

Review Problems

The first in-class test will take place on Wednesday **9/26/07** from **2:30 to 4:00** pm. There will be a recitation with test review on Friday **9/21/07**.

The test is 'closed book,' but if you wish you may bring a one-sided sheet of formulas. The test will be composed entirely from a subset of the following problems. Thus if you are familiar and comfortable with these problems, there will be no surprises!

You may find the following information helpful:

Physical Constants

Electron mass	$m_e \approx 9.1 \times 10^{-31} kg$	Proton mass	$m_p \approx 1.7 \times 10^{-27} kg$
Electron Charge	$e \approx 1.6 \times 10^{-19} C$	Planck's const./ 2π	$\hbar \approx 1.1 \times 10^{-34} Js^{-1}$
Speed of light	$c \approx 3.0 \times 10^8 ms^{-1}$	Stefan's const.	$\sigma \approx 5.7 \times 10^{-8} Wm^{-2}K^{-4}$
Boltzmann's const.	$k_B \approx 1.4 \times 10^{-23} JK^{-1}$	Avogadro's number	$N_0 \approx 6.0 \times 10^{23} mol^{-1}$

Conversion Factors

$$1 atm \equiv 1.0 \times 10^5 Nm^{-2} \qquad 1 \text{\AA} \equiv 10^{-10} m \qquad 1 eV \equiv 1.1 \times 10^4 K$$

Thermodynamics

$$dE = TdS + dW \qquad \text{For a gas: } dW = -PdV \qquad \text{For a wire: } dW = Jdx$$

Mathematical Formulas

$$\int_0^\infty dx x^n e^{-\alpha x} = \frac{n!}{\alpha^{n+1}} \qquad \left(\frac{1}{2}\right)! = \frac{\sqrt{\pi}}{2}$$

$$\int_{-\infty}^\infty dx \exp\left[-ikx - \frac{x^2}{2\sigma^2}\right] = \sqrt{2\pi\sigma^2} \exp\left[-\frac{\sigma^2 k^2}{2}\right] \qquad \lim_{N \rightarrow \infty} \ln N! = N \ln N - N$$

$$\langle e^{-ikx} \rangle = \sum_{n=0}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle \qquad \ln \langle e^{-ikx} \rangle = \sum_{n=1}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle_c$$

$$\cosh(x) = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \dots \qquad \sinh(x) = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \dots$$

$$\text{Surface area of a unit sphere in } d \text{ dimensions} \qquad S_d = \frac{2\pi^{d/2}}{(d/2-1)!}$$

1. *Surface tension:* Thermodynamic properties of the interface between two phases are described by a state function called the surface tension \mathcal{S} . It is defined in terms of the work required to increase the surface area by an amount dA through $dW = \mathcal{S}dA$.

(a) By considering the work done against surface tension in an infinitesimal change in radius, show that the pressure inside a spherical drop of water of radius R is larger than outside pressure by $2\mathcal{S}/R$. What is the air pressure inside a soap bubble of radius R ?

• The work done by a water droplet on the outside world, needed to increase the radius from R to $R + \Delta R$ is

$$\Delta W = (P - P_o) \cdot 4\pi R^2 \cdot \Delta R,$$

where P is the pressure inside the drop and P_o is the atmospheric pressure. In equilibrium, this should be equal to the increase in the surface energy $\mathcal{S}\Delta A = \mathcal{S} \cdot 8\pi R \cdot \Delta R$, where \mathcal{S} is the surface tension, and

$$\Delta W_{\text{total}} = 0, \quad \implies \quad \Delta W_{\text{pressure}} = -\Delta W_{\text{surface}},$$

resulting in

$$(P - P_o) \cdot 4\pi R^2 \cdot \Delta R = \mathcal{S} \cdot 8\pi R \cdot \Delta R, \quad \implies \quad (P - P_o) = \frac{2\mathcal{S}}{R}.$$

In a soap bubble, there are two air-soap surfaces with almost equal radii of curvatures, and

$$P_{\text{film}} - P_o = P_{\text{interior}} - P_{\text{film}} = \frac{2\mathcal{S}}{R},$$

leading to

$$P_{\text{interior}} - P_o = \frac{4\mathcal{S}}{R}.$$

Hence, the air pressure inside the bubble is larger than atmospheric pressure by $4\mathcal{S}/R$.

(b) A water droplet condenses on a solid surface. There are three surface tensions involved \mathcal{S}_{aw} , \mathcal{S}_{sw} , and \mathcal{S}_{sa} , where a , s , and w refer to air, solid and water respectively. Calculate the angle of contact, and find the condition for the appearance of a water film (complete wetting).

• When steam condenses on a solid surface, water either forms a droplet, or spreads on the surface. There are two ways to consider this problem:

Method 1: Energy associated with the interfaces

In equilibrium, the total energy associated with the three interfaces should be minimum, and therefore

$$dE = \mathcal{S}_{aw}dA_{aw} + \mathcal{S}_{as}dA_{as} + \mathcal{S}_{ws}dA_{ws} = 0.$$

Since the total surface area of the solid is constant,

$$dA_{as} + dA_{ws} = 0.$$

From geometrical considerations (see proof below), we obtain

$$dA_{ws} \cos \theta = dA_{aw}.$$

From these equations, we obtain

$$dE = (S_{aw} \cos \theta - S_{as} + S_{ws}) dA_{ws} = 0, \quad \implies \quad \cos \theta = \frac{S_{as} - S_{ws}}{S_{aw}}.$$

Proof of $dA_{ws} \cos \theta = dA_{aw}$: Consider a droplet which is part of a sphere of radius R , which is cut by the substrate at an angle θ . The areas of the involved surfaces are

$$A_{ws} = \pi(R \sin \theta)^2, \quad \text{and} \quad A_{aw} = 2\pi R^2(1 - \cos \theta).$$

Let us consider a small change in shape, accompanied by changes in R and θ . These variations should preserve the volume of water, i.e. constrained by

$$V = \frac{\pi R^3}{3} (\cos^3 \theta - 3 \cos \theta + 2).$$

Introducing $x = \cos \theta$, we can re-write the above results as

$$\begin{cases} A_{ws} = \pi R^2 (1 - x^2), \\ A_{aw} = 2\pi R^2 (1 - x), \\ V = \frac{\pi R^3}{3} (x^3 - 3x + 2). \end{cases}$$

