Question 1 (20 pts.):

Consider an ensemble of systems with a total of N members. The energy levels each system can occupy are denoted ε_i and are discrete. Each ensemble member is in one of the states. A configuration of the ensemble can be characterized by the occupation numbers $n_1, n_2, \ldots$ In terms of the occupation numbers the total energy and the total number of systems can be written:

$$\sum_i n_i = N, \qquad \sum_i n_i \varepsilon_i = E.$$

These two equations are constraints on the configurations.

- Write an expression for the number of ways W a particular configuration ($n_1, n_2, \ldots$) can be realized.
- Find the configuration for which W is the maximum given the constraints on the energy and the total number of systems. Assume that N is large, and use the Stirling formula: $\ln m! = m \ln m - m$. Maximize $\ln W$ using Lagrange multipliers for the constraints. (Let α denote the Lagrange multiplier for the constraint N and β denote the Lagrange multiplier for the constraint for E.)
- Determine the Lagrange multiplier α in terms of the other variables.
- Determine the probability $p_i = n_i/N$.

$$\boxed{W = \frac{N!}{n_1! n_2! \ldots}}$$

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

constraints: $\tilde{S} = \ln W + \alpha\left(\sum_i n_i - N\right) + \beta\left(\sum_i n_i \varepsilon_i - E\right)$

$$\frac{\partial \tilde{S}}{\partial n_i} = -\ln n_i - 1 + \alpha + \beta \varepsilon_i = 0$$

$$\boxed{n_i = e^{\alpha - 1} e^{+\beta \varepsilon_i}}$$

$$\sum_i n_i = e^{\alpha-1} \sum_i e^{\beta \varepsilon_i} = N$$

$$\Rightarrow \boxed{e^{\alpha - 1} = \frac{N}{\sum_i e^{+\beta \varepsilon_i}}} \Rightarrow \boxed{p_i = \frac{n_i}{N} = \frac{e^{+\beta \varepsilon_i}}{\sum_i e^{\beta \varepsilon_i}}}$$

Question 2 (20 pts.):

For the canonical ensemble, the probability of a state "i" with energy ε_i being occupied is given by

$$p_i = exp(-\beta\ \varepsilon_i)/Q \text{ where } Q = \sum_i exp(-\beta\ \varepsilon_i).$$

Show that the constant β is related to the temperature T as follows. Consider a process in which no work is done on the system meaning that the internal energy change dU is given by the thermodynamic relation

$$dU = TdS, \quad \text{(Eq. 1)}$$

where S denotes the entropy. Assuming that the entropy is given by $S = -k_B \sum_i p_i \ln p_i$ and the internal (average) energy is given by $U = \sum_i p_i\ \varepsilon_i$, use Equation 1 to derive a relation between β and T.

$$dU = TdS$$

$$S = -k_B \sum_i p_i \ln p_i$$

$$dS = -k_B \sum_i \ln p_i\, dp_i - k_B \sum_i dp_i = -k_B \sum_i \ln p_i\, dp_i$$

$$du = d\left[\sum_i p_i \varepsilon_i\right] = \sum_i \varepsilon_i dp_i + \underbrace{\sum_i p_i d\varepsilon_i}_{0}$$

(no work done on system)

$$\Rightarrow \sum_i \varepsilon_i\, dp_i = -k_B T \sum_i \ln p_i\, dp_i$$

$$p_i = \frac{\exp(-\beta\varepsilon_i)}{Q}$$

$$\ln p_i = -\beta\varepsilon_i - \ln Q$$

$$\Rightarrow \sum_i \varepsilon_i\, dp_i = k_B T\beta \sum_i \varepsilon_i\, dp_i + k_B T \ln Q \underbrace{\sum_i dp_i}_{0}$$

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

Question 3 (20 pts.):

Sethna Problem 5.7.

