

系統計力学 A VII

講義 XE

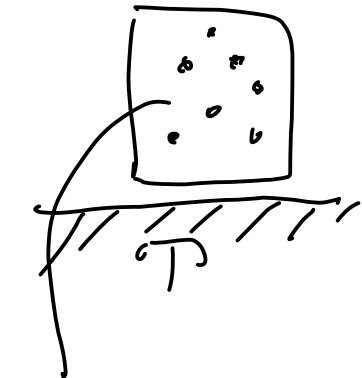
2023 / 11 / 14

§ 前回までの話と今日の目標

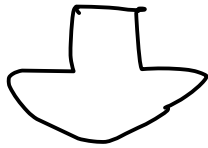
温度 T の熱浴と接する系の

確率分布 : カノニカル分布

$$\rho_{\beta, V, N}^C(\Gamma) = \frac{1}{Z(T, V, N)} e^{-\beta H(\Gamma; V, N)}$$



$$\Gamma = (r_1, \dots, r_N, p_1, \dots, p_N)$$



熱力学関係式

$$\begin{cases} F = E - TS \\ dF = -s dT - p dV \end{cases}$$

§ 分部积分法

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

$$\oint d\Gamma P_{\beta, V, N}^C(\Gamma) = 1$$

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

$$\Sigma(E, V, N) = \int d\Gamma \delta(H(\Gamma; V, N) - E)$$

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

or

$$S(E, V, N) = k_B \log \frac{\Sigma(E, V, N)}{N}$$

$$\therefore \frac{Z(T, V, N)}{N!} = \int dE e^{-\beta E + \frac{1}{k_B} S(E, V, N) + o(N)}$$

$I(u)$

$$= N \int du e^{-N \left(\beta u - \frac{1}{k_B} S(u, v) \right) + o(N)}$$

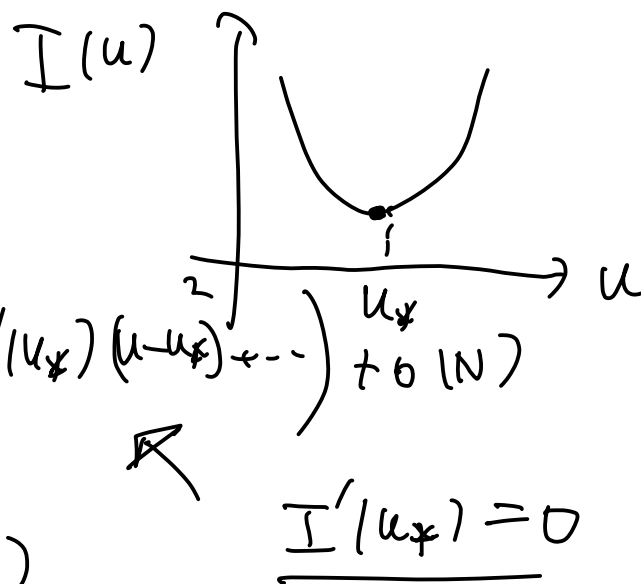
$$= N \int du e^{-N \underline{I(u)} + o(N)}$$

$$S(E, V, N) = N \bar{S} \left(\frac{E}{N}, \frac{V}{N} \right) + o(N)$$

$$\frac{Z(T, V, N)}{N!} = N \int du e^{-N I(u) + o(N)}$$

$$= N \int du e^{-N \left(I(u_*) + \frac{1}{2} I''(u_*) (u - u_*)^2 + \dots \right) + o(N)}$$

$$= e^{-N I(u_*) + o(N)}$$



$$\therefore \log \frac{Z(T, V, N)}{N!} = -N \left[\beta u_* - \bar{S}(u_*, V) \right] + o(N)$$

$$= -\beta E_* + S(E_*, V) + o(N)$$

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

E_* is det

$$= -\frac{1}{k_B T} \left[\underbrace{E_*(T, V) - S(E_*(T, V), V)}_{= F(T, V)} \right]$$

$$\therefore \bar{F}(T, V, N) = -k_B T \log \frac{Z(T, V, N)}{N!} \quad \text{とすると} \quad \bar{F} = E_* - TS(E_*, V, N)$$

参考: 前回の計算

$$\begin{aligned} Z &= \frac{\sum_{\text{tot}}}{N_B! e^{\frac{1}{k_B} S_B(E_{\text{tot}})}} \\ &= \frac{\sum_{\text{tot}}}{N_B! N!} \frac{N!}{e^{\frac{1}{k_B} S_B(E_{\text{tot}})}} \\ \frac{Z}{N!} &= e^{\frac{1}{k_B} (S_{\text{tot}}(E_{\text{tot}}) - S_B(E_{\text{tot}}))} \\ &= e^{\frac{1}{k_B} (S_{\text{tot}}(E_{\text{tot}}) - S_B(E_{B_*}) - \frac{\partial S_B}{\partial E_B} (E_{\text{tot}} - E_{B_*})) + o(N)} \\ &= e^{\frac{1}{k_B} (S(E_*) - \beta E_*) + o(N)} \quad \begin{array}{l} \text{I 系と II 系との} \\ \text{エネルギーの交換} \end{array} \\ &= e^{\frac{1}{k_B} (S(E_*) - \beta E_*) + o(N)} \quad \text{不確定性} \end{aligned}$$

