統計力学AⅩ

2020/12/15

今日の目標

✓ ゴムの例題での熱力学関係式

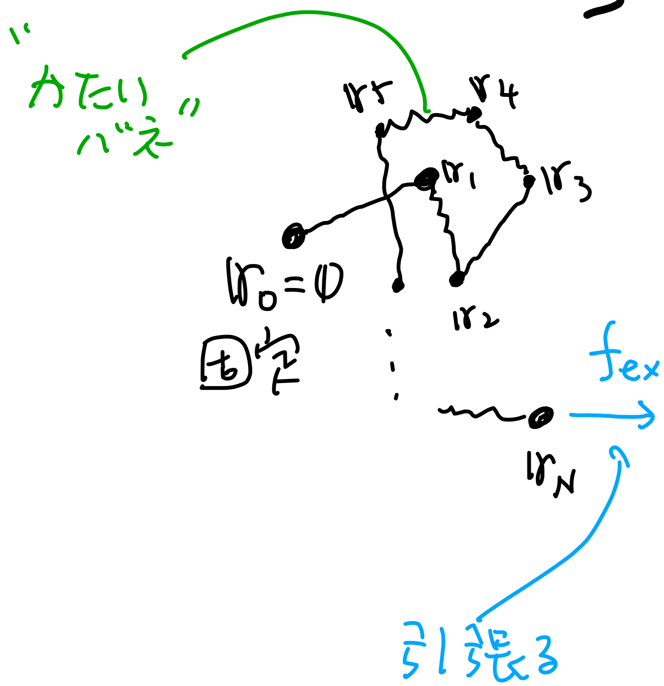
✓ 異なる設定での問題の再定式化

⇓

✓ "等価なアンサンブル"という考え方
(分布)

~ Intermission ~

§ 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

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

§ 公式のまとめ

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

✓ $\langle x_N \rangle^c_{\beta, f_{ex}, N} \equiv X = k_B T \frac{\partial}{\partial f_{ex}} \log Z(\beta, f_{ex}, N)$ 　公式I page6

✓ $\langle H \rangle^c_{\beta, f_{ex}, N} \equiv E = -\frac{\partial}{\partial \beta} \log Z(\beta, f_{ex}, N)$ 　公式II page14

✓ $S(T, f_{ex}, N) = k_B \log Z(\beta, f_{ex}, N) + \frac{E}{T}$ 　公式III page16

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

- $S(E, f_{ex}, N) = k_B \log \Sigma(E, f_{ex}, N) + o(N)$

§ 分配関数 何?

✓ $\langle x_N \rangle^c_{\beta, f_{ex}, N} \equiv X = k_B T \dfrac{\partial}{\partial f_{ex}} \log Z(\beta, f_{ex}, N)$ ✓ $\langle H \rangle^c_{\beta, f_{ex}, N} \equiv E = -\dfrac{\partial}{\partial \beta} \log Z(\beta, f_{ex}, N)$

✓ $S(T, f_{ex}, N) = k_B \log Z(\beta, f_{ex}, N) + \dfrac{E}{T}$

$$\boxed{F^*(T, f_{ex}, N) \equiv -k_B T \log Z(\beta, f_{ex}, N)}$$

$\Rightarrow$ ・ $X = -\dfrac{\partial F^*(T, f_{ex}, N)}{\partial f_{ex}}$

・ $F^* = E - TS$

・ $E = +T^2 \dfrac{\partial}{\partial T}\left(-\dfrac{F^*}{T}\right)$

$= F^* - T\dfrac{\partial F^*}{\partial T}$

$\therefore \quad S = -\dfrac{\partial F^*(T, f_{ex}, N)}{\partial T}$

§ 熱力学関係式

$$X = -\frac{\partial F^*(T, f_{ex}, N)}{\partial f_{ex}} \qquad S = -\frac{\partial F^*(T, f_{ex}, N)}{\partial T}$$

$$\Rightarrow \begin{cases} dF^* = -TdS - X\,df_{ex} \\ F^* = E - TS \end{cases}$$

