

Ch/ChE 164 Winter 2024 Homework Problem Set #2

Due Date: Thursday January 25, 2024 @ 11:59pm

1. The approximate partition function for a dense gas is of the form

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}N} (V - Nb)^N \exp \left[\frac{aN^2}{V kT} \right],$$

where a and b are constants that are given in terms of molecular parameters.

- (a) (10 pts.) Calculate the equation of state from this partition function. What equation of state is this?
- (b) (18 pts.) Calculate the Helmholtz free energy and the heat capacities, C_v and C_p .
2. (30 pts.) (The probability distribution for a thermodynamic system can be alternatively obtained directly from Gibb's definition of entropy. Entropy is defined as $S = -k \sum_{\nu} P_{\nu} \ln P_{\nu}$, where P_{ν} is the probability of finding the system in state ν . This is true regardless of the specification of the system. Thus for a (N, P, T) system, ν specifies the system's energy state and volume, while for a (μ , V, T) system it specifies the energy state and the number of particles. The probability distribution is obtained by the minimization of the characteristic potential (for example Gibbs free energy, Helmholtz free energy, etc.) for a particular specification of the system. Obtain the probability distributions for the (N, P, T) and (μ , V, T) systems using this approach.
3. The canonical partition function can be written in terms of energy levels as

$$Q(N, V, T) = \sum_E t_E = \sum_E \Omega(E, V, N) e^{-\beta E}. \quad (1)$$

E is the total energy of the system. Argue that in the thermodynamic limit, the dominant contribution to the partition function comes from the largest term, denoted by t_E^* , which corresponds to the most probable value of E , denoted E^* .

- a) (9 pts.) Show that about E^* , t_E can be approximated by

$$t_E = t_{E^*} \exp \left[\frac{-(E - E^*)^2}{2\sigma_E^2} \right]. \quad (2)$$

Find σ_E^2 by inspection. (Do not make use of the method illustrated in class.)

- b) (9 pts.) Now using the relation, $\sigma_E^2 = kT^2 C_V$ (obtained in class), and the result of part a), show that the error committed in replacing $\ln Q$ by $\ln t_{E^*}$ is only of order $\ln N$. (Hint: Consider the energy spacing as nearly continuous...)

4. (from Chandler 3.18) Consider a system of N localized non-interacting spins in a magnetic field H . Each spin has a magnetic moment of size μ , and each can point either parallel or antiparallel to the field. Thus the energy of a particular state is

$$E_\nu = \sum_{i=1}^N -n_i \mu H, \quad n_i = \pm 1, \quad (3)$$

where the vector $n = \{n_i\}$ specifies the state, ν , and $n_i \mu$ is the magnetic moment in the direction of the field.

- (a) (9 pts.) Determine the average internal energy of this system as a function of β , H , and N by employing an ensemble characterized by these variables.
- (b) (8 pts.) Determine the average entropy of this system as a function of β , H , and N .
- (c) (7 pts.) Determine the behavior of the energy and entropy for this system as $T \rightarrow 0$.

① Partition fxn

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3/2 N} (V - Nb)^N \exp \left[\frac{aN^2}{VKT} \right]$$

canonical

(a) partition fxn \rightsquigarrow thermo potential \rightsquigarrow EOS

$$F = -kT \ln Q = -kT \ln \left[\frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3/2 N} (V - Nb)^N \right] - \frac{aN^2}{V}$$

$$\begin{aligned} F &= -kT \left[\ln N! + \frac{3}{2} N \ln \left(\frac{2\pi mkT}{h^2} \right) + N \ln (V - Nb) \right] - \frac{aN^2}{V} \\ &= -kT \left[-N \ln N + N + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) N + N \ln (V - Nb) \right] - \frac{aN^2}{V} \end{aligned}$$

$$-\left(\frac{\delta F}{\delta V}\right)_{T,N} = P = \frac{kT}{V - Nb} - \frac{aN^2}{V^2}$$

$$P = \frac{kTN}{V - Nb} - a \left(\frac{N}{V} \right)^2$$

van der waals

$$(b) F, C_V, C_P ; \text{ given } C_P = C_V - T \frac{(\delta P / \delta T)_V^2}{(\delta P / \delta V)_T}$$

