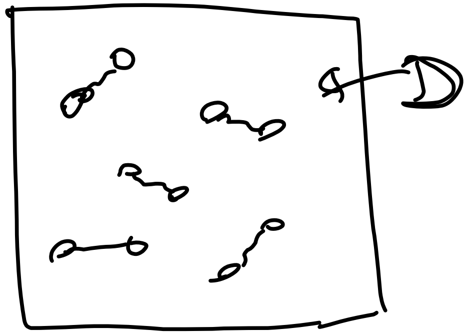
統計力学AV

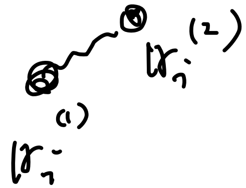
2020/11/10

問題



希薄2原子分子

$$\Gamma = (\mathbf{r}_1^{(1)}, \mathbf{r}_1^{(2)}, \ldots, \mathbf{r}_N^{(1)}, \mathbf{r}_N^{(2)}, \mathbf{P}_1^{(1)}, \mathbf{P}_2^{(2)} \ldots \mathbf{P}_N^{(1)}, \mathbf{P}_N^{(2)})$$



$$H(\Gamma; V, N) \equiv \sum_{i=1}^{N} \frac{|\mathbf{P}_i^{(1)}|^2 + |\mathbf{P}_i^{(2)}|^2}{2m} + \sum_{i=1}^{N} V_2(|\mathbf{r}_i^{(1)} - \mathbf{r}_i^{(2)}|)$$

$$+ \cancel{\sum_{i<j} V_{int}} + \underbrace{\sum_{\alpha} \sum_{i=1}^{N} V_{wall}(\mathbf{r}_i^{(\alpha)})}_{\to\ \mathbf{r}_i^{(1)},\ \mathbf{r}_i^{(2)} \in D}$$

熱容量を計算したい。

統計力学の公式

$$\Omega(E,V,N) \equiv \int d\Gamma\, \theta(E - H(\Gamma; V,N))$$

$$\Rightarrow \quad S(E,V,N) = k_B \log \frac{\Omega(E,V,N)}{N!}$$

$$\Rightarrow \quad \frac{1}{T} = \frac{\partial S(E,V,N)}{\partial E}$$

$$-\frac{1}{T^2}\left(\frac{\partial T}{\partial E}\right)_V = \frac{\partial^2 S(E,V,N)}{\partial E^2}$$

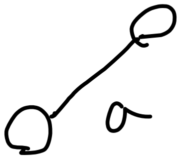
$$\left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial T}{\partial E}\right)_V^{-1}$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = -\frac{1}{T^2}\left(\frac{\partial^2 S(E,V,N)}{\partial E^2}\right)^{-1} \quad //$$

今日の目標

▷ $V_2(|\mathbf{r}^{(1)}-\mathbf{r}^{(2)}|)=\frac{K}{2}|\mathbf{r}^{(1)}-\mathbf{r}^{(2)}|^2$ なら計算できるが
それ以外は難しい。

▷ 特に、$V_2(|\mathbf{r}^{(1)}-\mathbf{r}^{(2)}|)=\frac{K}{2}\left(|\mathbf{r}^{(1)}-\mathbf{r}^{(2)}|-a\right)^2$



Kが"大きい"場合の計算をしたい。

⇩

新しい計算方法（公式）

（具体的な計算は来週）

~ Intermission ~

d次元球の体積

$$V_d(r) \equiv \int_{x_1^2+x_2^2+\cdots+x_d^2 \leq r^2} dx_1 \cdots dx_d$$ を計算する。

<u>Step-1</u>

$$V_d(\alpha r) = \int_{x_1^2+\cdots+x_d^2 \leq \alpha^2 r^2} dx_1 \cdots dx_d \qquad x_i = \alpha x_i'$$

$$= \alpha^d \int_{x_1'^2+\cdots+x_d'^2 \leq r^2} dx_1' \cdots dx_d' = \alpha^d V(r)$$

αで微分して, $\alpha=1$とおく

$$r \frac{dV_d(r)}{dr} = d\, V_d(r) \Rightarrow \frac{dV_d(r)}{V_d(r)} = d\,\frac{dr}{r}$$

$$\Rightarrow \log V_d(r) = d \log r + \mathrm{const}$$

$$\boxed{\therefore V_d(r) = C_d r^d}$$

C_dを求める

d 次元球の体積 2

書き直す。

$$V_d(r) = \int dx_1 \cdots dx_d \, \theta\left(r - \sqrt{x_1^2 + \cdots + x_d^2}\right) = C_d r^d$$

$$\theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \end{cases}$$

C_d 計算のアイデア!

