

Problem Set 2: Solutions

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1.) equation of motion follows from Liouvillean:

$$i \hbar \frac{\partial \rho^N(\vec{q}^N, \vec{p}^N; t)}{\partial t} = - \mathcal{L} \rho^N(\vec{q}^N, \vec{p}^N; t)$$

$$\frac{\partial n}{\partial t} = \sum_{i=1}^N \vec{q}_i \cdot \frac{\partial}{\partial \vec{q}_i} \delta(\vec{q}_i - \vec{R}) \quad \vec{q}_i - \text{coordinates}$$

no momentum dependence of density

$$\begin{aligned} \frac{\partial n}{\partial t} &= \sum_{i=1}^N \frac{\vec{p}_i}{m} \cdot \frac{\partial}{\partial \vec{q}_i} \delta(\vec{q}_i - \vec{R}) \\ &= - \vec{\nabla}_{\vec{R}} \left[\sum_{i=1}^N \frac{\vec{p}_i}{m} \delta(\vec{q}_i - \vec{R}) \right] \end{aligned}$$

(we can do this since

$$\begin{aligned} &\sum_{i=1}^N \vec{\nabla}_{\vec{q}_i} \delta(\vec{q}_i - \vec{R}) \\ &= - \sum_{i=1}^N \vec{\nabla}_{\vec{R}} \delta(\vec{q}_i - \vec{R}) \\ &= - \vec{\nabla}_{\vec{R}} \left[\sum_{i=1}^N \delta(\vec{q}_i - \vec{R}) \right] \end{aligned}$$

$$\frac{\partial n}{\partial t} = - \vec{\nabla}_{\vec{R}} \cdot \underbrace{\vec{J}(\vec{p}^N, \vec{q}^N; \vec{R})}_{\text{identifies as particle current}}$$

2. Palstra & Beale: 3.1

(1)

$$a.) \quad \Gamma = N! \sum_{\{n_s\}} \frac{\omega_0^{n_0} \omega_1^{n_1} \dots}{n_0! n_1! \dots}$$

rewrite $\omega = \sum_{\{n_s\}} A_{\{n_s\}} \omega_r^{n_r}$

$$[\omega_r \partial_{\omega_r}]^2 \ln \Gamma = [\omega_r \partial_{\omega_r}] \left[\frac{\omega_r}{r} \frac{\partial \Gamma}{\partial \omega_r} \right]$$

$$= \left[\frac{\omega_r}{r} \frac{\partial \Gamma}{\partial \omega_r} - \left[\frac{\omega_r}{r^2} \frac{\partial \Gamma}{\partial \omega_r} \right]^2 + \frac{\omega_r^2}{r} \frac{\partial^2 \Gamma}{\partial \omega_r^2} \right]$$

$$\Gamma = \sum_{\{n_s\}} A_{\{n_s\}} \omega_r^{n_r}$$

$$\frac{\partial \Gamma}{\partial \omega_r} = \sum_{\{n_s\}} A_{\{n_s\}} n_r \omega_r^{n_r-1}$$

$$\frac{\partial^2 \Gamma}{\partial \omega_r^2} = \sum_{\{n_s\}} A_{\{n_s\}} n_r (n_r - 1) \omega_r^{n_r-2}$$

$$= \frac{\sum_{\{n_s\}} A_{\{n_s\}} n_r \omega_r^{n_r}}{\sum_{\{n_s\}} A_{\{n_s\}} \omega_r^{n_r}} - \left[\frac{\sum_{\{n_s\}} A_{\{n_s\}} n_r \omega_r^{n_r}}{\sum_{\{n_s\}} A_{\{n_s\}} \omega_r^{n_r}} \right]^2$$

$$+ \frac{\sum_{\{n_s\}} A_{\{n_s\}} n_r (n_r - 1) \omega_r^{n_r}}{\sum_{\{n_s\}} A_{\{n_s\}} \omega_r^{n_r}}$$

$$= \frac{\sum_{\{n_s\}} A_{\{n_s\}} n_r^2 \omega_r^{n_r}}{\sum_{\{n_s\}} A_{\{n_s\}} \omega_r^{n_r}} - \left[\frac{\sum_{\{n_s\}} A_{\{n_s\}} n_r \omega_r^{n_r}}{\sum_{\{n_s\}} A_{\{n_s\}} \omega_r^{n_r}} \right]^2$$

$$= \langle n_r^2 \rangle - \langle n_r \rangle^2 = \langle n_r^2 \rangle$$

$$b.) \quad u = \frac{\sum_s w_s e^{-\beta E_s} \bar{E}_s}{\sum_s w_s e^{-\beta E_s}}$$