derived
in
thermo

Helmholtz : $F = -kT \ln Q$

$$F = -kT \ln \left[\frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3/2 N} (V - Nb)^N \right] - \frac{aN^2}{V}$$

$$C_V = \left(\frac{\delta U}{\delta T} \right)_V = \frac{\delta E}{\delta \beta} \cdot \frac{\delta \beta}{\delta T} = -\frac{1}{kT^2} \left(\frac{\delta E}{\delta \beta} \right)_V$$

$$\langle E \rangle = - \left(\frac{\delta \ln \varphi}{\delta \beta} \right)_{N,V}$$

$$C_V = + \frac{1}{kT^2} \left(\frac{\delta^2 \ln \varphi}{\delta \beta^2} \right)_{N,V}$$

$$\begin{aligned} \frac{\delta}{\delta \beta} \ln \varphi &= \frac{\delta}{\delta \beta} \left[\ln \frac{1}{N!} + \frac{3}{2} N \ln \left(\frac{2\pi m}{\beta h^2} \right) + \ln (V - Nb)^N + \beta \frac{aN^2}{V} \right] \\ &= -\frac{3}{2} \frac{N}{\beta} + \frac{aN^2}{V} \end{aligned}$$

$$\frac{\delta^2 \ln \varphi}{\delta \beta^2} = \frac{\delta}{\delta \beta} \left[-\frac{3}{2} N \cdot \frac{1}{\beta} + \frac{aN^2}{V} \right] = + \frac{3}{2} \frac{N}{\beta^2}$$

$$C_V = \frac{1}{kT^2} \left(\frac{3}{2} \frac{N}{\beta^2} \right) \rightarrow C_V = \frac{3}{2} kN$$

given:

$$C_P = C_V - T \frac{(\delta P / \delta T)_V^2}{(\delta P / \delta V)_T}$$

$$\left(\frac{\delta P}{\delta T} \right)_V^2 = \left(\frac{kN}{V-Nb} \right)^2, \quad \left(\frac{\delta P}{\delta V} \right)_T = -\frac{kNT}{(V-Nb)^2} + \frac{2aN^2}{V^3}$$

$$C_P = \frac{3}{2} kN - T \frac{(kN)^2}{(V-Nb)^2} \cdot \frac{(V-Nb)^2 (V^3)}{-kNTV^3 + 2aN^2(V-Nb)^2}$$

$$C_P - C_V = \frac{T k^2 N V^3}{kTV^3 - 2aN(V-Nb)^2}$$

$$C_P = kN \frac{\left(\frac{5}{2} - 3aNBV^{-3}(V-Nb)^2 \right)}{1 - 2aNBV^{-3}(V-Nb)^2}$$

(2)

2. (30 pts.) (The probability distribution for a thermodynamic system can be alternatively obtained directly from Gibb's definition of entropy. Entropy is defined as $S = -k \sum_{\nu} P_{\nu} \ln P_{\nu}$ where P_{ν} is the probability of finding the system in state ν . This is true regardless of the specification of the system. Thus for a (N, P, T) system, ν specifies the system's energy state and volume, while for a (μ , V, T) system it specifies the energy state and the number of particles. The probability distribution is obtained by the **minimization of the characteristic potential** (for example Gibbs free energy, Helmholtz free energy, etc.) for a particular specification of the system. Obtain the probability distributions for the (N, P, T) and (μ , V, T) systems using this approach.

Gibbs entropy: $S = -k \sum_{N,\nu} P_{N,\nu} \ln P_{N,\nu}$

• Probability dist $(N, P, T) \neq (\mu, V, T)$

• Gibbs minimization ($G = U + PV - TS$), $\sum P_{\nu} = 1$

$$\frac{\delta}{\delta P_{\nu}} (G - \alpha (\sum P_{\nu} - 1)) = 0$$

$$\frac{\delta}{\delta P_{\nu}} (U + PV + KT \sum_{\nu} P_{\nu} \ln P_{\nu} - \alpha (\sum P_{\nu} - 1)) = 0$$