Step 2

$$\int_{-\infty}^{\infty} dx \, e^{-x^2} = \sqrt{\pi}$$

$$I \equiv \int dx_1 \cdots dx_d \, e^{-(x_1^2 + \cdots + x_d^2)}$$

$$= \left(\int dx_1 e^{-x_1^2}\right) \cdots \left(\int dx_d e^{-x_d^2}\right)$$

$$= \pi^{\frac{d}{2}}$$

を C_d を使てあらわす。

d次元球の体積3

Step 3

$$I = \int dx_1 \cdots dx_d \, e^{-(x_1^2 + x_2^2 + \cdots + x_d^2)} \overbrace{\int_0^\infty dr \, \delta\left(r - \sqrt{x_1^2 + \cdots + x_d^2}\right)}^{=1 \text{ をかける}}$$

$$= \int_0^\infty dr \, e^{-r^2} \underbrace{\int dx_1 \cdots dx_d \, \delta\left(r - \sqrt{x_1^2 + \cdots + x_d^2}\right)}$$

$$\frac{dV_d(r)}{dr} = \int dx_1 \cdots dx_d \, \delta\left(r - \sqrt{x_1^2 + \cdots + x_d^2}\right) = d \, C_d \, r^{d-1}$$

$\therefore$

$$I = \int_0^\infty dr \, e^{-r^2} r^{d-1} \cdot d \, C_d$$

$$\Gamma(x) \equiv \int_0^\infty dt \, e^{-t} t^{x-1}$$

$r^2 = t, \quad 2r\,dr = dt$

$$= \int_0^\infty dt \, e^{-t} t^{\frac{d-2}{2}} \cdot \frac{d \, C_d}{2} = \Gamma\left(\frac{d}{2}\right) \cdot \frac{d}{2} \cdot C_d$$

d 次元球の体積4

Step4

$$\Gamma(x) = \int_0^\infty dt\, e^{-t} t^{x-1} = x\,\Gamma(x-1)$$
for $x > 1$

自然数 n $\quad \Gamma(n+1) = n!$

$$I = \Gamma\left(\frac{d}{2}\right) \cdot \frac{d}{2} C_d$$

d：偶数

$$= \left(\frac{d}{2}-1\right)!\, \frac{d}{2}\, C_d$$

$$= \left(\frac{d}{2}\right)!\, C_d$$

$I = \pi^{\frac{d}{2}}$ より， $\quad C_d = \dfrac{\pi^{\frac{d}{2}}}{\left(\frac{d}{2}\right)!}$

$$V_d(r) = \frac{\pi^{d}}{\left(\frac{d}{2}\right)!} r^d$$

～Intermission～

$\Omega(E,V,N)$ の計算

$$\Omega(E,V,N) \equiv \int d\Gamma\, \Theta(E - H(\Gamma;V,N))$$

- $d\Gamma = d\mathbf{r}_1 \cdots d\mathbf{r}_N\, d\mathbf{p}_1 \cdots d\mathbf{p}_N$ 6N次元積分
- $H(\Gamma;V,N) = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \sum_{i<j} V_{int}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=1}^{N} V_{wall}(\mathbf{r}_i)$

エネルギー面に囲まれる 6N次元領域の体積の計算

$\Longrightarrow$ 球の体積の計算と同じように考える

$\Omega(E,V,N)$の計算 2

$$Z(\beta, V, N) \equiv \int d\Gamma\, e^{-\beta H(\Gamma; V, N)}$$ を考える。

β：ある定数

※ $\Omega(E,V,N)$より計算しやすい。

$$\int dE\, \delta(H(\Gamma; V,N) - E) = 1$$ をかける.