The variations of these quantities are then obtained from

$$\begin{cases} dA_{ws} = 2\pi R \left[\frac{dR}{dx} (1 - x^2) - Rx \right] dx, \\ dA_{aw} = 2\pi R \left[2 \frac{dR}{dx} (1 - x) - R \right] dx, \\ dV = \pi R^2 \left[\frac{dR}{dx} (x^3 - 3x + 2) + R(x^2 - x) \right] dx = 0. \end{cases}$$

From the last equation, we conclude

$$\frac{1}{R} \frac{dR}{dx} = -\frac{x^2 - x}{x^3 - 3x + 2} = -\frac{x + 1}{(x - 1)(x + 2)}.$$

Substituting for dR/dx gives,

$$dA_{ws} = 2\pi R^2 \frac{dx}{x+2}, \quad \text{and} \quad dA_{aw} = 2\pi R^2 \frac{x \cdot dx}{x+2},$$

resulting in the required result of

$$dA_{aw} = x \cdot dA_{ws} = dA_{ws} \cos \theta.$$

Method 2: Balancing forces on the contact line

Another way to interpret the result is to consider the force balance of the equilibrium surface tension on the contact line. There are four forces acting on the line: (1) the surface tension at the water–gas interface, (2) the surface tension at the solid–water interface, (3) the surface tension at the gas–solid interface, and (4) the force downward by solid–contact line interaction. The last force ensures that the contact line stays on the solid surface, and is downward since the contact line is allowed to move only horizontally without friction. These forces should cancel along both the y –direction x –directions. The latter gives the condition for the contact angle known as *Young’s equation*,

$$\mathcal{S}_{as} = \mathcal{S}_{aw} \cdot \cos \theta + \mathcal{S}_{ws}, \quad \implies \quad \cos \theta = \frac{\mathcal{S}_{as} - \mathcal{S}_{ws}}{\mathcal{S}_{aw}}.$$

The critical condition for the complete wetting occurs when $\theta = 0$, or $\cos \theta = 1$, i.e. for

$$\cos \theta_C = \frac{\mathcal{S}_{as} - \mathcal{S}_{ws}}{\mathcal{S}_{aw}} = 1.$$

Complete wetting of the substrate thus occurs whenever

$$\mathcal{S}_{aw} \leq \mathcal{S}_{as} - \mathcal{S}_{ws}.$$

(c) In the realm of “large” bodies gravity is the dominant force, while at “small” distances surface tension effects are all important. At room temperature, the surface tension of water is $\mathcal{S}_o \approx 7 \times 10^{-2} \text{Nm}^{-1}$. Estimate the typical length-scale that separates “large” and “small” behaviors. Give a couple of examples for where this length-scale is important.

- Typical length scales at which the surface tension effects become significant are given by the condition that the forces exerted by surface tension and relevant pressures become comparable, or by the condition that the surface energy is comparable to the other energy changes of interest.

Example 1: Size of water drops not much deformed on a non-wetting surface. This is given by equalizing the surface energy and the gravitational energy,

$$S \cdot 4\pi R^2 \approx mgR = \rho V g R = \frac{4\pi}{3} R^4 g,$$

leading to

$$R \approx \sqrt{\frac{3S}{\rho g}} \approx \sqrt{\frac{3 \cdot 7 \times 10^{-2} \text{ N/m}}{10^3 \text{ kg/m}^3 \times 10 \text{ m/s}^2}} \approx 1.5 \times 10^{-3} \text{ m} = 1.5 \text{ mm}.$$

Example 2: Swelling of spherical gels in a saturated vapor: Osmotic pressure of the gel (about 1 atm) = surface tension of water, gives

$$\pi_{gel} \approx \frac{N}{V} k_B T \approx \frac{2S}{R},$$

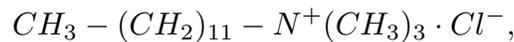
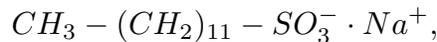
where N is the number of counter ions within the gel. Thus,

$$R \approx \left(\frac{2 \times 7 \times 10^{-2} \text{ N/m}}{10^5 \text{ N/m}^2} \right) \approx 10^{-6} \text{ m}.$$

2. Surfactants: Surfactant molecules such as those in soap or shampoo prefer to spread on the air-water surface rather than dissolve in water. To see this, float a hair on the surface of water and gently touch the water in its vicinity with a piece of soap. (This is also why a piece of soap can power a toy paper boat.)

(a) The air-water surface tension S_o (assumed to be temperature independent) is reduced roughly by $Nk_B T/A$, where N is the number of surfactant particles, and A is the area. Explain this result qualitatively.

- Typical surfactant molecules have a hydrophilic head and a hydrophobic tail, and prefer to go to the interface between water and air, or water and oil. Some examples are,



The surfactant molecules spread over the surface of water and behave as a two dimensional gas. The gas has a pressure proportional to the density and the absolute temperature, which comes from the two dimensional degrees of freedom of the molecules. Thus the surfactants lower the free energy of the surface when the surface area is increased.

$$\Delta F_{\text{surfactant}} = \frac{N}{A} k_B T \cdot \Delta A = (S - S_o) \cdot \Delta A, \implies S = S_o - \frac{N}{A} k_B T.$$

(Note that surface tension is defined with a sign opposite to that of hydrostatic pressure.)

(b) Place a drop of water on a clean surface. Observe what happens to the air-water-surface contact angle as you gently touch the droplet surface with a small piece of soap, and explain the observation.

- As shown in the previous problem, the contact angle satisfies

$$\cos \theta = \frac{\mathcal{S}_{as} - \mathcal{S}_{ws}}{\mathcal{S}_{aw}}.$$

Touching the surface of the droplet with a small piece of soap reduces \mathcal{S}_{aw} , hence $\cos \theta$ increases, or equivalently, the angle θ decreases.

(c) More careful observations show that at higher surfactant densities

$$\left. \frac{\partial \mathcal{S}}{\partial A} \right|_T = \frac{Nk_B T}{(A - Nb)^2} - \frac{2a}{A} \left(\frac{N}{A} \right)^2, \quad \text{and} \quad \left. \frac{\partial T}{\partial \mathcal{S}} \right|_A = -\frac{A - Nb}{Nk_B};$$

where a and b are constants. Obtain the expression for $\mathcal{S}(A, T)$ and explain qualitatively the origin of the corrections described by a and b .