$$\frac{\partial f(\rho)}{\partial t} = -\nabla \cdot [f(\rho)\vec{V}] \qquad \text{(continuity equation)}$$

$$= -\sum_i \frac{\partial}{\partial p_i}[f(\rho)\dot{p}_i] - \sum_i \frac{\partial}{\partial q_i}[f(\rho)\dot{q}_i]$$

$$= -\sum_i \frac{\partial f(\rho)}{\partial \rho}\frac{\partial \rho}{\partial p_i}\dot{p}_i - \sum_i f(\rho)\frac{\partial \dot{p}_i}{\partial p_i} - \sum_i \frac{\partial f(\rho)}{\partial \rho}\frac{\partial \rho}{\partial q_i}\dot{q}_i$$

$$- \sum_i f(\rho)\frac{\partial \dot{q}_i}{\partial q_i}$$

use: $\dot{p}_i = -\frac{\partial H}{\partial q_i} \qquad \dot{q}_i = \frac{\partial H}{\partial p_i}$

$$= -\sum_i \frac{\partial f(\rho)}{\partial \rho}\left(\frac{\partial \rho}{\partial p_i}\dot{p}_i + \frac{\partial \rho}{\partial q_i}\dot{q}_i\right) - \sum_i f(\rho)\cancelto{0}{\left[-\frac{\partial^2 H}{\partial p_i \partial q_i} + \frac{\partial^2 H}{\partial p_i q_i}\right]}$$

$$\frac{\partial f(\rho)}{\partial t} = -\sum_i \frac{\partial f(\rho)}{\partial \rho}\left(\frac{\partial \rho}{\partial p_i}\dot{p}_i + \frac{\partial \rho}{\partial q_i}\dot{q}_i\right)$$

$$\Rightarrow \quad \frac{\partial f(\rho)}{\partial t} + \sum_i \frac{\partial f(\rho)}{\partial \rho}\frac{\partial \rho}{\partial p_i}\dot{p}_i + \frac{\partial f(\rho)}{\partial \rho}\frac{\partial \rho}{\partial q_i}\dot{q}_i = 0$$

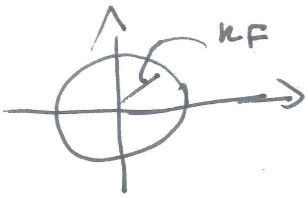
$$\Rightarrow \quad \underline{\frac{d f(\rho)}{dt} = 0} \quad \Rightarrow \quad \frac{d}{dt}\int f(\rho)\, dP\, dQ = 0$$

so $S = -k_B \int \rho \log \rho \, dP dQ \Rightarrow$ constant in time

Question 4 (20 pts.):

Consider a system of free bosons in two dimensions in the grand canonical ensemble. The particles have mass m, and they occupy a square of side L. Calculate the number of particles as a function of temperature T and chemical potential μ.

Need $g(\varepsilon)\,d\varepsilon$ $\qquad \varepsilon = \frac{\hbar^2 k^2}{2m}$



$\Rightarrow$ volume in k-space

πk_F^2

number of particles within this volume

$$\tilde{N} = \frac{\pi k_F^2}{(2\pi/L)^2} = \frac{A k_F^2}{4\pi}$$

number of particles/states with wavevector $k < k' < k + dk$

$$d\tilde{N} = \frac{A}{2\pi} k\,dk$$

using $\varepsilon = \frac{\hbar^2 k^2}{2m} \rightarrow d\varepsilon = \frac{2\hbar^2 k}{2m} = \frac{\hbar^2 k\,dk}{m}$

$$\rightarrow k = \frac{\sqrt{2m\varepsilon}}{\hbar} \rightarrow k\,dk = \frac{m\,d\varepsilon}{\hbar^2}$$

$$d\tilde{N} = \frac{A}{2\pi}\frac{m}{\hbar^2}\,d\varepsilon \Rightarrow g(\varepsilon) = \frac{Am}{2\pi\hbar^2}$$

$$N(\mu, T) = \int_0^\infty \frac{g(\varepsilon)\,d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1} = \frac{Am}{2\pi\hbar^2}\int_0^\infty \frac{d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$$

Question 5 (20 pts.)

Sethna, Problem 6.8 (a).