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

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

$$\frac{\partial \Omega(E,V,N)}{\partial E} = \Sigma(E,V,N)$$

$\Omega(E,V,N)$の計算3

熱力学極限

$$
\begin{cases}
\dfrac{\Omega(E,V,N)}{N!} = e^{N\omega\left(\frac{E}{N},\frac{V}{N}\right)+o(N)} \\[2ex]
\dfrac{\Sigma(E,V,N)}{N!} = e^{N\omega\left(\frac{E}{N},\frac{V}{N}\right)+o(N)}
\end{cases}
$$

$$
\therefore \quad \frac{Z(\beta,V,N)}{N!} = \int dE\, e^{-\beta E}\, \frac{\Sigma(E,V,N)}{N!}
$$

$$
= \int dE\, e^{-\beta E + N\omega\left(\frac{E}{N},\frac{V}{N}\right)+o(N)}
$$

$$
= \cancel{N}\int du\, e^{-N[\beta u - \omega(u,v)]+o(N)}
$$

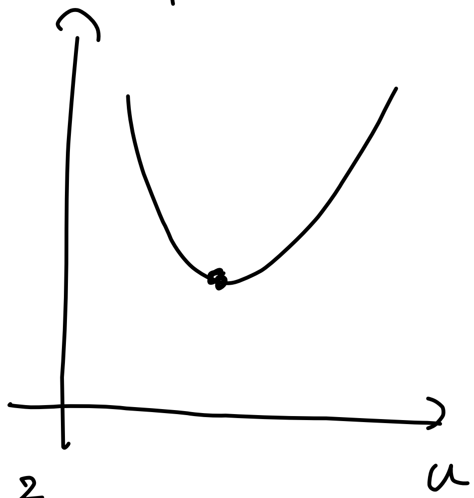
$$
u = \frac{E}{N},\quad v = \frac{V}{N}
$$

$$
N = e^{\log N} = e^{o(N)}
$$

$\Omega(E,V,N)$の計算4

$$\frac{1}{N!}Z(\beta,V,N) = \int du\, e^{-N(\beta u - w(u,v)) + o(N)}$$
$$= e^{-N(\beta u_* - w(u_*,v)) + o(N)}$$

$I(u) \equiv \beta u - w(u,v)$



u_* : $I(u)$の最小値

$\Longrightarrow \quad I'(u)\big|_{u_*} = 0$

$$\beta = \frac{\partial w(u,v)}{\partial u}\bigg|_{u_*}$$

$u_* = u_*(\beta, v)$

逆に解く : $\beta = \beta(u_*, v)$

- $\frac{\partial^2 w(u,v)}{\partial u^2} < 0$

条件／仮定

$\Omega(E,V,N)$の計算5

$$\frac{1}{N!}Z(\beta,V,N) = e^{N m(\beta,\frac{V}{N}) + o(N)}$$

が計算できたとする

$$\Rightarrow \quad m(\beta,v) = \omega(u_*(\beta,v),v) - \beta u_*(\beta,v)$$

$$\omega(u_*,v) = m(\beta(u_*,v),v) + \beta(u_*,v)\cdot u_*$$

$$\left.\frac{\partial \omega(u,v)}{\partial u}\right|_{u_*} = \left.\frac{\partial m}{\partial \beta}\right|_{\beta(u_*,v)} \left.\frac{\partial \beta(u,v)}{\partial u}\right|_{u_*} + \beta(u_*,v) + u_*\left.\frac{\partial \beta}{\partial u}\right|_{u_*}$$

$$\left.\frac{\partial \omega(u,v)}{\partial u}\right|_{u_*} = \beta \iff \left.\frac{\partial m}{\partial \beta}\right|_{\beta(u_*,v)} = -u_*$$

$$\therefore \quad \begin{cases} \omega(u,v) = m(\beta,v) + \beta u \\ \dfrac{\partial m}{\partial \beta} = -u \Leftrightarrow \beta = \beta(u,v) \end{cases}$$

