

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 ?

(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).

(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.

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 \mathcal{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.

(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.

(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 .

(d) Find an expression for $C_{\mathcal{S}} - C_A$ 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 $\left. \frac{\partial E}{\partial T} \right|_A = \left. \frac{\partial E}{\partial T} \right|_{\mathcal{S}}$.

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.
- (b) Calculate the volume expansion factor in an adiabatic process as a function of Θ .
- (c) Show that $Q_H/Q_C = \Theta_H/\Theta_C$.

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 .
- (b) What is the most general equation of state consistent with an internal energy that depends only on temperature?
- (c) Show that for a van der Waals gas C_V is a function of temperature alone.

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. 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

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

- (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 $dTdL/dT$ must equal the work $W = VdP$, equal to LdT/T from eq.(1). Hence $dL/dT = L/T$ implying that L is proportional to $T!$ ”

- (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 $P(T)$.

- (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 $2.3 \times 10^6 Jkg^{-1}$.)

(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.

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

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 .

(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 $T \leq T_m$.

(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 $T \leq T_m$.

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

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

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

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;

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

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

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

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

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

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 $|x - \lambda| < n\sigma$.

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 $x = \max\{r_1, \dots, r_n\}$.

(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 .

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