- When the surfactant molecules are dense their interaction becomes important, resulting in

$$\left. \frac{\partial \mathcal{S}}{\partial A} \right|_T = \frac{Nk_B T}{(A - Nb)^2} - \frac{2a}{A} \left(\frac{N}{A} \right)^2,$$

and

$$\left. \frac{\partial T}{\partial \mathcal{S}} \right|_A = -\frac{A - Nb}{Nk_B}.$$

Integrating the first equation, gives

$$\mathcal{S}(A, T) = f(T) - \frac{Nk_B T}{A - Nb} + a \left(\frac{N}{A} \right)^2,$$

where $f(T)$ is a function of only T , while integrating the second equation, yields

$$\mathcal{S}(A, T) = g(A) - \frac{Nk_B T}{A - Nb},$$

with $g(A)$ a function of only A . By comparing these two equations we get

$$\mathcal{S}(A, T) = \mathcal{S}_o - \frac{Nk_B T}{A - Nb} + a \left(\frac{N}{A} \right)^2,$$

where \mathcal{S}_o represents the surface tension in the absence of surfactants and is independent of A and T . The equation resembles the van der Waals equation of state for gas-liquid systems. The factor Nb in the second term represents the excluded volume effect due to the finite size of the surfactant molecules. The last term represents the binary interaction

between two surfactant molecules. If surfactant molecules attract each other the coefficient a is positive the surface tension increases.

(d) Find an expression for $C_S - C_A$ in terms of $\left.\frac{\partial E}{\partial A}\right|_T$, \mathcal{S} , $\left.\frac{\partial \mathcal{S}}{\partial A}\right|_T$, and $\left.\frac{\partial T}{\partial \mathcal{S}}\right|_A$, for $\left.\frac{\partial E}{\partial T}\right|_A = \left.\frac{\partial E}{\partial T}\right|_S$.

• Taking A and T as independent variables, we obtain

$$\delta Q = dE - \mathcal{S} \cdot dA, \quad \implies \quad \delta Q = \left.\frac{\partial E}{\partial A}\right|_T dA + \left.\frac{\partial E}{\partial T}\right|_A dT - \mathcal{S} \cdot dA,$$

and

$$\delta Q = \left(\left.\frac{\partial E}{\partial A}\right|_T - \mathcal{S} \right) dA + \left.\frac{\partial E}{\partial T}\right|_A dT.$$

From the above result, the heat capacities are obtained as

$$\begin{cases} C_A \equiv \left.\frac{\delta Q}{\delta T}\right|_A = \left.\frac{\partial E}{\partial T}\right|_A \\ C_S \equiv \left.\frac{\delta Q}{\delta T}\right|_S = \left(\left.\frac{\partial E}{\partial A}\right|_T - \mathcal{S} \right) \left.\frac{\partial A}{\partial T}\right|_S + \left.\frac{\partial E}{\partial T}\right|_S \end{cases},$$

resulting in

$$C_S - C_A = \left(\left.\frac{\partial E}{\partial A}\right|_T - \mathcal{S} \right) \left.\frac{\partial A}{\partial T}\right|_S.$$

Using the chain rule relation

$$\left.\frac{\partial T}{\partial \mathcal{S}}\right|_A \cdot \left.\frac{\partial \mathcal{S}}{\partial A}\right|_T \cdot \left.\frac{\partial A}{\partial T}\right|_S = -1,$$

we obtain

$$C_S - C_A = \left(\left.\frac{\partial E}{\partial A}\right|_T - \mathcal{S} \right) \cdot \left(\frac{-1}{\left.\frac{\partial T}{\partial \mathcal{S}}\right|_A \cdot \left.\frac{\partial \mathcal{S}}{\partial A}\right|_T} \right).$$

3. Temperature scales: Prove the equivalence of the ideal gas temperature scale Θ , and the thermodynamic scale T , by performing a Carnot cycle on an ideal gas. The ideal gas satisfies $PV = Nk_B\Theta$, and its internal energy E is a function of Θ only. However, *you may not assume that $E \propto \Theta$* . You may wish to proceed as follows:

(a) Calculate the heat exchanges Q_H and Q_C as a function of Θ_H , Θ_C , and the volume expansion factors.

• The ideal gas temperature is defined through the equation of state

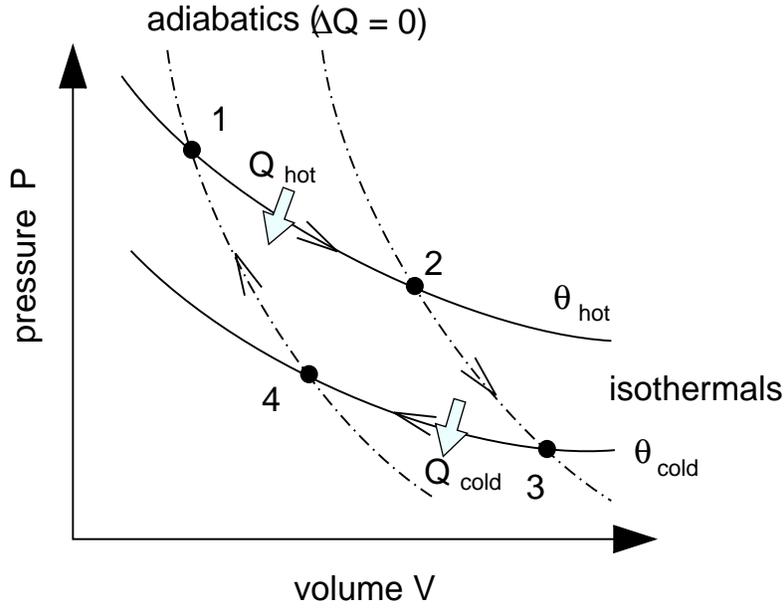
$$\theta = \frac{PV}{Nk_B}.$$

The thermodynamic temperature is defined for a reversible Carnot cycle by

$$\frac{T_{hot}}{T_{cold}} = \frac{Q_{hot}}{Q_{cold}}.$$

For an ideal gas, the internal energy is a function only of θ , i.e. $E = E(\theta)$, and

$$dQ = dE - dW = \frac{dE}{d\theta} \cdot d\theta + PdV.$$



Consider the Carnot cycle indicated in the figure. For the segment 1 to 2, which undergoes an isothermal expansion, we have

$$d\theta = 0, \implies dQ_{hot} = PdV, \quad \text{and} \quad P = \frac{Nk_B\theta_{hot}}{V}.$$