$$E_{\nu} + PV + KT \ln P_{\nu} + KT - \alpha = 0$$

solve for $P_{\nu} \dots$

$$\exp \left[\frac{\alpha - E_{\nu} - KT - PV}{KT} \right] = P_{\nu}$$

$$P_{\nu} = \exp (\beta \alpha - \beta E_{\nu} - 1 - \beta PV)$$

$$\sum P_{\nu} = 1 = e^{\beta \alpha - 1} \sum e^{-\beta PV - \beta E_{\nu}}$$

$$Z = \sum e^{-\beta PV - \beta E_{\nu}} = \frac{1}{e^{\beta \alpha - 1}}$$

$$P_V(N, P, T) = \frac{1}{Z} \exp(-\beta E_V - \beta PV)$$

probability distribution
for isothermal -
isobaric ensemble

• Grand minimization ($W = U - \mu N - TS$)
wrt $\sum P_V = 1 \rightsquigarrow (\mu, V, T)$

$$\frac{\delta}{\delta P_V} (U - \mu N - TS - \alpha(\sum P_V - 1)) = 0$$

$$E_V - \mu N + KT \ln P_V + KT - \alpha = 0$$

$$P_V = \exp\left(\frac{\alpha - KT + \mu N - E_V}{KT}\right)$$

$$P_V = \exp(\alpha \beta - 1 + \beta \mu N - \beta E_V)$$

$$\sum P_V = 1 \rightarrow 1 = e^{\alpha \beta - 1} \sum e^{\beta \mu N - \beta E_V}$$

$$\sum = \sum e^{\beta \mu N - \beta E_V} = 1/e^{\alpha \beta - 1}$$

$$P_V(\mu, V, T) = \frac{1}{Z} \exp(-\beta E_V + \beta \mu N)$$

probability distribution of grand canonical ensemble

3. The canonical partition function can be written in terms of energy levels as

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E is the total energy of the system. Argue that in the thermodynamic limit, the dominant contribution to the partition function comes from the largest term, denoted by t_E^* , which corresponds to the most probable value of E , denoted E^* .

a) (9 pts.) Show that about E^* , t_E can be approximated by

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b) (9 pts.) Now using the relation, $\sigma_E^2 = kT^2 C_V$ (obtained in class), and the result of part a), show that the error committed in replacing $\ln Q$ by $\ln t_{E^*}$ is only of order $\ln N$. (Hint: Consider the energy spacing as nearly continuous...)

(a) $\sum_E t_E = \sum_E \Omega(E, V, N) e^{-\beta E}$, Ω # microstates
 ↓
 increasing decreasing w/ E w/ E

$$t_E = \Omega(E) e^{-\beta E} \rightsquigarrow \text{some maximum}$$

$$\ln t_E = \ln \Omega(E) - \beta E, \quad \beta \text{ is constant (parameter of bath)}$$

$$\begin{aligned} \text{TE. } \ln t_E &= \ln \Omega(E^*) - \beta E^* + (E - E^*) \left[\frac{\delta \ln \Omega}{\delta E} - \beta \right] \\ \text{Bath} &+ \frac{1}{2} (E - E^*)^2 \left[\frac{\delta^2 \ln \Omega}{\delta E^2} \right] + O(E^3) \end{aligned}$$

↓
vanish

$$E^* \text{ when } t_E \text{ @ max.} \quad \frac{\delta \ln t_E}{\delta E} \Big|_{E^*} = 0 = \frac{\delta \ln \Omega}{\delta E} \Big|_{E^*} - \beta_{\text{bath}}$$

rewrite
 $\ln t_E^* = \ln \Omega(E^*) - \beta E^*$

$$\ln t_E = \ln t_E^* + \frac{1}{2} (E - E^*)^2 \left(\frac{\delta^2 \ln \Omega}{\delta E^2} \right)$$

get 2nd derivative term

$$\ln t_E = \ln \Omega(E) - \beta E = \frac{S(E)}{K} - \beta E$$

$$\frac{\delta \ln t_E}{\delta E} = \frac{1}{K} \frac{\delta S(E)}{\delta E} - \beta_{\text{bath}}$$

$$\frac{\delta^2 \ln t_E}{\delta E^2} = \frac{1}{K} \frac{\delta^2 S(E)}{\delta E^2}$$

$$\text{we know } \left(\frac{\delta S}{\delta E}\right)_{N,V} = \frac{1}{T}$$

$$\frac{\delta^2 S(E)}{\delta E^2} = \frac{\delta(\frac{1}{T})}{\delta E} = -\frac{1}{T^2} \frac{\delta T}{\delta E} = -\frac{1}{T^2} \cdot \frac{1}{C_V}$$

