$

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

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

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

§ 計算のまとめ

$$X = N\frac{a^2}{3k_BT}f_{ex} = Na\cdot\frac{af_{ex}}{\underline{3k_BT}}$$

a伸長変位させるとき
外力のする仕事

1自由度あたりの
運動エネルギー

$$= \frac{1}{K_{macro}}f_{ex}$$

復元力

$$f = -K_{macro}X$$

$$\underset{\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim}{K_{macro} = \frac{3k_BT}{Na^2}}$$

マクロなバネ定数が
あらわれた!!

~Intermission~

§ 分配関数

$$Z(\beta, f_{ex}, N) = \int d\Gamma\, e^{-\beta\left[\sum_i \frac{|p_i|^2}{2m} + \sum_i \frac{K}{2}\left(|r_i - r_{i-1}| - a\right)^2 - \beta f_{ex} x_N\right]}$$

$$= \left(\int dp\, e^{-\beta\frac{p^2}{2m}}\right)^{3N} \cdot \left(\frac{4\pi a^2}{\beta f_{ex}} \sinh \beta f_{ex} a \sqrt{\frac{2\pi}{\beta K a^2}}\right)^N$$

$$= \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}} \left(\frac{\sinh \beta f_{ex} a}{\beta f_{ex} a}\right)^N \left(4\pi a^3\right)^N \left(\frac{2\pi}{\beta K a^2}\right)^{\frac{N}{2}}$$

$$\log Z(\beta, f_{ex}, N) = -2N \log \beta + N \underbrace{\log \frac{\sinh(\beta f_{ex} a)}{\beta f_{ex} a}} + N c_0$$

定数

$$\sim \log\left(1 + \frac{1}{6}(\beta f_{ex} a)^2 + \cdots\right) = \frac{1}{6}(\beta f_{ex} a)^2 = \frac{1}{2}\beta \frac{\cancel{X}}{N} f_{ex}$$

$$X = N \frac{a^2}{3 k_B T} f_{ex}$$

§ エネルギー

$$\log Z(\beta, f_{ex}, N) = -2N\log\beta + N\log\frac{\sinh(\beta f_{ex} a)}{\beta f_{ex} a} + N c_0$$ 定数

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

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

$$= 2Nk_BT + Nk_BT - N\frac{\cosh(\beta f_{ex} a)}{\sinh(\beta f_{ex} a)} f_{ex} a$$

$$= 3Nk_BT - \frac{N}{\beta a f_{ex}}\left(1 + \frac{1}{3}(\beta f_{ex} a)^2 + \cdots\right) f_{ex} a$$

$$= 2Nk_BT - \frac{N}{3}(\beta f_{ex} a)^2 k_BT$$

$$X = N\frac{a^2}{3k_BT} f_{ex}$$

$$= 2Nk_BT - X\cdot f_{ex}$$

//

§ エントロピー －公式－

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

$$= \int d\Gamma \underbrace{\int dE\, \delta(E - H(\Gamma; f_{ex}, N))}_{=1} e^{-\beta H(\Gamma; f_{ex}, N)}$$

$$= \int dE\, e^{-\beta E}\, \Sigma(E, f_{ex}, N)$$

$$\Sigma(E, f_{ex}, N) \equiv \int d\Gamma\, \delta(E - H(\Gamma; f_{ex}, N))$$

(N! いらずない。)

$$\fallingdotseq e^{\frac{1}{k_B} S(E, f_{ex}, N)}$$

$$Z(\beta, f_{ex}, N) = \int dE\, e^{-\beta E + \frac{1}{k_B} S(E, f_{ex}, N)}$$

$$= e^{-\beta E_* + \frac{1}{k_B} S(E_*, f_{ex}, N) + o(N)}$$

$$\left.\frac{\partial S(E, f_{ex}, N)}{\partial E}\right|_{E_*} = \beta \implies E_*(\beta, f_{ex}, N)$$

§ エントロピー - 計算

$$\frac{\partial}{\partial\beta}\log Z(\beta, f_{ex}, N) = -E_* - \beta\frac{\partial E_*}{\partial\beta} + \frac{1}{k_B}\left.\frac{\partial S(E, f_{ex}, N)}{\partial E}\right|_{E_*}\frac{\partial E_*}{\partial\beta}$$

$$= -E_*$$

$$\therefore\quad E_* = \langle H\rangle^c_{\beta, v, N}$$

$$S(T, f_{ex}, N) = k_B \log Z(\beta, f_{ex}, N) + \frac{1}{T}\langle H\rangle^c_{\beta, v N}$$

$$= 2N k_B \log T + k_B \frac{1}{2}\beta(x f_{ex})$$

$$+ 2N k - \frac{1}{T} X f_{ex} \quad + \text{const}$$

$$\begin{cases} \log Z(\beta, f_{ex}, N) = -2N\log\beta + \overbrace{N\log\dfrac{\sinh(\beta f_{ex} a)}{\beta f_{ex} a}}^{\frac{1}{2}\beta x f_{ex}} + N c_0^{\text{定数}} \\ \langle H\rangle^c_{\beta, f_{ex}, N} = 2N k_B T - X\cdot f_{ex} \end{cases}$$

§ エントロピー －結果－

$$S(T, f_{ex}, N) = 2N k_B \log T - \frac{1}{2T}\frac{f_{ex}^2}{K_{macro}} + \text{const}$$

(or)

$$S(T, X, N) = 2N k_B \log T - \frac{K_{macro}}{2T} X^2 + \text{const}$$

マクロな変位の関数とにみる。

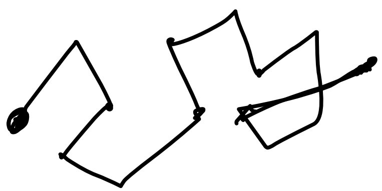
運動量空間の相空間体積のlog
＝"状態数"のlog
＝運動の激しさ

配置空間の相空間のlog
＝配置の複雑さ

§ 現象の解釈

$$S(T, X, N) = 2Nk_B \log T - \frac{K_{nano}}{2T} X^2 + const$$

温度T一定で変位を与える（$f_{ex} \neq 0$）



⇒ { ・配置の"複雑さ"が減少
　　・運動の"激しさ"が一定

⇒ ・拘束をはずすと、もっとも状態数（$f_{ex} = 0$）が大きい状態（$X=0$）に変化する

復元力！　エントロピー力！

~Intermission~

まとめ

▷ 統計力学模型にもとづいて
エントロピー力としての復元力
を具体的に計算した。

▷ エネルギー，エントロピーを計算した。

⇒ 来週，この例での熱力学関係式へ
（"混乱する部分!!"）