$S(N,V,E)$ is extensive

$\rightarrow \quad \lambda S(N,V,E) = S(\lambda N, \lambda V, \lambda E)$

take derivative of both sides with respect to λ and set $\lambda = 1$

$$S(N,V,E) = \frac{\partial S}{\partial N} N + \frac{\partial S}{\partial V} V + \frac{\partial S}{\partial E} E$$

since: $T\,dS = dE + P\,dV - \mu\,dN$

$$dS = \frac{dE}{T} + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN$$

$$\Downarrow \qquad \Downarrow \qquad \Downarrow$$

$$\frac{\partial S}{\partial E} = \frac{1}{T} \qquad \frac{\partial S}{\partial V} = \frac{P}{T} \qquad \frac{\partial S}{\partial N} = -\frac{\mu}{T}$$

$$S = -\frac{\mu N}{T} + \frac{PV}{T} + \frac{E}{T}$$

$$\Rightarrow \quad \boxed{E = TS - PV + \mu N}$$

Question 6:

For problem 7.10 in Sethna (crystal defects), calculate the canonical partition function, the mean energy, the fluctuations in the energy, the entropy, and the specific heat as a function of temperature.

$$\bar{\bar{H}} = \begin{pmatrix} 0 & & & \\ & \epsilon & & \\ & & \epsilon & \\ & & & \ddots \end{pmatrix} \qquad Z(T) = \mathrm{Tr}\, e^{-\beta H} \qquad \left(\beta = \frac{1}{k_B T}\right)$$

$$\boxed{Z(T) = 1 + M e^{-\beta\epsilon}}$$

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\left(\frac{1}{1+Me^{-\beta\epsilon}}\right) M e^{-\beta\epsilon}(-\epsilon) = \underline{\underline{\frac{M e^{-\beta\epsilon}\,\epsilon}{1+Me^{-\beta\epsilon}}}}$$

energy fluctuations: $\sigma_E = \overline{E^2} - \bar{E}^2 = \frac{\partial \ln Z}{\partial \beta^2}$

$$\ln Z = \ln(1 + M e^{-\beta\epsilon})$$

$$\frac{\partial \ln Z}{\partial \beta} = \frac{1}{1+Me^{-\beta\epsilon}} M e^{-\beta\epsilon}(-\epsilon)$$

$$\frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{M e^{-\beta\epsilon}(-\epsilon)^2}{1+Me^{-\beta\epsilon}} - \frac{M e^{-\beta\epsilon}(-\epsilon)\, M e^{-\beta\epsilon}(-\epsilon)}{(1+Me^{-\beta\epsilon})^2}$$

$$= \frac{M e^{-\beta\epsilon}(-\epsilon)^2 + \cancel{M^2 e^{-2\beta\epsilon}(-\epsilon)^2} - \cancel{M^2 e^{-2\beta\epsilon}(-\epsilon)^2}}{(1+Me^{-\beta\epsilon})^2}$$

$$\boxed{\sigma_E^2 = \frac{M e^{-\beta\epsilon}\,\epsilon^2}{(1+Me^{-\beta\epsilon})^2}}$$

Worksheet:

entropy: $A = \bar{E} - TS \Rightarrow TS = A - \bar{E}$

$$S = \frac{A}{T} - \frac{\bar{E}}{T}$$

$$A = -k_B T \ln Z$$

$$S = -\frac{k_B T \ln(1 + M e^{-\beta\epsilon})}{T} - \frac{k_B \beta M e^{-\beta\epsilon} \epsilon}{1 + M e^{-\beta\epsilon}}$$

$$S = -k_B \ln(1 + M e^{-\beta\epsilon}) - \frac{k_B \beta\epsilon M e^{-\beta\epsilon}}{1 + M e^{-\beta\epsilon}}$$

$$C = \frac{\partial \bar{E}}{\partial T} = \frac{\partial \bar{E}}{\partial \beta}\left(-\frac{1}{k_B T^2}\right) = \frac{\sigma_E^2}{k_B T^2}$$

$$\boxed{C = \frac{M \epsilon^2 e^{-\beta\epsilon}}{k_B T^2 (1 + M e^{-\beta\epsilon})^2}}$$