$$t_E = t_E^* \exp \left[-\frac{(E-E^*)^2}{2} \cdot \frac{1}{K} \cdot \frac{1}{T^2} \cdot \frac{1}{C_V} \right]$$

$$t_E = t_E^* \exp \left[-\frac{(E-E^*)^2}{2\sigma_E^2} \right]$$

$$[\sigma_E^2 = kT^2 C_V]$$

(b) replace $\ln Q$ by $\ln t_E^*$, error $\ln N$

$\rightsquigarrow C_V$ intensive, scales w/ N

$$\ln C_V \approx \ln N$$

$$Q = \sum_E t_E = t_E^* \sum \exp \left[-\frac{(E-E^*)^2}{2\sigma_E^2} \right]$$

$$\ln Q - \ln t_E^* = \ln \sum_E \exp \left[-\frac{(E-E^*)^2}{2\sigma_E^2} \right]$$

$$\approx \ln \int_{-\infty}^{\infty} \exp \left[-\frac{(E-E^*)^2}{2\sigma_E^2} \right] dE$$

$$= \ln (\sqrt{2\pi\sigma_E^2}) = \ln (\sqrt{2\pi kT^2 C_V})$$

k, T intensive but C_V extensive

$$= \ln (C_V^{1/2}) \sim \ln (N^{1/2}) = 1/2 \ln N$$

$$\boxed{\text{error} \approx \ln N}$$

(4)

$$E_V = \sum_{i=1}^N -n_i \mu H, n_i = \pm 1$$

(a) $Q(N, T, H) = \sum_{\forall n_1, n_2, \dots, n_N} e^{-\beta E_V} = \sum_{\forall n_1, n_2, \dots, n_N} \exp[-\beta \sum_{i=1}^N \mu H n_i]$

$$= \sum_{n_1=-1}^1 e^{\beta \mu H n_1} \sum_{n_2=-1}^1 e^{\beta \mu H n_2} \dots \sum_{n_N=-1}^1 e^{\beta \mu H n_N}$$

$$= \sum_{n_1=-1}^1 \sum_{n_2=-1}^1 \sum_{n_3=-1}^1 \dots \sum_{n_N=-1}^1 e^{\beta \mu H n_i} = (e^{\beta \mu H} + e^{-\beta \mu H})^N$$

$$\langle E \rangle = -\frac{\delta \ln Q}{\delta \beta} = \frac{N \delta \ln (e^{\beta \mu H} + e^{-\beta \mu H})}{\delta \beta}$$

$$\langle E \rangle = -\mu H N \frac{e^{\beta \mu H} - e^{-\beta \mu H}}{(e^{\beta \mu H} + e^{-\beta \mu H})}$$

(b) $S(\beta, H, N)$

$$F = U - TS = -KT \ln Q$$

$$S = K \ln Q + \frac{1}{T} \langle E \rangle$$

$$S = K N \ln (e^{\beta \mu H} + e^{-\beta \mu H}) - \frac{\mu H N}{T} \left[\frac{e^{\beta \mu H} - e^{-\beta \mu H}}{e^{\beta \mu H} + e^{-\beta \mu H}} \right]$$

(C)

$$\lim_{\substack{T \rightarrow 0 \\ (\beta \rightarrow \infty)}} \langle E \rangle = -\mu H N \left(\frac{e^\beta - 0}{e^\beta - 0} \right)$$

$$\boxed{\lim_{T \rightarrow 0} \langle E \rangle = -\mu H N}$$

$$\begin{aligned} \lim_{\substack{T \rightarrow 0 \\ (\beta \rightarrow \infty)}} S &= k N \ln \left(e^{\beta M H} + e^{-\beta M H} \right) - \frac{H N}{T} \left(\frac{e^{\beta M H}}{e^{\beta M H} + e^{-\beta M H}} - \frac{e^{-\beta M H}}{e^{\beta M H} + e^{-\beta M H}} \right) \\ &= \lim_{\substack{T \rightarrow 0 \\ (\beta \rightarrow \infty)}} \frac{N K \beta M H}{T} - \frac{H N}{T} = 0 \end{aligned}$$

$$\boxed{\lim_{T \rightarrow 0} S = 0}$$