cf 前回 page14

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

cf: ばねの熱力学

復元力

$f_{ex} = -f$

$$\begin{cases} dF = -TdS - f\,dX \\ F = U - TS \end{cases}$$

自由エネルギー

内部エネルギー

☆ Eは内部エネルギーではないし、

F^*は等温準静的仕事で決まるFでない

§ 熱力学関数

$$E = \underbrace{2Nk_BT}_{\text{内部エネルギー}} - \underbrace{X \cdot f_{ex}}_{\text{外場によるポテンシャルエネルギー}}$$

$$\Rightarrow \quad E = U + fX$$

(f が圧力；気体・液体の場合
E : エンタルピー)

$$F^* = F + fX$$

$$\Rightarrow \quad dF^* = -SdT - \cancel{f}dX + \cancel{f}dX + (df)X$$

$$= -SdT + \underbrace{X\,df}_{(= -X\,df_{ex})}$$

F^* : 外場のポテンシャルエネルギーを加えた
自由エネルギー

(気体・液体の場合： F^* : ギブスの自由エネルギー)

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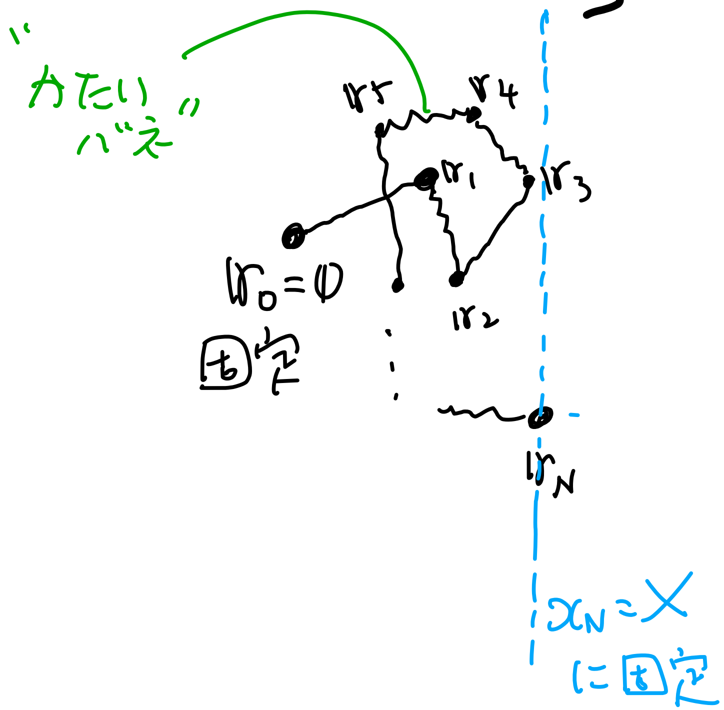
§ 設定 II



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

$$H_0(\Gamma) = \sum_{i=1}^{N} \frac{|p_i|^2}{2m} + \sum_{i=1}^{N} \frac{K}{2} \left(|r_i - r_{i-1}| - a \right)^2$$

$x_N = X$ fix

$r_i = (x_i, y_i, z_i)$

$$\rho^c_{\beta X N}(\Gamma) = \frac{1}{\tilde{Z}(\beta, X, N)} e^{-\beta H_0(\Gamma)} \cdot \delta(x_N - X)$$

復元力 $\tilde{f} \equiv -\dfrac{\partial H_0(\Gamma)}{\partial x_N}$

$$f \equiv \langle \tilde{f} \rangle^c_{\beta, X, N} = \int d\Gamma \, \tilde{f}(\Gamma) \rho^c_{\beta, X, N}$$

を計算する。

§ 計算 ー公式ー

$$f = -\frac{1}{\tilde{Z}} \int d\Gamma \, \frac{\partial H(\Gamma)}{\partial x_N} e^{-\beta H_0(\Gamma)} \cdot \delta(x_N - X)$$

$$= \frac{k_B T}{\tilde{Z}} \int d\Gamma \left(\frac{\partial}{\partial x_N} e^{-\beta H_0(\Gamma)} \right) \delta(x_N - X)$$

$$= \frac{k_B T}{\tilde{Z}} \int d\Gamma \, e^{-\beta H_0(\Gamma)} \frac{\partial}{\partial X} \delta(x_N - X)$$

$$= k_B T \frac{1}{\tilde{Z}} \frac{\partial}{\partial X} \tilde{Z}$$

$$= k_B T \frac{\partial}{\partial X} \log \tilde{Z}$$

§ 計算のトリック

$$\tilde{Z}(\beta, X, N) = \int d\Gamma \, e^{-\beta H_0(\Gamma)} \delta(x_N - X)$$