（ルジャンドル変換）

βの意味

$$\left.\frac{\partial w(u,v)}{\partial u}\right|_{u_*} = \beta \iff \left.\frac{\partial m}{\partial \beta}\right|_{\beta(u_*,v)} = -u_*$$

$\because$
$$\begin{cases} w(u,v) = m(\beta,v) + \beta u \\ \dfrac{\partial m}{\partial \beta} = -u \iff \beta = \beta(u,v) \end{cases}$$

Boltzmann公式

$$S(E,V,N) = k_B \log \frac{\Omega(E,V,N)}{N!} = k_B N w\left(\frac{E}{N}, \frac{V}{N}\right) + o(N)$$

熱力学関係式

$$\frac{\partial S(E,V,N)}{\partial E} = k_B N \left.\frac{\partial w(u,v)}{\partial u}\right| \frac{1}{N} = k_B \beta$$

$$\| \quad \frac{1}{T}$$

$$\therefore \quad \beta = \frac{1}{k_B T}$$

逆温度

公式

$$\frac{Z(\beta, V, N)}{N!} = e^{N m(\beta, \frac{V}{N}) + o(N)}$$ が計算できたとする。

$\beta = \frac{1}{k_B T}$

$$\frac{\partial m(\beta, v)}{\partial \beta} = -u \quad \Rightarrow \quad \beta = \beta(u, v)$$

※ Eとℐの関係

$$\omega(u, v) = m(\beta, v) + \beta u$$

$$\begin{aligned} S(E, V, N) &= N k_B\, \omega(u, v) + o(N) \\ &= N k_B [m(\beta, v) + \beta u] \\ &= N k_B\, m(\beta, v) + \frac{E}{T} \end{aligned}$$

自由エネルギー

$$S(E,V,N) = N k_B m(\beta,v) + \frac{E}{T}$$

$$\frac{\partial m(\beta,v)}{\partial\beta} = -u$$

$$\Downarrow$$

- $u = u(\beta,v)$
- $\beta = \frac{1}{k_B T}$
- $w = m + \beta u$

$$F(T,V,N) \equiv E - TS(E,V,N)$$

$$\Rightarrow \quad F(T,V,N) = -N k_B T m(\beta,v) + o(N)$$

つまり

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

$$dE = TdS - pdV$$

$$dF = -SdT - pdV \Longleftrightarrow \begin{cases} S = -\left(\frac{\partial F}{\partial T}\right)_V \\ p = -\left(\frac{\partial F}{\partial V}\right)_T \end{cases}$$

付録： 熱力学関係式の確認

$$\frac{\partial m(\beta,v)}{\partial \beta} = -u$$

$$\Downarrow$$

- $u = u(\beta, v)$
- $\beta = \frac{1}{k_B T}$
- $w = m + \beta u$

$$F(T,V,N) = -N k_B T\, m(\beta, v) + o(N)$$

- $$\frac{\partial F(T,V,N)}{\partial T} = -N k_B T \frac{\partial m(\beta,v)}{\partial \beta}\left(-\frac{1}{k_B}\frac{1}{T^2}\right) - N k_B\, m(\beta, v)$$

$$= -k_B(\beta u + m)N$$

$$= -k_B w N = -S$$

$$\frac{\partial w(\beta,v)}{\partial \beta} = -u$$

- $$\frac{\partial F(T,V,N)}{\partial V} = -N k_B T \frac{\partial m(\beta,v)}{\partial v}$$

$$= -N k_B T\left[\frac{\partial\, w(u(\beta,v),v)}{\partial v} - \beta\frac{\partial u(\beta,v)}{\partial v}\right]$$

$$= -T\frac{\partial S(E,V,N)}{\partial V} = -P$$

まとめ

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

$$F(T, V, N) = -k_B T \log \frac{Z(\beta, V, N)}{N!}, \quad \beta = \frac{1}{k_B T}$$

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

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N}$$

来週、希薄な原子分子で

C_V を計算する!!