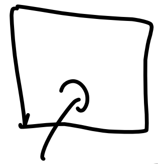
グランドカノニカル分布に対する補足メモ

23/01/24

§ 準備1



領域D

$$H(\Gamma;V,N)=H_0(\Gamma;N)+\sum_{i=1}^{N}V_{wall}(\mathbf{r}_i;D)$$

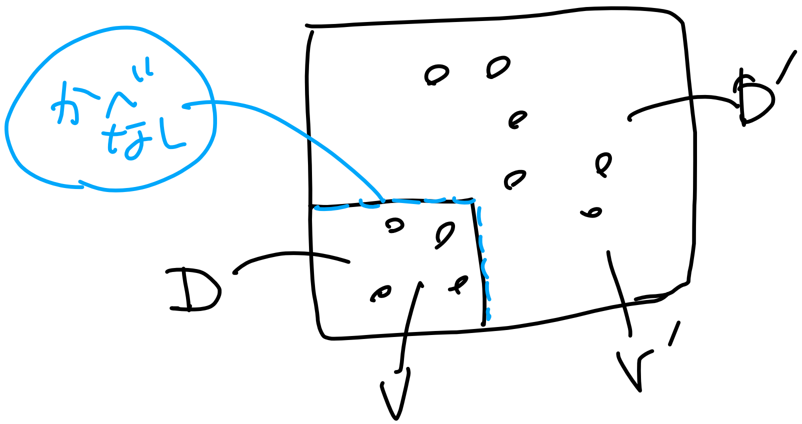
$$\rho^{c}_{TVN}(\Gamma)=\frac{1}{Z(T,V,N)}e^{-\beta H(\Gamma;V,N)}$$

$$=\frac{1}{Z(T,V,N)}e^{-\beta H_0(\Gamma;N)}\prod_{i=1}^{N}\chi(\mathbf{r}_i\in D)$$

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

$$\chi(A)=\begin{cases} 1 & \text{if } A \text{ is true} \\ 0 & \text{if } A \text{ is false} \end{cases}$$

考える系



$$D\cup D'=D_{tot}$$

$$V+V'=V_{tot}$$

$$\Gamma_{tot}=(\tilde{\mathbf{r}}_1,\cdots\tilde{\mathbf{r}}_{N_{tot}},\tilde{\mathbf{p}}_1\cdots\tilde{\mathbf{p}}_{N_{tot}})$$

$$H_{tot}(\Gamma_{tot};V_{tot},N_{tot})$$

§ 準備 2

- $\sigma : (1, \cdots, N_{tot}) \to (1, \cdots, N_{tot})$ 置換

  such that $\sigma(1) < \sigma(2) \cdots < \sigma(N)$

  $\sigma(N+1) < \sigma(N+2) \cdots < \sigma(N_{tot})$

  G : この置換全体　N_{tot} 個から N 個選ぶ方法を指定

- 領域 D に N 個の粒子が入っている $\tilde{\Gamma}_{tot}$ の条件

$$\exists \sigma \in G, \quad \tilde{\mathbb{r}}_{\sigma(i)} \in D \quad \text{for} \quad 1 \leq i \leq N$$

$$\tilde{\mathbb{r}}_{\sigma(i)} \in D' \quad \text{for} \quad 1 \leq i \leq N+1$$

- $\Gamma_N = (\mathbb{r}_1 \cdots \mathbb{r}_N, \mathbb{p}_1 \cdots \mathbb{p}_N)$: 領域 D に N 個あって力学状態が Γ_N である確率密度

  $\Rightarrow \rho(\Gamma_N, N)$

§ 定義

$$\rho(\Gamma_N, N) = \int d\tilde{\Gamma}_{tot} \frac{1}{Z_{tot}} e^{-\beta H_{tot,0}(\tilde{\Gamma}_{tot};\, N_{tot})}$$

