CHEM/CHPH/PHYS 703: Introduction to Nonequilibrium Statistical Physics

PROBLEM SET # 1, due at the start of class, Thursday, February 20, 2020

**Problem 1**

In a simple model of a rubber band the tension ($\mathcal{F}$) and internal energy ($U$) are given by:

$$\mathcal{F} = bT(L - L_0) \qquad , \qquad U = cT \, , \tag{1}$$

where $L \geq L_0$ denotes length, $T$ is temperature, and $L_0$, $b$, $c > 0$ are constants. The work required to stretch the rubber band is given by $đW = \mathcal{F}\mathrm{d}L$. When the rubber band at temperature $T$ is surrounded by air at temperature $T_0$, it absorbs heat from the air at a rate $đQ/\mathrm{d}t = -\alpha(T - T_0)$, where $\alpha > 0$ is a constant. To answer the questions below, neglect the mass of the rubber band and any internal friction generated by stretching and contraction.

(a) Letting $S_0$ denote the entropy of the rubber band at length $L_0$ and temperature $T_0$, solve for its entropy $S(L,T)$ for arbitrary length $L \geq L_0$ and temperature $T$.

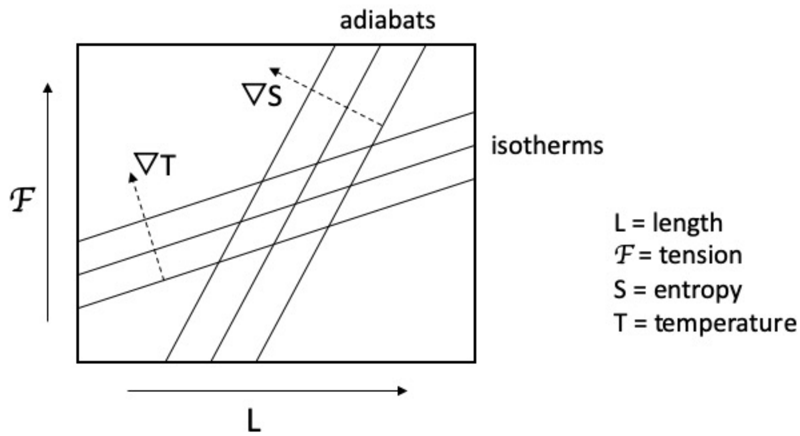
Now imagine that a mass $m$ is suspended from a ceiling by a rubber band. Initially, the mass is held in place at a distance $L_0$ below the ceiling, and the rubber band is in equilibrium with the surrounding air at temperature $T_0$. The mass is released at time $t = 0$, it falls, and it bounces up and down at the end of the rubber band. Let $x = L - L_0$ denote the vertical position of the mass and $p = m\dot{x}$ its momentum.

(b) Obtain a set of coupled equations for $\dot{x}$, $\dot{p}$ and $\dot{T}$ that govern the motion of the mass and the temperature of the rubber band.

(c) When $\alpha = 0$, show that $x$ and $p$ evolve under an effective Hamiltonian $H(x,p) = p^2/2m + V(x)$, and solve for $V(x)$.

(d) When $\alpha > 0$, use the second law of thermodynamics to write down an explicit function $f(x,p,T)$ whose value never increases with time. Verify directly from the equations you obtained in part (b) that $\mathrm{d}f/\mathrm{d}t \leq 0$. At what values of $x$, $p$, and $T$ does the minimum of $f(x,p,T)$ occur? Briefly explain why these values make sense.

(e) From $t = 0$ to $t = \infty$, what is the net change in: (i) the internal energy of the rubber band, (ii) the kinetic + potential energy of the mass, (iii) the internal energy of the surrounding air, (iv) the entropy of the rubber band, and (v) the entropy of the air? Verify that your answers agree with the first and second laws of thermodynamics. Assume $\alpha > 0$.




**Problem 2**

The figure above shows a portion of the $\mathcal{F}L$-diagram for a rubber band. As discussed in class and illustrated in the figure, adiabats (lines of constant entropy) are steeper than isotherms (lines of constant temperature), as a result of the Kelvin-Planck statement of the second law. The dashed arrows indicate temperature and entropy gradients.

(a) Imagine "deforming" the $\mathcal{F}L$-plane to obtain a figure like the one shown above, but with $S$ on the horizontal axis and $T$ on the vertical axis. Sketch this figure. Draw a few lines of constant tension and a few lines of constant length, analogous to the isotherms and adiabats shown above. Draw arrows to indicate the directions of increasing $S$, $T$, $L$ and $\mathcal{F}$. Using your figure, determine which is greater, $C_L$ or $C_{\mathcal{F}}$? Here

$$C_L = T \left.\frac{\partial S}{\partial T}\right)_L \quad \text{and} \quad C_{\mathcal{F}} = T \left.\frac{\partial S}{\partial T}\right)_{\mathcal{F}} \tag{2}$$

denote the heat capacity of the rubber band at fixed length and tension, respectively.

(b) For the state function $U(S, L)$ (internal energy) the first law gives: $dU = TdS + \mathcal{F}dL$. Use the first law to derive the Maxwell relation $(\partial T/\partial L)_S = (\partial \mathcal{F}/\partial S)_L$.

(c) Since temperature can be viewed as a function of length and entropy, and length can be viewed as a function of tension and entropy, we can express temperature as follows:

$$T = T(L(\mathcal{F}, S), S) \tag{3}$$

Use the chain rule for derivatives, the Maxwell relation from part (b), and various partial derivative identities to answer the same question as in part (a): which is greater, $C_L$ or $C_{\mathcal{F}}$? Note that $\partial^2 U/\partial S^2 > 0$ and $\partial^2 U/\partial L^2 > 0$, by thermodynamic stability.

**Problem 3**

Consider an ideal gas of $N \gg 1$ point particles of mass $m$, confined within a three-dimensional container of volume $V$.

(a) Show that the classical density of states, $\Sigma(E) = \int \delta(E - H)$, is given by

$$\Sigma(E) = \frac{(2\pi m)^k}{\Gamma(k)} V^N E^{k-1} \tag{4}$$

where $k = 3N/2$ and $\Gamma(k) = \int_0^\infty e^{-t} t^{k-1} \mathrm{d}t$ denotes the gamma function.

(b) Use Eq. 4 to evaluate the microcanonical entropy $S = k_B \ln(\Sigma/N!)$, keeping only those terms that do not vanish when $S/N$ is evaluated in the thermodynamic limit $N \to \infty$, with $E/N$ and $V/N$ held fixed. Compare your result with the Sackur-Tetrode equation.

(c) Now evaluate the canonical entropy $S = -k_B \int \pi^c \ln(N! \pi^c)$ where $\pi^c$ is the canonical distribution at temperature $T$. Keep only those terms that do not vanish when $S/N$ is evaluated in the thermodynamic limit $N \to \infty$, with $T$ and $V/N$ held fixed.

(d) Show that the canonical distribution of energies $\rho^c(E) = \Sigma(E) e^{-\beta E}/Z$ can be written in the large deviation form

$$\rho^c(E) \sim e^{-N\phi(\epsilon;T)} \qquad , \qquad \epsilon = \frac{E}{N} \tag{5}$$

and obtain an explicit expression for $\phi(\epsilon; T)$. Verify that $\phi$ is convex, i.e. $\partial^2\phi/\partial\epsilon^2 > 0$.