Thermodynamics

1. *Non-Carnot Engine:*   Consider an engine that operates between a set of temperatures $T_{\max} = T_1 > T_2 > T_3 > \cdots > T_n = T_{\min}$. For a subset of these temperatures $\{T_\alpha^+\}$, the engine takes in heat $\{Q_\alpha^+\}$; while at the remaining temperatures $\{T_\beta^-\}$, heat $\{Q_\beta^-\}$ is released. The engine does a net work $W = Q^+ - Q^-$, and its efficiency is given by $\eta = W/Q_+$, where $Q^+ = \sum_\alpha Q_\alpha^+$ and $Q^- = \sum_\beta Q_\beta^-$. Show that this efficiency is less than that of a Carnot engine operating between $T_{\max}$ and $T_{\min}$.

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2. *Heat exchange between identical bodies:*   A collection of n identical bodies, of temperature independent heat capacity C, are initially at temperatures $\{\theta_1, \theta_2, \cdots, \theta_n\}$.

(a) If these bodies are brought into contact such that the only heat exchange is allowed between them, what is the final temperature T_F, and what is the change in entropy.

(b) What is the final temperature if a Carnot engine is used to transfer heat between the n bodies? What is the amount of work done by the engine in this case?

(c) What is the theoretical maximum temperature T_H to which one of the bodies can be raised at the expense of the other $(n-1)$ bodies? (Any work generated in the process can in principle be stored and reused.) You can leave the answer in the form of an implicit equation for T_H without solving it.

(d) For the case of $n = 3$, with $\theta_1 = \theta_2 = \theta_H$, and $\theta_3 = \theta_C < \theta_H$, find the explicit solution for $T_H(\theta_H, \theta_C)$.

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3.   *Hard core gas:*   A gas obeys the equation of state $P(V - Nb) = Nk_BT$, and has a heat capacity C_V independent of temperature. (N is kept fixed in the following.)

(a) Find the Maxwell relation involving $\partial S/\partial V|_{T,N}$.

(b) By calculating $dE(T, V)$, show that E is a function of T (and N) only.

(c) Show that $\gamma \equiv C_P/C_V = 1 + Nk_B/C_V$ (independent of T and V).

(d) By writing an expression for $E(P, V)$, or otherwise, show that an adiabatic change satisfies the equation $P(V - Nb)^\gamma =$ constant.

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4. *Superconducting transition:* Many metals become superconductors at low temperatures T, and magnetic fields B. The heat capacities of the two phases at zero magnetic field are approximately given by

$$\begin{cases} C_s(T) = V\alpha T^3 & \text{in the superconducting phase} \\ C_n(T) = V\left[\beta T^3 + \gamma T\right] & \text{in the normal phase} \end{cases},$$

where V is the volume, and $\{\alpha, \beta, \gamma\}$ are constants. (There is no appreciable change in volume at this transition, and mechanical work can be ignored throughout this problem.)

(a) Calculate the entropies $S_s(T)$ and $S_n(T)$ of the two phases at zero field, using the third law of thermodynamics.

(b) Experiments indicate that there is no latent heat ($L = 0$) for the transition between the normal and superconducting phases at zero field. Use this information to obtain the transition temperature T_c, as a function of α, β, and γ.

(c) At zero temperature, the electrons in the superconductor form bound Cooper pairs. As a result, the internal energy of the superconductor is reduced by an amount $V\Delta$, i.e. $E_n(T = 0) = E_0$ and $E_s(T = 0) = E_0 - V\Delta$ for the metal and superconductor, respectively. Calculate the internal energies of both phases at finite temperatures.

(d) By comparing the Gibbs free energies (or chemical potentials) in the two phases, obtain an expression for the energy gap Δ in terms of α, β, and γ.

(e) In the presence of a magnetic field B, inclusion of magnetic work results in $dE = TdS + BdM + \mu dN$, where M is the magnetization. The superconducting phase is a perfect diamagnet, expelling the magnetic field from its interior, such that $M_s = -VB/(4\pi)$ in appropriate units. The normal metal can be regarded as approximately non-magnetic, with $M_n = 0$. Use this information, in conjunction with previous results, to show that the superconducting phase becomes normal for magnetic fields larger than

$$B_c(T) = B_0 \left(1 - \frac{T^2}{T_c^2}\right),$$

giving an expression for B_0.

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5. *Photon gas Carnot cycle:* The aim of this problem is to obtain the blackbody radiation relation, $E(T, V) \propto VT^4$, starting from the equation of state, by performing an infinitesimal Carnot cycle on the photon gas.
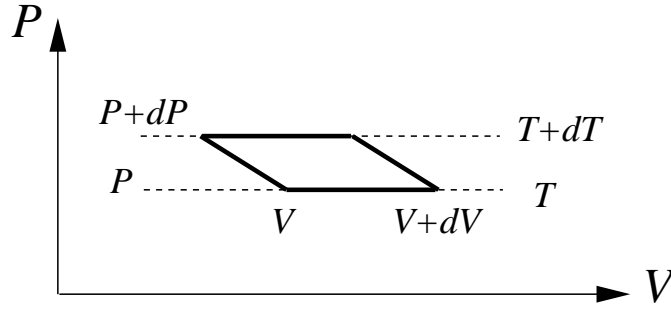
(a) Express the work done, W, in the above cycle, in terms of dV and dP.