Hence, the heat input of the cycle is related to the expansion factor by

$$Q_{hot} = \int_{V_1}^{V_2} Nk_B\theta_{hot} \frac{dV}{V} = Nk_B\theta_{hot} \ln \left(\frac{V_2}{V_1} \right).$$

A similar calculation along the low temperature isotherm yields

$$Q_{cold} = \int_{V_4}^{V_3} Nk_B\theta_{cold} \frac{dV}{V} = Nk_B\theta_{cold} \ln \left(\frac{V_3}{V_4} \right),$$

and thus

$$\frac{Q_{hot}}{Q_{cold}} = \frac{\theta_{hot}}{\theta_{cold}} \frac{\ln(V_2/V_1)}{\ln(V_3/V_4)}.$$

(b) Calculate the volume expansion factor in an adiabatic process as a function of Θ .

- Next, we calculate the volume expansion/compression ratios in the adiabatic processes. Along an adiabatic segment

$$dQ = 0, \quad \implies \quad 0 = \frac{dE}{d\theta} \cdot d\theta + \frac{Nk_B\theta}{V} \cdot dV, \quad \implies \quad \frac{dV}{V} = -\frac{1}{Nk_B\theta} \frac{dE}{d\theta} \cdot d\theta.$$

Integrating the above between the two temperatures, we obtain

$$\begin{cases} \ln\left(\frac{V_3}{V_2}\right) = -\frac{1}{Nk_B} \int_{\theta_{cold}}^{\theta_{hot}} \frac{1}{\theta} \frac{dE}{d\theta} \cdot d\theta, & \text{and} \\ \ln\left(\frac{V_4}{V_1}\right) = -\frac{1}{Nk_B} \int_{\theta_{cold}}^{\theta_{hot}} \frac{1}{\theta} \frac{dE}{d\theta} \cdot d\theta. \end{cases}$$

While we cannot explicitly evaluate the integral (since $E(\theta)$ is arbitrary), we can nonetheless conclude that

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}.$$

(c) Show that $Q_H/Q_C = \Theta_H/\Theta_C$.

- Combining the results of parts (a) and (b), we observe that

$$\frac{Q_{hot}}{Q_{cold}} = \frac{\theta_{hot}}{\theta_{cold}}.$$

Since the thermodynamic temperature scale is defined by

$$\frac{Q_{hot}}{Q_{cold}} = \frac{T_{hot}}{T_{cold}},$$

we conclude that θ and T are proportional. If we further define $\theta(\text{triple point}_{\text{H}_2\text{O}}) = T(\text{triple point}_{\text{H}_2\text{O}}) = 273.16$, θ and T become identical.

4. Equations of State: The equation of state constrains the form of internal energy as in the following examples.

(a) Starting from $dE = TdS - PdV$, show that the equation of state $PV = Nk_B T$, in fact implies that E can only depend on T .

- Since there is only one form of work, we can choose any two parameters as independent variables. For example, selecting T and V , such that $E = E(T, V)$, and $S = S(T, V)$, we obtain

$$dE = TdS - PdV = T \left. \frac{\partial S}{\partial T} \right|_V dT + T \left. \frac{\partial S}{\partial V} \right|_T dV - PdV,$$

resulting in

$$\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial S}{\partial V} \right|_T - P.$$

Using the Maxwell's relation[†]

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V,$$

we obtain

$$\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial P}{\partial T} \right|_V - P.$$

Since $T \left. \frac{\partial P}{\partial T} \right|_V = T \frac{Nk_B}{V} = P$, for an ideal gas, $\left. \frac{\partial E}{\partial V} \right|_T = 0$. Thus E depends only on T , i.e. $E = E(T)$.

(b) What is the most general equation of state consistent with an internal energy that depends only on temperature?

- If $E = E(T)$,

$$\left. \frac{\partial E}{\partial V} \right|_T = 0, \quad \implies \quad T \left. \frac{\partial P}{\partial T} \right|_V = P.$$

The solution for this equation is $P = f(V)T$, where $f(V)$ is any function of only V .

(c) Show that for a van der Waals gas C_V is a function of temperature alone.

- The van der Waals equation of state is given by

$$\left[P - a \left(\frac{N}{V} \right)^2 \right] \cdot (V - Nb) = Nk_B T,$$

or

$$P = \frac{Nk_B T}{(V - Nb)} + a \left(\frac{N}{V} \right)^2.$$

From these equations, we conclude that

$$C_V \equiv \left. \frac{\partial E}{\partial T} \right|_V, \quad \implies \quad \left. \frac{\partial C_V}{\partial V} \right|_T = \frac{\partial^2 E}{\partial V \partial T} = \frac{\partial}{\partial T} \left\{ T \left. \frac{\partial P}{\partial T} \right|_V - P \right\} = T \left. \frac{\partial^2 P}{\partial T^2} \right|_V = 0.$$

5. Clausius–Clapeyron equation describes the variation of boiling point with pressure. It is usually derived from the condition that the chemical potentials of the gas and liquid phases are the same at coexistence.

