PHYS 650 S'24 Problem Set 5 Solutions

Kardar:

3.3 a) $\rho_N = \prod_{i=1}^{N} \rho_1(\vec{q}_i, \vec{p}_i, t) \equiv \prod_{i=1}^{N} \rho_1(\vec{x}_i, t)$

Normalization! $\int d^3q_i \, d^3p_i \, \rho_1 = \int d^6x_i \, \rho_1(\vec{x}_i) = 1$

$$\boxed{f_s(\{\underbrace{\vec{p}_i, \vec{q}_i}_{\vec{x}_i}, t\})} = \frac{N!}{(N-s)!} \int \prod_{i=s+1}^{N} d^6x_i \, \rho(\{\vec{x}_i\}, t)$$

$$= \frac{N!}{(N-s)!} \int \prod_{i=s+1}^{N} d^6x_i \prod_{j=1}^{N} \rho_1(\vec{x}_i, t)$$

$$\boxed{= \frac{N!}{(N-s)!} \prod_{j=1}^{s} \rho_1(\vec{x}_i, t)}$$

b) $$\left[\frac{\partial}{\partial t} + \sum_{n=1}^{s}\left(\frac{\vec{p}_n}{m} \cdot \frac{\partial}{\partial \vec{q}_n} - \frac{\partial U}{\partial \vec{q}_n} \cdot \frac{\partial}{\partial \vec{p}_n}\right)\right] f_s$$

$$= \sum_{n=1}^{s} \left\{ \int \underbrace{dV_{s+1}}_{d^6x_{s+1}} \frac{\partial \mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial \vec{q}_n} \cdot \frac{\partial f_{s+1}}{\partial \vec{p}_n} \right\}$$

Use $f_{s+1} = \dfrac{(N-s)!}{(N-s-1)!} f_s \, \rho_1(\vec{x}_{s+1}) \approx N f_s \, \rho_1(\vec{x}_{s+1})$

$$\to \boxed{\left[\frac{\partial}{\partial t} + \sum_{n=1}^{s}\left(\frac{\vec{p}_n}{m}\cdot\frac{\partial}{\partial \vec{q}_n} - \frac{\partial U}{\partial \vec{q}_n}\cdot\frac{\partial}{\partial \vec{p}_n}\right)\right] f_s}$$

$$= \sum_{n=1}^{s}\left[\int dV_{s+1}\, \frac{\partial \mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial \vec{q}_n}\cdot \underbrace{\frac{(N-s)!}{(N-s-1)!}}_{\approx N}\, \frac{\partial}{\partial \vec{p}_n}\left(f_s \rho_1(\vec{x}_{s+1})\right)\right]$$

$$\boxed{\approx \sum_{n=1}^{s}\left[\frac{\partial}{\partial \vec{q}_n}\int dV_{s+1}\, \rho_1(\vec{x}_{s+1})\, \mathcal{V}(\vec{q}_n - \vec{q}_{s+1})\right]\cdot N \frac{\partial f_s}{\partial \vec{p}_n}}$$

$$\to \frac{\partial}{\partial t} + \sum_{n=1}^{s}\left(\frac{\vec{p}_n}{m}\cdot\frac{\partial}{\partial \vec{q}_n} - \frac{\partial U_{eff}}{\partial \vec{q}_n}\cdot\frac{\partial}{\partial \vec{p}_n}\right) f_s = 0,$$

where

$$\boxed{U_{eff}(\vec{q}) = U(\vec{q}) + N\int d^3q'\, d^3p'\, \rho_1(\vec{x}_1')\, \mathcal{V}(\vec{q}_n - \vec{q}\,')}$$

4.7 a) N diatomic molecules aligned either along $\hat{x}$ or $\hat{y}$ with energy 0, or $\hat{z}$ with energy $\varepsilon > 0$.

Ground state: $E_{min} = 0$, each molecule aligned along $\hat{x}$ or $\hat{y}$.

$\rightarrow$ $\boxed{(2^N) \text{ configurations}}$

Largest energy: $E_{max} = N\epsilon$, all molecules aligned along $\hat{z}$

$\rightarrow$ $\boxed{1 \text{ configuration}}$

b) Energy $E \rightsquigarrow$ # molecules along $\hat{z}$, $N_z = E/\epsilon$

$$\Omega(E,N) = \frac{N!}{N_z!\,(N-N_z)!} \cdot 2^{N-N_z}$$

from molecules along $\hat{z}$

from remaining molecules along $\hat{x}$, $\hat{y}$

$$S(E,N) = k_B \ln\left(\frac{N!}{N_z!\,(N-N_z)!}\right) + (N-N_z)k_B \ln 2$$

$$\approx -Nk_B\left[\frac{E}{N\epsilon}\ln\frac{E}{N\epsilon} + \left(1-\frac{E}{N\epsilon}\right)\ln\left(1-E/N\epsilon\right)\right]$$

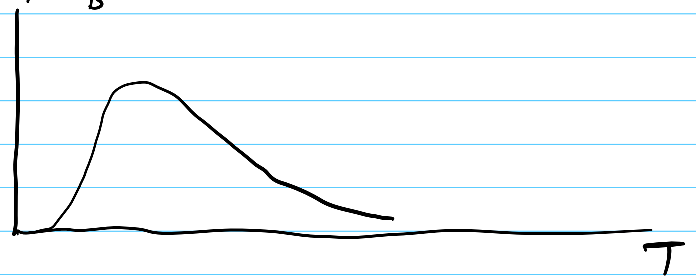
$$+ k_B\left(N - \frac{E}{\epsilon}\right)\ln 2$$

c) $\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_N = -\frac{k_B}{\epsilon}\ln\left(\frac{E}{N\epsilon - E}\right) - \frac{k_B}{\epsilon}\ln 2$

Solve for $E(T)$:

$$E(T) = \frac{N\epsilon}{\exp\left(\frac{\epsilon}{k_B T} + \ln 2\right) + 1} = \frac{N\epsilon}{2\exp\left(\frac{\epsilon}{k_B T}\right) + 1}$$

$$\boxed{C(T) = \frac{dE}{dT} = N k_B \left(\frac{\epsilon}{k_B T}\right)^2 \frac{2\exp(\epsilon/k_B T)}{\left(2\exp(\epsilon/k_B T) + 1\right)^2}}$$



d) $\boxed{p(\text{molecule along } \hat{z})} = \frac{\Omega(E-\epsilon, N-1)}{\Omega(E, N)}$ remaining molecules

$$= \left(\frac{(N-1)!}{(N_z-1)!\,\cancel{\left((N-1)-(N_z-1)\right)!}}\, \cancel{2^{((N-1)-(N_z-1))}}\right)\left(\frac{N_z!\,\cancel{(N-N_z)!}}{N!}\, \cancel{\frac{1}{2^{N-N_z}}}\right)$$

$$= \frac{N_z}{N} = \frac{E}{N\epsilon} = \boxed{\frac{1}{2\exp(\epsilon/k_B T) + 1}}$$

e) Largest possible internal energy w/ $T>0$:

$\frac{dE}{dT} > 0 \rightarrow$ Maximum at $T \rightarrow \infty$:

$$\boxed{E_{max}(T>0)} = \frac{N\epsilon}{2+1} \boxed{= \frac{N\epsilon}{3}}$$