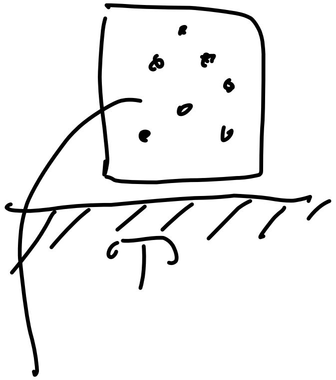
統計力学A VII

講義メモ

2022/11/29

§ 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

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

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

熱力学関係式

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

§ 分配関数

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

$\leftarrow \int d\Gamma\, \rho^{c}_{\beta,V,N}(\Gamma) = 1$

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

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

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

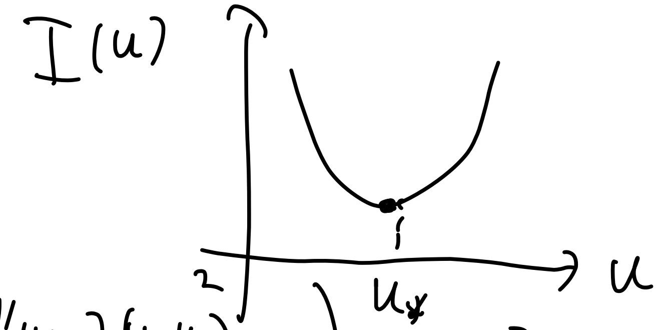
$S(E,V,N) = k_B \log \frac{\Sigma(E,V,N)}{N!} + o(N)$

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

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

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

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



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

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

$\underline{I'(u_*) = 0}$

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

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

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

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

E_* a det

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

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

参考: 前回の計算

(← page 5 の (…) はまちがっています)

$$Z = \frac{\Sigma_{tot}}{N_B!\, e^{\frac{1}{k_B} S_B(E_{tot})}}$$

$$= \frac{\Sigma_{tot}}{N_B!\, N!} \frac{N!}{e^{\frac{1}{k_B} S_B(E_{tot})}}$$

$$\frac{Z}{N!} = e^{\frac{1}{k_B}\left(S_{tot}(E_{tot}) - S_B(E_{tot})\right)}$$

$$= e^{\frac{1}{k_B}\left(S_{tot}(E_{tot}) - S_B(E_{B*}) - \frac{\partial S_B}{\partial E_B}\cdot(E_{tot} - E_{B*})\right) + o(N)}$$

エネルギー配分の不確定値

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

今回の計算と consistent

§ 圧力

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

$$p = \langle \hat{p} \rangle^{c}_{\beta, V, N} = -\int d\Gamma \frac{\partial H(\Gamma; V, N)}{\partial V} \frac{1}{Z} e^{-\beta H(\Gamma; V, N)}$$

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

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

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

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

$$= -\frac{\partial}{\partial V} F(T, V, N)$$

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§ エネルギー

$$E = \langle H \rangle^{c}_{\beta,V,N} = \frac{1}{Z}\int d\Gamma\, H(\Gamma)\, e^{-\beta H(\Gamma)}$$

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

$$= -\frac{\partial}{\partial \beta}\log Z$$

ここまでの式が計算簡単

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

$$= +\frac{\partial}{\partial \beta}(\beta F)$$

熱力学関係式

$$= F + \beta \frac{\partial F}{\partial \beta}$$

$$= F - T\frac{\partial F}{\partial T}$$

$$= F + TS$$

$$\therefore\ S = -\frac{\partial F}{\partial T}$$

まとめると

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

$$\Rightarrow \begin{cases} \cdot\ F = E_* - TS(E_*, V, N) \\ \cdot\ dF = -S\,dT - p\,dV \\ \cdot\ F(T, \lambda V, \lambda N) = \lambda F(T, V, N) + o(N) \end{cases}$$

$F(T,V,N)$：ヘルムホルツの自由エネルギー

例: 単原子希薄気体

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

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

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

これまでのト
で抜けていたかも

$$=\int_{\mathbb{r}_i\in D}d^3\mathbb{r}_1\cdots d^3\mathbb{r}_N\int d^3\mathbb{p}_1\cdots d^3\mathbb{p}_N\,e^{-\beta\sum_{i=1}^{N}\frac{(\mathbb{p}_i)^2}{2m}}$$

$$=V^N\left(\int_{-\infty}^{\infty}dp\,e^{-\beta\frac{p^2}{2m}}\right)^{3N}$$

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

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

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

$$= -k_B T N \log \frac{T^{3/2} V}{N} + c_0' N + o(N)$$

$$S = -\frac{\partial \bar{F}}{\partial T} = k_B N \log \frac{T^{3/2} V}{N} + c_0' N + o(N)$$

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

例：エネルギーのゆらぎ

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

$$\begin{aligned}
\langle H^2 \rangle_\beta^c &= \frac{1}{Z} \int d\Gamma \, H^2 e^{-\beta H} \\
&= \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z \\
&= \frac{1}{Z} \frac{\partial}{\partial \beta} \left(Z \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) \\
&= -\frac{1}{Z} \frac{\partial}{\partial \beta} \left(Z E \right) \\
&= E^2 - \frac{\partial}{\partial \beta} E
\end{aligned}$$

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

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

$$\sigma_E = \langle (H-E)^2 \rangle$$
$$= \langle H^2 \rangle - E^2$$
$$= k_B T^2 C_V \quad //$$

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)