$\longrightarrow$ 直接計算不可

ところが、

$$Z(\beta, f_{ex}, N) = \int d\Gamma \, e^{-\beta H_0(\Gamma) + \beta f_{ex} x_N}$$

計算可能

$$= \int d\Gamma \int dX \, \delta(x_N - X) e^{-\beta H_0(\Gamma) + \beta f_{ex} x_N}$$

$$= \int dX \, e^{\beta f_{ex} X} \tilde{Z}(\beta, X, N)$$

$$= \int dX \, e^{\beta \left(f_{ex} X + k_B T \log \tilde{Z}(\beta, X, N)\right)}$$

$$f_{ex} + k_B T \frac{\partial}{\partial X} \log \tilde{Z}(\beta, X, N) \Big|_{X_*} = 0$$

$$= e^{\beta \left[f_{ex} X_* + k_B T \log \tilde{Z}(\beta, X_*, N) + o(N)\right]}$$

§ 計算結果

$$e^{\beta\left[f_{ex} X_* + k_B T \log \tilde{Z}(\beta, X_*, N) + o(N)\right]}$$

$$k_B T \log \tilde{Z}(\beta, X, N) = k_B T \log Z(\beta, f_{ex}, N) - f_{ex} X$$

復元力

$$f_{ex} = -k_B T \frac{\partial}{\partial X} \log \tilde{Z}(\beta, X, N)$$ ☆

$$\Rightarrow \quad k_B T \frac{\partial}{\partial X} \log \tilde{Z}(\beta, X, N) = -f_{ex} + \frac{\partial f_{ex}}{\partial X}\left[k_B T \frac{\partial}{\partial f_{ex}} \log Z(\beta, f_{ex}, N) - X\right]$$

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

計算済

つまり f_{ex} を加えて、X を求める結果を

逆解きして、$f_{ex} = f_{ex}(X, T, N)$ を書く。

$\Rightarrow$ $k_B T \log \tilde{Z}(\beta, X, N)$ が求まる

$\Rightarrow$ 復元力が分かる。 $f = -f_{ex}$

§ 熱力学

$$k_B T \log \tilde{Z}(\beta, X, N) = -F^*(\beta, f_{ex}, N) - f_{ex} X$$
$$= -F^*(\beta, f_{ex}, N) + f X$$

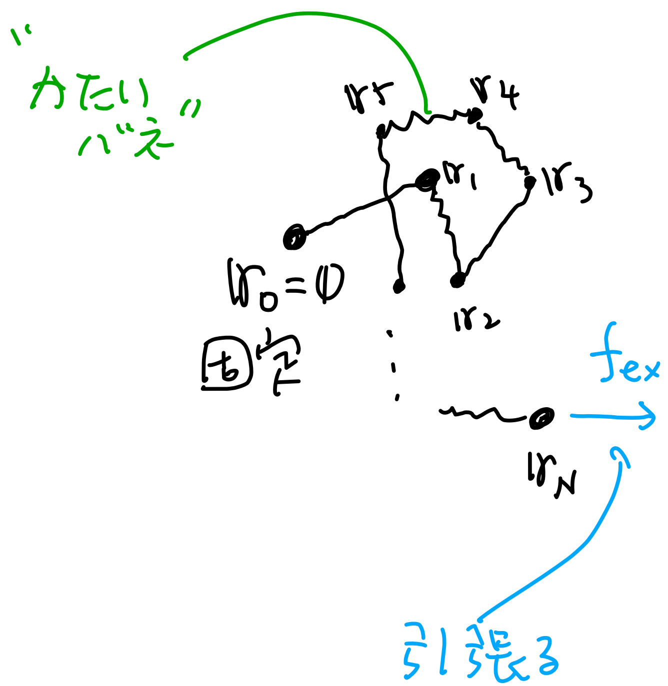
$$\therefore \ F(\beta, X, N) = -k_B T \log \tilde{Z}(\beta, X, N)$$