[†] $dL = X dx + Y dy + \dots, \quad \implies \quad \left. \frac{\partial X}{\partial y} \right|_x = \left. \frac{\partial Y}{\partial x} \right|_y = \frac{\partial^2 L}{\partial x \cdot \partial y}.$

- From the equations

$$\mu_{liquid}(P, T) = \mu_{gas}(P, T),$$

and

$$\mu_{liquid}(P + dP, T + dT) = \mu_{gas}(P + dP, T + dT),$$

we conclude that along the coexistence line

$$\left. \frac{dP}{dT} \right|_{\text{coX}} = \frac{\left. \frac{\partial \mu_g}{\partial T} \right|_P - \left. \frac{\partial \mu_l}{\partial T} \right|_P}{\left. \frac{\partial \mu_l}{\partial P} \right|_T - \left. \frac{\partial \mu_g}{\partial P} \right|_T}.$$

The variations of the Gibbs free energy, $G = N\mu(P, T)$ from the extensivity condition, are given by

$$V = \left. \frac{\partial G}{\partial P} \right|_T, \quad S = - \left. \frac{\partial G}{\partial T} \right|_P.$$

In terms of intensive quantities

$$v = \frac{V}{N} = \left. \frac{\partial \mu}{\partial P} \right|_T, \quad s = \frac{S}{N} = - \left. \frac{\partial \mu}{\partial T} \right|_P,$$

where s and v are molar entropy and volume, respectively. Thus, the coexistence line satisfies the condition

$$\left. \frac{dP}{dT} \right|_{\text{coX}} = \frac{S_g - S_l}{V_g - V_l} = \frac{s_g - s_l}{v_g - v_l}.$$

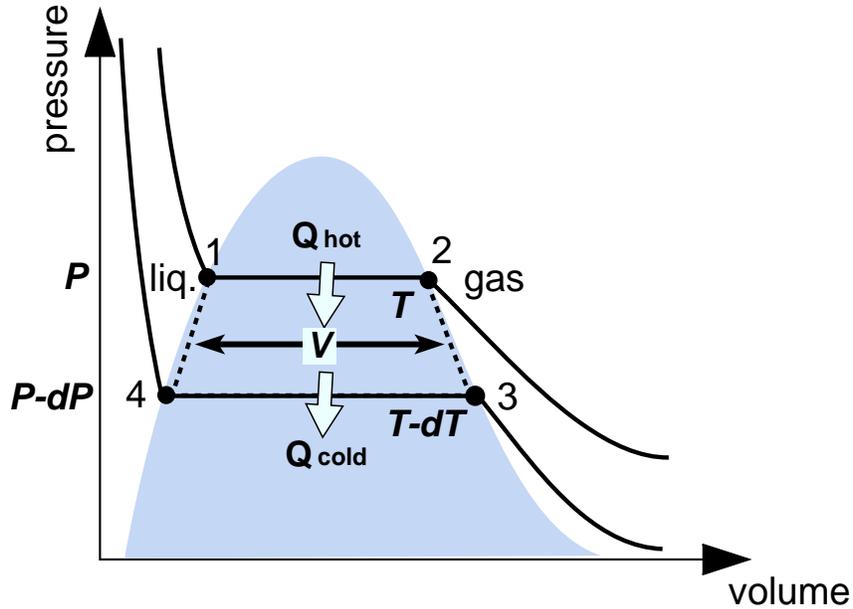
For an alternative derivation, consider a Carnot engine using one mole of water. At the source (P, T) the latent heat L is supplied converting water to steam. There is a volume increase V associated with this process. The pressure is adiabatically decreased to $P - dP$. At the sink $(P - dP, T - dT)$ steam is condensed back to water.

(a) Show that the work output of the engine is $W = VdP + \mathcal{O}(dP^2)$. Hence obtain the Clausius–Clapeyron equation

$$\left. \frac{dP}{dT} \right|_{\text{boiling}} = \frac{L}{TV}. \quad (1)$$

- If we approximate the adiabatic processes as taking place at constant volume V (vertical lines in the $P - V$ diagram), we find

$$W = \oint PdV = PV - (P - dP)V = VdP.$$



Here, we have neglected the volume of liquid state, which is much smaller than that of the gas state. As the error is of the order of

$$\left. \frac{\partial V}{\partial P} \right|_S dP \cdot dP = O(dP^2),$$

we have

$$W = VdP + O(dP^2).$$

The efficiency of any Carnot cycle is given by

$$\eta = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H},$$

and in the present case,

$$Q_H = L, \quad W = VdP, \quad T_H = T, \quad T_C = T - dT.$$

Substituting these values in the universal formula for efficiency, we obtain the Clausius-Clapeyron equation

$$\frac{VdP}{L} = \frac{dT}{T}, \quad \text{or} \quad \left. \frac{dP}{dT} \right|_{coX} = \frac{L}{T \cdot V}.$$

(b) What is wrong with the following argument: “The heat Q_H supplied at the source to convert one mole of water to steam is $L(T)$. At the sink $L(T - dT)$ is supplied to condense one mole of steam to water. The difference $dT dL/dT$ must equal the work $W = VdP$, equal to LdT/T from eq.(1). Hence $dL/dT = L/T$ implying that L is proportional to T !”

- The statement “At the sink $L(T - dT)$ is supplied to condense one mole of water” is incorrect. In the $P - V$ diagram shown, the state at “1” corresponds to pure water, “2” corresponds to pure vapor, but the states “3” and “4” have two phases coexisting. In going from the state 3 to 4 less than one mole of steam is converted to water. Part of the steam has already been converted into water during the adiabatic expansion $2 \rightarrow 3$, and the remaining portion is converted in the adiabatic compression $4 \rightarrow 1$. Thus the actual latent heat should be less than the contribution by one mole of water.

(c) Assume that L is approximately temperature independent, and that the volume change is dominated by the volume of steam treated as an ideal gas, i.e. $V = Nk_B T/P$. Integrate equation (1) to obtain $P(T)$.

- For an ideal gas

$$V = \frac{Nk_B T}{P}, \quad \Rightarrow \quad \left. \frac{dP}{dT} \right|_{coX} = \frac{LP}{Nk_B T^2}, \quad \text{or} \quad \frac{dP}{P} = \frac{L}{Nk_B T^2} dT.$$

Integrating this equation, the boiling temperature is obtained as a function of the pressure P , as

$$P = C \cdot \exp\left(-\frac{L}{k_B T_{Boiling}}\right).$$

(d) A hurricane works somewhat like the engine described above. Water evaporates at the warm surface of the ocean, steam rises up in the atmosphere, and condenses to water at the higher and cooler altitudes. The Coriolis force converts the upwards suction of the air to spiral motion. (Using ice and boiling water, you can create a little storm in a tea cup.) Typical values of warm ocean surface and high altitude temperatures are $80^{\circ}F$ and $-120^{\circ}F$ respectively. The warm water surface layer must be at least 200 feet thick to provide sufficient water vapor, as the hurricane needs to condense about 90 million tons of water vapor per hour to maintain itself. Estimate the maximum possible efficiency, and power output, of such a hurricane. (The latent heat of vaporization of water is about $2.3 \times 10^6 Jkg^{-1}$.)