$$\frac{\partial u}{\partial w_r} = 0 = \frac{e^{-\beta E_r} E_r}{\sum_s w_s e^{-\beta E_s}} + \frac{\sum_s w_s E_s e^{-\beta E_s}}{\sum_s w_s e^{-\beta E_s}} \left(-E_s \frac{\partial \beta}{\partial w_r} \right)$$

$$= \frac{\sum_s w_s e^{-\beta E_s} E_s}{\left(\sum_s w_s e^{-\beta E_s} \right)^2} \left[w_r e^{-\beta E_r} + \sum_s w_s e^{-\beta E_s} \left(-E_s \frac{\partial \beta}{\partial w_r} \right) \right]$$

$$= \frac{n_r E_r}{N} \bar{E}^2 \frac{\partial \beta}{\partial w_r} - \frac{\bar{E} n_r}{N} + \bar{E}^2 \frac{\partial \beta}{\partial w_r} = 0$$

$$\boxed{\frac{\partial \beta}{\partial w_r} = \frac{n_r}{N} \frac{(E_r - \bar{E})}{\bar{E}^2 - \bar{E}^2}} \quad \checkmark$$

second part: derive $\langle \Delta n_r^2 \rangle$

$$\langle \Delta n_r^2 \rangle = \left[w_r \frac{\partial}{\partial w_r} \left[\frac{w_r \exp(-\beta E_r)}{Q} + (u - \bar{E}) w_r \frac{\partial \beta}{\partial w_r} \right] \right]_{w_r=1}$$

$$= \left[w_r \frac{\partial}{\partial w_r} \left(\frac{w_r \exp(-\beta E_r)}{Q} \right) + \left(w_r \frac{\partial}{\partial w_r} (u - \bar{E}) \right) w_r \frac{\partial \beta}{\partial w_r} + \cancel{w_r \frac{\partial}{\partial w_r} (u - \bar{E}) w_r \frac{\partial}{\partial w_r} w_r \frac{\partial \beta}{\partial w_r}} \right]_{w_r=1}$$

$$= \left[w_r \frac{\partial}{\partial w_r} \left[\frac{w_r \exp(-\beta E_r)}{Q} \right] + \left(w_r \frac{\partial}{\partial w_r} (u - \bar{E}) \right) w_r \frac{\partial \beta}{\partial w_r} \right]_{w_r=1}$$

first term:

$$\begin{aligned} \omega_r \partial_{\omega_r} \left[\frac{\omega_r e^{-\beta E_r}}{Q} \right]_{\omega_r=1} &= \left[\frac{\omega_r e^{-\beta E_r}}{Q} + \frac{\omega_r^2 e^{-\beta E_r}}{Q} (-E_r \frac{\partial \beta}{\partial \omega_r}) \right. \\ &\quad \left. - \frac{\omega_r e^{-\beta E_r}}{Q^2} \left(\omega_r e^{-\beta E_r} + \sum_s \omega_s e^{-\beta E_s} (-E_s \frac{\partial \beta}{\partial \omega_r}) \right) \right]_{\omega_r=1} \\ &= \left[\frac{n_r}{N} - n_r E_r \frac{\partial \beta}{\partial \omega_r} - \left(\frac{n_r}{N} \right)^2 + \frac{\bar{E} n_r}{N} \frac{\partial \beta}{\partial \omega_r} \right] \end{aligned} \quad (4)$$

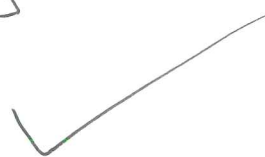
second term:

$$\begin{aligned} &\left[\left(\omega_r \partial_{\omega_r} (\mu - \bar{E}) \right) \omega_r \frac{\partial \beta}{\partial \omega_r} \right]_{\omega_r=1} \\ &= \left[\left(-\omega_r \partial_{\omega_r} \bar{E} \right) \omega_r \frac{\partial \beta}{\partial \omega_r} \right]_{\omega_r=1} \\ &= \left[-\omega_r^2 \frac{\partial \beta}{\partial \omega_r} \left(\frac{e^{-\beta E_r}}{Q} E_r + \frac{\sum_s e^{-\beta E_s}}{Q} E_s (-E_s \frac{\partial \beta}{\partial \omega_r}) \right) \right. \\ &\quad \left. - \frac{\sum_s e^{-\beta E_s}}{Q^2} E_s \left(e^{-\beta E_r} + \sum_s \omega_s e^{-\beta E_s} (-E_s \frac{\partial \beta}{\partial \omega_r}) \right) \right]_{\omega_r=1} \\ &= \left[-\frac{\partial \beta}{\partial \omega_r} \left(\frac{n_r}{N} E_r - \bar{E} \frac{\partial \beta}{\partial \omega_r} - \frac{\bar{E} n_r}{N} + \bar{E}^2 \frac{\partial \beta}{\partial \omega_r} \right) \right] \\ &= \left[-\frac{\partial \beta}{\partial \omega_r} \left(\frac{n_r}{N} (E_r - \bar{E}) + \frac{\partial \beta}{\partial \omega_r} (\bar{E}^2 - \bar{E}^2) \right) \right] \\ &= \left[-\frac{\partial \beta}{\partial \omega_r} \left(\frac{n_r}{N} (E_r - \bar{E}) + \frac{n}{N} (\bar{E} - E_r) \right) \right] = 0 \end{aligned}$$