壁をとってよい
があるから

$$\times \sum_{\sigma\in G} \prod_{i=1}^{N} \chi(\tilde{\mathbf{r}}_{\sigma(i)} \in D) \prod_{i=N+1}^{N_{tot}} \chi(\tilde{\mathbf{r}}_{\sigma(i)} \in D')$$

$$\times\ \delta(\mathbf{r}_1 - \mathbf{r}_{\sigma(1)})\,\delta(\mathbf{p}_1 - \mathbf{p}_{\sigma(1)}) \cdots\cdots \delta(\mathbf{r}_N - \mathbf{r}_{\sigma(N)})\,\delta(\mathbf{p} - \mathbf{p}_{\sigma(N)})$$

$$\tilde{\Gamma}_\sigma = (\tilde{\mathbf{r}}_{\sigma(1)}, \ldots, \tilde{\mathbf{r}}_{\sigma(N)}, \tilde{\mathbf{p}}_{\sigma(1)} \cdots \tilde{\mathbf{p}}_{\sigma(N)})$$

$$\tilde{\Gamma}'_\sigma = (\tilde{\mathbf{r}}_{\sigma(N+1)}, \cdots \tilde{\mathbf{r}}_{\sigma(N_{tot})}\ \tilde{\mathbf{p}}_{\sigma(N+1)} \cdots \tilde{\mathbf{p}}_{\sigma(N_{tot})})$$

熱力学
極限で
無視

$$H_{tot,0}(\tilde{\Gamma};\, V_{tot}, N_{tot}) = H_0(\tilde{\Gamma}_\sigma; N) + H(\tilde{\Gamma}'_\sigma; N') + \cancel{H_{int}}$$

§ 書き換え

$$\rho(\Gamma_N, N) = \int d\tilde{\Gamma}_{tot} \frac{1}{Z_{tot}} \sum_{\sigma\in G} e^{-\beta H_0(\tilde{\Gamma}_\sigma ; N)} e^{-\beta H_0(\tilde{\Gamma}'_\sigma ; N')}$$

$$\times \prod_{i=1}^{N} \chi(\tilde{\mathbf{r}}_{\sigma(i)} \in D) \prod_{i=N+1}^{N_{tot}} \chi(\tilde{\mathbf{r}}_{\sigma(i)} \in D')$$

$$\times \quad \delta(\tilde{\Gamma}_\sigma - \Gamma_N)$$

$$= \frac{1}{Z_{tot}} e^{-\beta H_0(\Gamma_N ; N)} \prod_{i=1}^{N} \chi(\mathbf{r}_i \in D)$$

$$\sum_{\sigma\in G} \int d\tilde{\Gamma}'_\sigma e^{-\beta H_0(\tilde{\Gamma}'_\sigma ; N')} \prod_{i=N+1}^{N_{tot}} \chi(\tilde{\mathbf{r}}_{\sigma(i)} \in D')$$

$$= \frac{1}{Z_{tot}} e^{-\beta H(\Gamma_N ; V, N)} \sum_{\sigma\in G} Z(T, V', N')$$

$$= \frac{1}{Z_{tot}} e^{-\beta H(\Gamma_N ; V, N)} Z(T, V', N') \frac{N_{tot}!}{N! \, N'!}$$

§ 展開

$$\frac{Z(T, V_{tot}-V, N_{tot}-N)}{Z_{tot}(T, V_{tot}, N_{tot})} \frac{N_{tot}!}{N!\,(N_{tot}-N)!}$$

$$= \frac{1}{N!} e^{-\beta\left(F(T, V_{tot}-V, N_{tot}-N) - F(T, V_{tot}, N_{tot})\right)}$$

$$= \frac{1}{N!} e^{-\beta(pV-\mu N) + o(N_*)}$$

よって

$$\rho(\Gamma_N, N) = \frac{1}{N!} e^{-\beta(H(\Gamma_N, N)-\mu N)} \cdot e^{-\beta pV}$$

$$= \frac{1}{\Xi(T, V, \mu)} \frac{1}{N!} e^{-\beta(H(\Gamma_N, N)-\mu N)}$$

$$\Xi(T, V, \mu) = e^{\beta pV}$$

規格化因子

$$\therefore \underbrace{-pV}_{\Omega} = -k_B T \log \Xi$$

Ω: グランドポテンシャル