- For $T_C = -120^{\circ}F = 189^{\circ}K$, and $T_H = 80^{\circ}F = 300^{\circ}K$, the limiting efficiency, as that of a Carnot engine, is

$$\eta_{max} = \frac{T_H - T_C}{T_H} = 0.37.$$

The output power, is equal to (input power) x (efficiency). The input in this case is the energy obtained from evaporation of warm ocean temperature; hence

$$\begin{aligned} \text{Power output} &= \frac{dW}{dt} = \frac{dQ_c}{dt} \times \frac{T_H - T_C}{T_C} \\ &= \frac{90 \times 10^6 \text{ tons}}{\text{hr}} \cdot \frac{1 \text{ hr}}{3600 \text{ sec}} \cdot \frac{1000 \text{ kg}}{\text{ton}} \cdot \frac{2.3 \times 10^6 \text{ J}}{\text{kg}} \times 0.67 \approx 4 \times 10^{13} \text{ watts}. \end{aligned}$$

(e) Due to gravity, atmospheric pressure $P(h)$ drops with the height h . By balancing the forces acting on a slab of air (behaving like a perfect gas) of thickness dh , show that $P(h) = P_0 \exp(-mgh/kT)$, where m is the average mass of a molecule in air.

- Consider a horizontal slab of area A between heights h and $h + dh$. The gravitational force due to mass of particles in the slab is

$$dF_{\text{gravity}} = mg \frac{N}{V} A dh = mg \frac{P}{k_B T} A dh,$$

where we have used the ideal gas law to relate the density (N/V) to the pressure. The gravitational force is balanced in equilibrium with the force due to pressure

$$dF_{\text{pressure}} = A [P(h) - P(h + dh)] = - \frac{\partial P}{\partial h} \Big| A dh.$$

Equating the two forces gives

$$\frac{\partial P}{\partial h} \Big| = -mg \frac{P}{k_B T}, \quad \implies \quad P(h) = p_0 \exp\left(-\frac{mgh}{k_B T}\right),$$

assuming that temperature does not change with height.

(f) Use the above results to estimate the boiling temperature of water on top of Mount Everest ($h \approx 9\text{km}$). The latent heat of vaporization of water is about $2.3 \times 10^6 \text{Jkg}^{-1}$.

- Using the results from parts (c) and (e), we conclude that

$$\frac{P_{\text{Everest}}}{P_{\text{sea}}} \approx \exp\left(-\frac{mg}{k_B T}(h_{\text{Everest}} - h_{\text{sea}})\right) \approx \exp\left[-\frac{L}{k_B} \left(\frac{1}{T_{\text{Everest}}(\text{boil})} - \frac{1}{T_{\text{sea}}(\text{boil})}\right)\right].$$

Using the numbers provided, we find $T_{\text{Everest}}(\text{boil}) \approx 346^\circ\text{K}$ ($74^\circ\text{C} \approx 163^\circ\text{F}$).

6. Glass: Liquid quartz, if cooled slowly, crystallizes at a temperature T_m , and releases latent heat L . Under more rapid cooling conditions, the liquid is supercooled and becomes glassy.

(a) As both phases of quartz are almost incompressible, there is no work input, and changes in internal energy satisfy $dE = TdS + \mu dN$. Use the extensivity condition to obtain the expression for μ in terms of E , T , S , and N .

- Since in the present context we are considering only chemical work, we can regard entropy as a function of two independent variables, e.g. E , and N , which appear naturally from $dS = dE/T - \mu dN/T$. Since entropy is an extensive variable, $\lambda S = S(\lambda E, \lambda N)$.

Differentiating this with respect to λ and evaluating the resulting expression at $\lambda = 1$, gives

$$S(E, N) = \left. \frac{\partial S}{\partial E} \right|_N E + \left. \frac{\partial S}{\partial N} \right|_E N = \frac{E}{T} - \frac{N\mu}{T},$$

leading to

$$\mu = \frac{E - TS}{N}.$$

(b) The heat capacity of crystalline quartz is approximately $C_X = \alpha T^3$, while that of glassy quartz is roughly $C_G = \beta T$, where α and β are constants.

Assuming that the third law of thermodynamics applies to both crystalline and glass phases, calculate the entropies of the two phases at temperatures $T \leq T_m$.

• Finite temperature entropies can be obtained by integrating dQ/T , starting from $S(T = 0) = 0$. Using the heat capacities to obtain the heat inputs, we find

$$\begin{cases} C_{crystal} = \alpha T^3 = \frac{T}{N} \frac{dS_{crystal}}{dT}, & \implies S_{crystal} = \frac{N\alpha T^3}{3}, \\ C_{glass} = \beta T = \frac{T}{N} \frac{dS_{glass}}{dT}, & \implies S_{glass} = \beta NT. \end{cases}$$

(c) At zero temperature the local bonding structure is similar in glass and crystalline quartz, so that they have approximately the same internal energy E_0 . Calculate the internal energies of both phases at temperatures $T \leq T_m$.

• Since $dE = TdS + \mu dN$, for $dN = 0$, we have

$$\begin{cases} dE = TdS = \alpha NT^3 dT & (crystal), \\ dE = TdS = \beta NT dT & (glass). \end{cases}$$

Integrating these expressions, starting with the same internal energy E_0 at $T = 0$, yields

$$\begin{cases} E = E_0 + \frac{\alpha N}{4} T^4 & (crystal), \\ E = E_0 + \frac{\beta N}{2} T^2 & (glass). \end{cases}$$

(d) Use the condition of thermal equilibrium between two phases to compute the equilibrium melting temperature T_m in terms of α and β .

• From the condition of chemical equilibrium between the two phases, $\mu_{crystal} = \mu_{glass}$, we obtain

$$\left(\frac{1}{3} - \frac{1}{4}\right) \cdot \alpha T^4 = \left(1 - \frac{1}{2}\right) \cdot \beta T^2, \implies \frac{\alpha T^4}{12} = \frac{\beta T^2}{2},$$

resulting in a transition temperature

$$T_{melt} = \sqrt{\frac{6\beta}{\alpha}}.$$

(e) Compute the latent heat L in terms of α and β .