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$$\begin{aligned} \langle \Delta n_r^2 \rangle &= \left[\frac{n_r}{N} - \left(\frac{n_r}{N} \right)^2 + \frac{n_r}{N} (\bar{E} - E_r) \frac{\partial \beta}{\partial \omega_r} \right] \\ &= \left[\frac{n_r}{N} - \left(\frac{n_r}{N} \right)^2 + \left(\frac{n_r}{N} \right)^2 \frac{(\bar{E} - E_r)^2}{(\bar{E}^2 - \bar{E}^2)} \right] \end{aligned}$$



$$g''(x_0) = \left(\frac{f''(x_0)}{f(x_0)} - \left[\frac{f'(x_0)}{f(x_0)} \right]^2 \right) + \frac{Nu+1}{Nx_0^2}$$

x_0 defined by: $u = x_0 \frac{f'(x_0)}{f(x_0)}$

$$= \left(\frac{f''(x_0)}{f(x_0)} - \frac{u^2}{x_0^2} \right) + \frac{Nu+1}{Nx_0^2}$$

since $f(r) = \sum_r \omega_r r^{E_r}$ (Eq. 3.7.22)

$$f(x_0) = \sum_r \omega_r x_0^{E_r}$$

$$f'(x_0) = \sum_r \omega_r E_r x_0^{E_r-1}$$

$$f''(x_0) = \sum_r \omega_r E_r(E_r-1) x_0^{E_r-2}$$

$$\frac{f''(x_0)}{f(x_0)} = \frac{\sum_r \omega_r E_r(E_r-1) x_0^{E_r}}{\sum_r \omega_r x_0^{E_r}} = \frac{\overline{E^2}}{\overline{x_0^2}} - \frac{\overline{E}}{\overline{x_0}}$$

$$g''(x_0) = \left[\frac{\overline{E^2}}{\overline{x_0^2}} - \frac{\overline{E}}{\overline{x_0}} - \frac{u^2}{x_0^2} + \frac{u}{x_0} + \frac{1}{Nx_0^2} \right]$$

$$= \left[\frac{\overline{E^2} - \overline{E}^2}{\overline{x_0^2}} \right] + \frac{1}{Nx_0^2} \quad \text{for } N \rightarrow \infty \quad \frac{1}{Nx_0^2} = 0$$

using $x_0 = e^{-\beta}$

$$g''(x_0) = e^{2\beta} (\overline{E^2} - \overline{E}^2)$$

second order term: $-\frac{1}{2\beta} \ln(2\pi N (\overline{E^2} - \overline{E}^2) e^{2\beta}) =$

$$-\frac{kT}{2\beta} \ln(2\pi kT^2 C_V) = 2\beta \ln(2\pi kT^2 C_V)$$

3.6.9

second order term:

$$= \ln(2\pi kT^2 C_V e^{2\beta})$$

$$C_V = N \frac{\partial \overline{E}}{\partial T} = N \frac{\partial \overline{E}}{\partial \beta} \frac{\partial \beta}{\partial T} = \frac{N(\overline{E^2} - \overline{E}^2)}{kT^2}$$

$$kT^2 C_V = N(\overline{E^2} - \overline{E}^2)$$

Ratna & Beale: 3.3

(5)

$$G(z) = e^z = \sum_{u=0}^{\infty} \frac{z^u}{u!}$$

$$\frac{1}{i\pi} \oint_{\gamma} \frac{G(z)}{z^{u+1}} dz = \frac{1}{i\pi} \oint_{\gamma} \frac{e^z}{z^{u+1}} dz = \frac{1}{u!}$$

$$g(z) = \ln \frac{e^z}{z^{u+1}} = z - (u+1) \ln z$$

$$g'(z) = 1 - \frac{(u+1)}{z} = 0 \quad z_0 = u+1$$

$$\frac{e^{u+1}}{(u+1)^{u+1}} \frac{1}{i\pi} \oint_{\gamma}$$

$$g'(z_0) = 1 - \frac{(u+1)}{z_0} = 0$$

$$g''(z_0) = \frac{(u+1)}{z_0^2} \quad z_0 = u+1$$

$$g''(z_0) = \frac{1}{u+1}$$

$$\Gamma(u) = \frac{e^{u+1}}{(u+1)^{u+1}} \frac{1}{i\pi} \oint_{\gamma} \exp\left(-\frac{1}{2} \left(\frac{1}{u+1}\right) y^2\right) dy$$