(b) Express the heat absorbed, Q, in expanding the gas *along an isotherm*, in terms of P, dV, and an appropriate derivative of $E(T, V)$.

(c) Using the efficiency of the Carnot cycle, relate the above expressions for W and Q to T and dT.

(d) Observations indicate that the pressure of the photon gas is given by $P = AT^4$, where $A = \pi^2 k_B^4 / 45 \, (\hbar c)^3$ is a constant. Use this information to obtain $E(T, V)$, assuming $E(T, 0) = 0$.

(e) Find the relation describing the *adiabatic paths* in the above cycle.

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6. (Optional) *Irreversible Processes:*

(a) Consider two substances, initially at temperatures T_1^0 and T_2^0, coming to equilibrium at a final temperature T_f through heat exchange. By relating the direction of heat flow to the temperature difference, show that the change in the total entropy, which can be written as

$$\Delta S = \Delta S_1 + \Delta S_2 \geq \int_{T_1^0}^{T_f} \frac{dQ_1}{T_1} + \int_{T_2^0}^{T_f} \frac{dQ_2}{T_2} = \int \frac{T_1 - T_2}{T_1 T_2} dQ,$$

must be positive. This is an example of the more general condition that "*in a closed system, equilibrium is characterized by the maximum value of entropy S.*"

(b) Now consider a gas with adjustable volume V, and diathermal walls, embedded in a heat bath of constant temperature T, *and* fixed pressure P. The change in the entropy of the bath is given by

$$\Delta S_{\text{bath}} = \frac{\Delta Q_{\text{bath}}}{T} = -\frac{\Delta Q_{\text{gas}}}{T} = -\frac{1}{T} \left(\Delta E_{\text{gas}} + P \Delta V_{\text{gas}} \right).$$

By considering the change in entropy of the combined system establish that *"the equilibrium of a gas at fixed T and P is characterized by the minimum of the Gibbs free energy $G = E + PV - TS$."*

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7. *Relaxation dynamics:* Consider a mechanical system described by displacements $\mathbf{x} = \{x_i\}$ and potential energy $U(\mathbf{x})$. When subject to conjugate external forces $\mathbf{J} = \{J_i\}$, a stable equilibrium is obtained by minimizing $H = U - \mathbf{J} \cdot \mathbf{x}$.

(a) What are the conditions on the first and second derivatives of $U(\mathbf{x})$ at the equilibrium point $\mathbf{x}_0$?

Following a small displacement away from equilibrium to $\delta\mathbf{x} = \mathbf{x} - \mathbf{x}_0$, (in linear response) the displacements relax back to equilibrium with 'velocities' $v_i = \dot{x}_i = -\sum_k \gamma_{ik}\delta J_k$; where $\mathbf{\Gamma} \equiv \{\gamma_{ik}\}$ are *kinetic coefficients*, and $\delta J_k = \frac{\partial U}{\partial x_k} - J_k$ is the difference between internal and external force.

(b) Assuming dissipative relaxation always proceeds such that H is decreased; what is the constraint on $\mathbf{\Gamma} \equiv \{\gamma_{ik}\}$?

The above discussion can be extended to a thermodynamic system, in which case internal energy can change by both mechanical work and heat. At a temperature T, equilibrium is obtained by minimizing $G = E - \mathbf{J} \cdot \mathbf{x} - TS$. With the entropy S as an additional coordinate,

$$\dot{x}_i = -\sum_k \gamma_{ik}\delta J_k - \theta_i \, \delta T,$$

with $\mathbf{\Theta} = \{\theta_i\}$ as kinetic coefficients relating velocities to temperature differences in the linear regime. Similarly the heat flux into the system can be written as

$$\dot{Q} = T\dot{S} = -\kappa\delta T - \sum_i \lambda_i \delta J_i.$$

(c) What is the stability constraint for the parameters $\mathbf{\Gamma}$, $\mathbf{\Theta}$, $\mathbf{\Lambda} = \{\lambda_i\}$, and κ?

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8. (Optional) *The solar system* originated from a dilute gas of particles, sufficiently separated from other such clouds to be regarded as an isolated system. Under the action of gravity the particles coalesced to form the sun and planets.

(a) The motion and organization of planets is much more ordered than the original dust cloud. Why does this not violate the second law of thermodynamics?

(b) The nuclear processes of the sun convert protons to heavier elements such as carbon. Does this further organization lead to a reduction in entropy?

(c) The evolution of life and intelligence requires even further levels of organization. How is this achieved on earth without violating the second law?

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† Reviewing the problems and solutions provided on the course web-page for preparation for *Test 1* should help you with the above problems.