• From the assumptions of the previous parts, we obtain the latent heats for the glass to crystal transition as

$$\begin{aligned} L &= T_{melt} (S_{glass} - S_{crystal}) = NT_{melt} \left(\beta T_{melt} - \frac{\alpha T_{melt}^3}{3} \right) \\ &= NT_{melt}^2 \left(\beta - \frac{\alpha T_{melt}^2}{3} \right) = NT_{melt}^2 (\beta - 2\beta) = -N\beta T_{melt}^2 < 0. \end{aligned}$$

(f) Is the result in the previous part correct? If not, which of the steps leading to it is most likely to be incorrect?

• The above result implies that the entropy of the crystal phase is larger than that of the glass phase. This is clearly unphysical, and one of the assumptions must be wrong. The questionable step is the assumption that the glass phase is subject to the third law of thermodynamics, and has zero entropy at $T = 0$. In fact, glass is a non-ergodic state of matter which does not have a unique ground state, and violates the third law.

7. Characteristic functions: Calculate the characteristic function, the mean, and the variance of the following probability density functions:

(a) *Uniform* $p(x) = \frac{1}{2a}$ for $-a < x < a$, and $p(x) = 0$ otherwise;

• A *uniform* probability distribution,

$$p(x) = \begin{cases} \frac{1}{2a} & \text{for } -a < x < a \\ 0 & \text{otherwise} \end{cases},$$

for which there exist many examples, gives

$$\begin{aligned} f(k) &= \frac{1}{2a} \int_{-a}^a \exp(-ikx) dx = \frac{1}{2a} \frac{1}{-ik} \exp(-ikx) \Big|_{-a}^a \\ &= \frac{1}{ak} \sin(ka) = \sum_{m=0}^{\infty} (-1)^m \frac{(ak)^{2m}}{(2m+1)!}. \end{aligned}$$

Therefore,

$$m_1 = \langle x \rangle = 0, \quad \text{and} \quad m_2 = \langle x^2 \rangle = \frac{1}{3} a^2.$$

(b) *Laplace* $p(x) = \frac{1}{2a} \exp\left(-\frac{|x|}{a}\right)$;

• The *Laplace* PDF,

$$p(x) = \frac{1}{2a} \exp\left(-\frac{|x|}{a}\right),$$

for example describing light absorption through a turbid medium, gives

$$\begin{aligned} f(k) &= \frac{1}{2a} \int_{-\infty}^{\infty} dx \exp\left(-ikx - \frac{|x|}{a}\right) \\ &= \frac{1}{2a} \int_0^{\infty} dx \exp(-ikx - x/a) + \frac{1}{2a} \int_{-\infty}^0 dx \exp(-ikx + x/a) \\ &= \frac{1}{2a} \left[\frac{1}{-ik + 1/a} - \frac{1}{-ik - 1/a} \right] = \frac{1}{1 + (ak)^2} \\ &= 1 - (ak)^2 + (ak)^4 - \dots \end{aligned}$$

Therefore,

$$m_1 = \langle x \rangle = 0, \quad \text{and} \quad m_2 = \langle x^2 \rangle = 2a^2.$$

(c) *Cauchy* $p(x) = \frac{a}{\pi(x^2 + a^2)}$.

• The *Cauchy*, or *Lorentz* PDF describes the spectrum of light scattered by diffusive modes, and is given by

$$p(x) = \frac{a}{\pi(x^2 + a^2)}.$$

For this distribution,

$$\begin{aligned} f(k) &= \int_{-\infty}^{\infty} \exp(-ikx) \frac{a}{\pi(x^2 + a^2)} dx \\ &= \frac{1}{2\pi i} \int_{-\infty}^{\infty} \exp(-ikx) \left[\frac{1}{x - ia} - \frac{1}{x + ia} \right] dx. \end{aligned}$$

The easiest method for evaluating the above integrals is to close the integration contours in the complex plane, and evaluate the residue. The vanishing of the integrand at infinity determines whether the contour has to be closed in the upper, or lower half of the complex plane, and leads to

$$f(k) = \left\{ \begin{array}{ll} -\frac{1}{2\pi i} \int_C \frac{\exp(-ikx)}{x + ia} dx = \exp(-ka) & \text{for } k \geq 0 \\ \frac{1}{2\pi i} \int_B \frac{\exp(-ikx)}{x - ia} dx = \exp(ka) & \text{for } k < 0 \end{array} \right\} = \exp(-|ka|).$$

Note that $f(k)$ is not an analytic function in this case, and hence does not have a Taylor expansion. The moments have to be determined by another method, e.g. by direct evaluation, as

$$m_1 = \langle x \rangle = 0, \quad \text{and} \quad m_2 = \langle x^2 \rangle = \int dx \frac{\pi}{a} \cdot \frac{x^2}{x^2 + a^2} \rightarrow \infty.$$

The first moment vanishes by symmetry, while the second (and higher) moments diverge, explaining the non-analytic nature of $f(k)$.

The following two probability density functions are defined for $x \geq 0$. Compute only the mean and variance for each.

(d) *Rayleigh* $p(x) = \frac{x}{a^2} \exp(-\frac{x^2}{2a^2})$,

- The *Rayleigh* distribution,

$$p(x) = \frac{x}{a^2} \exp\left(-\frac{x^2}{2a^2}\right), \quad \text{for } x \geq 0,$$

can be used for the length of a random walk in two dimensions. Its characteristic function is

$$\begin{aligned} f(k) &= \int_0^\infty \exp(-ikx) \frac{x}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx \\ &= \int_0^\infty [\cos(kx) - i \sin(kx)] \frac{x}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx. \end{aligned}$$

The integrals are not simple, but can be evaluated as

$$\int_0^\infty \cos(kx) \frac{x}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx = \sum_{n=0}^\infty \frac{(-1)^n n!}{(2n)!} (2a^2 k^2)^n,$$

and

$$\begin{aligned} \int_0^\infty \sin(kx) \frac{x}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx &= \frac{1}{2} \int_{-\infty}^\infty \sin(kx) \frac{x}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx \\ &= \sqrt{\frac{\pi}{2}} ka \exp\left(-\frac{k^2 a^2}{2}\right), \end{aligned}$$

resulting in

$$f(k) = \sum_{n=0}^\infty \frac{(-1)^n n!}{(2n)!} (2a^2 k^2)^n - i \sqrt{\frac{\pi}{2}} ka \exp\left(-\frac{k^2 a^2}{2}\right).$$

The moments can also be calculated directly, from

$$\begin{aligned} m_1 = \langle x \rangle &= \int_0^\infty \frac{x^2}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx = \int_{-\infty}^\infty \frac{x^2}{2a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx = \sqrt{\frac{\pi}{2}} a, \\ m_2 = \langle x^2 \rangle &= \int_0^\infty \frac{x^3}{a^2} \exp\left(-\frac{x^2}{2a^2}\right) dx = 2a^2 \int_0^\infty \frac{x^2}{2a^2} \exp\left(-\frac{x^2}{2a^2}\right) d\left(\frac{x^2}{2a^2}\right) \\ &= 2a^2 \int_0^\infty y \exp(-y) dy = 2a^2. \end{aligned}$$

(e) *Maxwell* $p(x) = \sqrt{\frac{2}{\pi}} \frac{x^2}{a^3} \exp(-\frac{x^2}{2a^2})$.