$$\ln \left\{ \frac{e^{u+1}}{(u+1)^{u+1}} \frac{1}{(2\pi/(u+1))^{1/2}} \right\}$$

$$(u+1) - (u+1) \ln(u+1) - \frac{1}{2} \ln[2\pi/(u+1)]$$

$$\text{as } u \rightarrow \infty \quad u - u \ln u = \frac{1}{u!} \quad (\text{Stirling!})$$

$$\Gamma(N, U) = \sum_{\{n_i\}} W(\{n_i\})$$

$$= \sum_{\{n_i\}} \frac{N!}{n_1! \dots}$$

largest term in sum

$\ln N! - \sum_i \ln n_i!$ needs to be maximized without any constraints

apply Stirling's approximation

$$\ln W = N \ln N - \sum_i n_i \ln n_i$$

$$\text{maximize } \frac{\partial \ln W}{\partial n_i} = -1 - \ln n_i = 0$$

$$n_i = e^{-1} = \text{constant}$$

$$\text{normalization } n_i = \frac{1}{\sum_i n_i} = \frac{1}{N}$$

verifies that it corresponds to mean entropy:

$$S = - \sum_{i=1}^N n_i \ln n_i = - \sum_{i=1}^N \frac{1}{N} \ln \frac{1}{N} = - \ln \frac{1}{N} = \underline{\ln N}$$

N-number of states

a) Ω microstates

assume each has same probability of occurrence

$P_i \Rightarrow$ entropy from 3.3.13

$$S = -k \sum_{i=1}^{\Omega} P_i \ln P_i \rightarrow \text{set } k=1$$

maximize under constraint $\sum_{i=1}^{\Omega} P_i = 1$

$$\tilde{S} = -k \sum_{i=1}^{\Omega} P_i \ln P_i + \alpha \left(\sum_{i=1}^{\Omega} P_i - 1 \right)$$

$$\frac{\partial \tilde{S}}{\partial P_j} = -k (1 + \ln P_j) + \alpha = 0$$

$\Rightarrow P_j = \text{constant}$

normalization condition fixes α
(or constant)

$$P_j = \frac{1}{\Omega}$$

all states are equally likely to occur

b.) minimize under constraint $\sum_i P_i E_i = \bar{E}$ (+ normalization)

$$\tilde{S} = -k \sum_{i=1}^{\Omega} P_i \ln P_i + \alpha \left(\sum_{i=1}^{\Omega} P_i - 1 \right) + \beta \left(\sum_{i=1}^{\Omega} P_i E_i - \bar{E} \right)$$

$$\frac{\partial \tilde{S}}{\partial P_i} = -k (\ln P_i + 1) + \alpha + \beta E_i = 0$$

$$P_i = \frac{e^{-\beta E_i}}{\sum_{i=1}^{\Omega} e^{-\beta E_i}}$$

c.) minimize under two constraints (+ normalization)

$$\tilde{S} = -k \sum_{i=1}^{\Omega} P_i \ln P_i + \alpha \left(\sum_{i=1}^{\Omega} P_i - 1 \right) + \beta \left(\sum_{i=1}^{\Omega} P_i E_i - \bar{E} \right) + \gamma \left(\sum_{i=1}^{\Omega} P_i N_i - \bar{N} \right)$$

~~$\Rightarrow \phi$~~

(8)

$$\sum_i \sum_j P_{ij} E_i = \bar{E}$$

$$\sum_{ij} P_{ij} = 1$$

$$\sum_i \sum_j P_{ij} U_j = \bar{U}$$

$$\tilde{J} = -k \sum_{ij} P_{ij} \ln P_{ij} + \alpha \left(\sum_{ij} P_{ij} - 1 \right) + \beta \left(\sum_{ij} P_{ij} E_i - \bar{E} \right) + \gamma \left(\sum_{ij} P_{ij} U_j - \bar{U} \right) \Rightarrow$$

$$\frac{\partial \tilde{J}}{\partial P_{ij}} = -k(\ln P_{ij} + 1) + \alpha + \beta E_i + \gamma U_j = 0 \quad \text{let } k=1$$

$$\Rightarrow P_{ij} = e^{-\frac{\alpha + \beta E_i + \gamma U_j}{1}}$$

normalization

$$P_{ij} = \frac{e^{-\beta E_i - \gamma U_j}}{\sum_{ij} e^{-\beta E_i - \gamma U_j}}$$