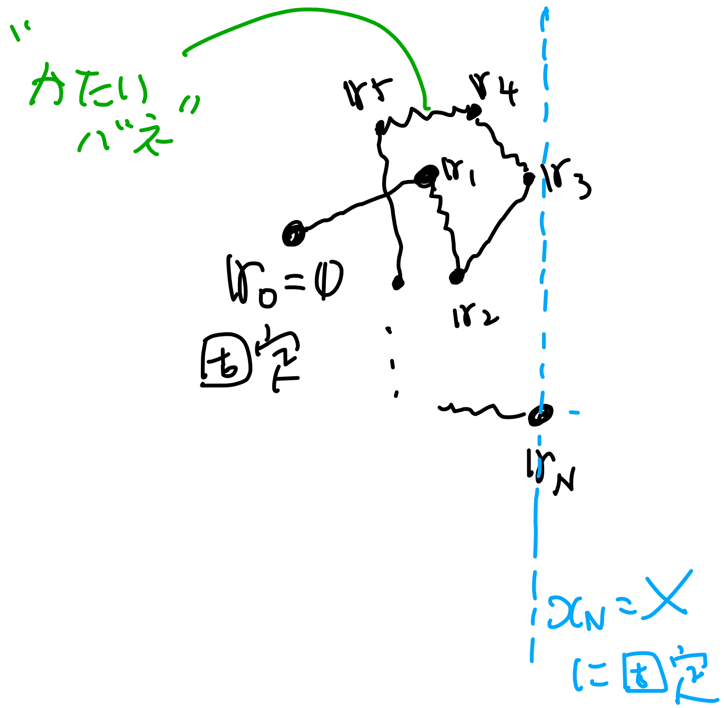
自由エネルギー!!

$$dF = -S dT - f dX$$

~ Intermission ~

まとめ





$$\rho^{c}_{\beta, f_{ex}, N}(\Gamma) = \frac{1}{Z(\beta, f_{ex}, N)} e^{-\beta H_0(\Gamma) + \beta f_{ex} x_N}$$

$$\rho^{c}_{\beta, X, N}(\Gamma) = \frac{1}{\tilde{Z}(\beta, X, N)} e^{-\beta H_0(\Gamma)} \delta(x_N - X)$$

‘T-p分布’ (T-f_{ex}分布)
とよばれることもある.

まとめⅡ

$$\rho^{c}_{\beta, f_{ex}, N}(\Gamma) = \frac{1}{Z(\beta, f_{ex}, N)} e^{-\beta H_0(\Gamma) + \beta f_{ex} x_N}$$

$$\rho^{c}_{\beta, X, N}(\Gamma) = \frac{1}{\tilde{Z}(\beta, X, N)} e^{-\beta H_0(\Gamma)} \delta(x_N - X)$$

$$F^*(T, f_{ex}, N) = -k_B T \log Z(\beta, f_{ex}, N)$$

$$F(T, X, N) = -k_B T \log \tilde{Z}(\beta, X, N)$$

$$dF^* = -S\,dT - X\,df_{ex}$$

$$dF = -S\,dT - f\,dX$$

$$F^* = F + fX$$

ルジャンドル変換

熱力学の完全な熱力学関数の変換

に対応する確率分布の変換

まとめⅢ

$$\rho^{c}_{\beta, f_{ex}, N}(\Gamma) = \frac{1}{Z(\beta, f_{ex}, N)} e^{-\beta H_0(\Gamma) + \beta f_{ex} x_N} \qquad \rho^{c}_{\beta, X, N}(\Gamma) = \frac{1}{\tilde{Z}(\beta, X, N)} e^{-\beta H_0(\Gamma)} \delta(x_N - X)$$

指数型 $\longleftrightarrow$ 拘束型

"等価なアンサンブル"の典型例

計算量の非対称性