今回の計算と consistent

§ 圧力

$$\hat{p}(P) \equiv - \frac{\partial H(P; V, N)}{\partial V}$$

$$p = \langle \hat{p} \rangle_{\beta, V, N}^c = \int dP \frac{\partial H(P; V, N)}{\partial V} \frac{1}{Z} e^{-\beta H(P; V, N)}$$

$$Z = \int dP e^{-\beta H(P; V, N)}$$

$$p = \frac{1}{Z} \frac{\partial Z}{\partial V} \beta^{-1}$$

$$= k_B T \frac{\partial}{\partial V} \log Z$$

$$= - \left(- k_B T \frac{\partial}{\partial V} \log \frac{Z}{N!} \right)$$

$$= - \frac{\partial}{\partial V} \bar{F}(\tau, V, N) //$$

§ I 系 1 粒子 -

$$\bar{H} = \langle H \rangle_{\beta, V, N} = \frac{1}{Z} \int d\Gamma H(\Gamma) e^{-\beta H(\Gamma)}$$

$$= \frac{1}{Z} \frac{\partial Z}{\partial \beta} (-1)$$

$$= - \frac{\partial}{\partial \beta} \log Z \quad \leftarrow \text{ここまでの式が計算簡単}$$

$$= - \frac{\partial}{\partial \beta} \left(\beta \cdot k_B T \cdot \log \frac{Z}{N!} \right)$$

$$= + \frac{\partial}{\partial \beta} (\beta \bar{H}) \quad \leftarrow \text{熱力学関係式}$$

$$= \bar{H} + \beta \frac{\partial \bar{H}}{\partial \beta}$$

$$= \bar{H} - T \frac{\partial \bar{H}}{\partial T}$$

$$= \bar{H} + TS$$

$$\therefore \underline{\underline{S = - \frac{\partial \bar{H}}{\partial T}}}$$

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$$\bar{F} = -k_B T \log \frac{Z(T, V, N)}{N!} .$$

$$\Rightarrow \left\{ \begin{array}{l} \cdot \bar{F} = E_* - TS(E_*, V, N) \\ \cdot d\bar{F} = -SdT - pdV \\ \cdot F(T, \lambda V, \lambda N) = \lambda F(T, V, N) + o(N) \end{array} \right.$$

$\bar{F}(T, V, N)$: N 個の自由エネルギー

例: 単原子希薄気体

$$H(\mathbf{P}; V, N) = \sum_{i=1}^N \frac{|\mathbf{P}_i|^2}{2m} + \sum_{i < j} V_{int}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_i V_{wall}(\mathbf{r}_i; D)$$

$$Z(T, V, N) = \int d\mathbf{P} e^{-\beta \left(\sum_{i=1}^N \frac{|\mathbf{P}_i|^2}{2m} + \sum_i V_{wall}(\mathbf{r}_i; D) \right)}$$

$$V_{wall}(\mathbf{r}_i; D) = \begin{cases} 0 & \mathbf{r}_i \in D \\ \infty & \mathbf{r}_i \notin D \end{cases}$$

この積分は
2^N 次元空間に
なっている

$$= \int_{\mathbf{r}_i \in D} d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \int d^3\mathbf{P}_1 \dots d^3\mathbf{P}_N e^{-\beta \sum_{i=1}^N \frac{|\mathbf{P}_i|^2}{2m}}$$

$$= V^N \left(\int_{-\infty}^{\infty} d\mathbf{P} e^{-\beta \frac{\mathbf{P}^2}{2m}} \right)^{3N}$$

$$= V^N \left(\frac{2m\pi}{\beta} \right)^{\frac{3N}{2}}$$

$$\bar{F}(T, V, N) = -k_B T \log \frac{V^N T^{\frac{3N}{2}}}{N!} + c_0 N$$

$$= -k_B T \log \frac{V^N T^{\frac{3N}{2}}}{N^N} + c_0 N + o(N)$$

$$= -k_B T N \log \frac{T^{3/2} V}{N} + c'_0 N + o(N)$$

$$S = -\frac{\partial \bar{F}}{\partial T} = k_B N \log \frac{T^{3/2} V}{N} + c'_0 N + o(N)$$

$$P = -\frac{\partial \bar{F}}{\partial V} = \frac{k_B T N}{V}$$

例 : エネルギーのゆらぎ

$$\sigma_E \equiv \left\langle (H - \langle H \rangle_\beta^c)^2 \right\rangle_\beta^c \quad E = \langle H \rangle_\beta^c$$

$$\langle H^2 \rangle_\beta^c = \frac{1}{Z} \int d\Gamma H^2 e^{-\beta H}$$

$$= \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z$$

$$= \frac{1}{Z} \frac{\partial}{\partial \beta} \left(Z \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)$$

$$= \frac{1}{Z} \frac{\partial}{\partial \beta} (Z E)$$

$$= E^2 - \frac{\partial}{\partial \beta} E$$

$$\frac{\partial}{\partial \beta} E = -k_B T^2 \frac{\partial}{\partial T} E = -k_B T^2 C_V$$

$$\langle H^2 \rangle = E^2 + k_B T^2 C_V$$

$$\begin{aligned} \sigma_E &= \langle (H - E)^2 \rangle \\ &= \langle H^2 \rangle - E^2 \\ &= k_B T^2 C_V \quad // \end{aligned}$$

熱容量はエネルギーのゆらぎ強度である

(ゆらぎ-応答関係の例)