- It is difficult to calculate the characteristic function for the *Maxwell* distribution

$$p(x) = \sqrt{\frac{2}{\pi}} \frac{x^2}{a^3} \exp\left(-\frac{x^2}{2a^2}\right),$$

say describing the speed of a gas particle. However, we can directly evaluate the mean and variance, as

$$\begin{aligned} m_1 = \langle x \rangle &= \sqrt{\frac{2}{\pi}} \int_0^\infty \frac{x^3}{a^3} \exp\left(-\frac{x^2}{2a^2}\right) dx \\ &= 2\sqrt{\frac{2}{\pi}} a \int_0^\infty \frac{x^2}{2a^2} \exp\left(-\frac{x^2}{2a^2}\right) d\left(\frac{x^2}{2a^2}\right) \\ &= 2\sqrt{\frac{2}{\pi}} a \int_0^\infty y \exp(-y) dy = 2\sqrt{\frac{2}{\pi}} a, \end{aligned}$$

and

$$m_2 = \langle x^2 \rangle = \sqrt{\frac{2}{\pi}} \int_0^\infty \frac{x^4}{a^3} \exp\left(-\frac{x^2}{2a^2}\right) dx = 3a^2.$$

8. Tchebycheff inequality: Consider any probability density $p(x)$ for $(-\infty < x < \infty)$, with mean λ , and variance σ^2 . Show that the total probability of outcomes that are more than $n\sigma$ away from λ is less than $1/n^2$, i.e.

$$\int_{|x-\lambda| \geq n\sigma} dx p(x) \leq \frac{1}{n^2}.$$

Hint: Start with the integral defining σ^2 , and break it up into parts corresponding to $|x - \lambda| > n\sigma$, and $|x - \lambda| < n\sigma$.

- By definition, for a system with a PDF $p(x)$, and average λ , the variance is

$$\sigma^2 = \int (x - \lambda)^2 p(x) dx.$$

Let us break the integral into two parts as

$$\sigma^2 = \int_{|x-\lambda| \geq n\sigma} (x - \lambda)^2 p(x) dx + \int_{|x-\lambda| < n\sigma} (x - \lambda)^2 p(x) dx,$$

resulting in

$$\sigma^2 - \int_{|x-\lambda| < n\sigma} (x - \lambda)^2 p(x) dx = \int_{|x-\lambda| \geq n\sigma} (x - \lambda)^2 p(x) dx.$$

Now since

$$\int_{|x-\lambda|\geq n\sigma} (x-\lambda)^2 p(x) dx \geq \int_{|x-\lambda|\geq n\sigma} (n\sigma)^2 p(x) dx,$$

we obtain

$$\int_{|x-\lambda|\geq n\sigma} (n\sigma)^2 p(x) dx \leq \sigma^2 - \int_{|x-\lambda|< n\sigma} (x-\lambda)^2 p(x) dx \leq \sigma^2,$$

and

$$\int_{|x-\lambda|\geq n\sigma} p(x) dx \leq \frac{1}{n^2}.$$

9. Optimal selection: In many specialized populations, there is little variability among the members. Is this a natural consequence of optimal selection?

(a) Let $\{r_\alpha\}$ be n random numbers, each independently chosen from a probability density $p(r)$, with $r \in [0, 1]$. Calculate the probability density $p_n(x)$ for the largest value of this set, i.e. for $x = \max\{r_1, \dots, r_n\}$.

• The probability that the maximum of n random numbers falls between x and $x + dx$ is equal to the probability that one outcome is in this interval, while all the others are smaller than x , i.e.

$$p_n(x) = p(r_1 = x, r_2 < x, r_3 < x, \dots, r_n < x) \times \binom{n}{1},$$

where the second factor corresponds to the number of ways of choosing which $r_\alpha = x$. As these events are independent

$$\begin{aligned} p_n(x) &= p(r_1 = x) \cdot p(r_2 < x) \cdot p(r_3 < x) \cdots p(r_n < x) \times \binom{n}{1} \\ &= p(r = x) [p(r < x)]^{n-1} \times \binom{n}{1}. \end{aligned}$$

The probability of $r < x$ is just a cumulative probability function, and

$$p_n(x) = n \cdot p(x) \cdot \left[\int_0^x p(r) dr \right]^{n-1}.$$

(b) If each r_α is uniformly distributed between 0 and 1, calculate the mean and variance of x as a function of n , and comment on their behavior at large n .

- If each r_α is uniformly distributed between 0 and 1, $p(r) = 1$ ($\int_0^1 p(r)dr = \int_0^1 dr = 1$). With this PDF, we find

$$p_n(x) = n \cdot p(x) \cdot \left[\int_0^x p(r)dr \right]^{n-1} = n \left[\int_0^x dr \right]^{n-1} = nx^{n-1},$$

and the mean is now given by

$$\langle x \rangle = \int_0^1 xp_n(x)dx = n \int_0^1 x^n dx = \frac{n}{n+1}.$$

The second moment of the maximum is

$$\langle x^2 \rangle = n \int_0^1 x^{n+1} dx = \frac{n}{n+2},$$

resulting in a variance

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{n}{n+2} - \left(\frac{n}{n+1} \right)^2 = \frac{n}{(n+1)^2(n+2)}.$$

Note that for large n the mean approaches the limiting value of unity, while the variance vanishes as $1/n^2$. There is too little space at the top of the distribution for a wide variance.

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