- The restoring force is linear in L. The longer the chain, the larger is the tendency to crumple
- The tension in the chain is greater at higher temperatures. Therefore, increasing the temperature should cause the chain to fold up. This is the opposite behavior that we find in an ideal gas which wants to expand as the temperature is increased.
- We have assumed adiabatic stretching - the total entropy should be constant. But, as the chain contracts, the configurational entropy increases. Therefore, the vibrational entropy must decrease to compensate for the increase in configurational entropy. The reduction in the total number of vibrational states available to the chain corresponds to a decrease in the effective temperature of the chain.

The last point has some interesting physical consequences. Consider a rubber band which is pretty much a network of simple polymer chains like the one we've been modeling. As you stretch the rubber band, you are *decreasing* the configurational entropy (chain is straightening out). This must be compensated for (in the adiabatic approximation) by an *increase* in the vibrational entropy - an increase in the temperature of the rubber band! Conversely, as you allow the rubber band to shrink, the configurational entropy goes up, the vibrational entropy goes down, and the temperature of the rubber band goes down! You can check this by stretching and relaxing a rubber band that is just barely touching your lips. You can usually feel the temperature changes on those fat rubber bands. Not so much on the thin ones.

12.5 Diffusive Equilibrium

We've learned that there is an equilibrium as well as a state variable associated with maximizing the entropy with respect to energy U (defines temperature) and volume V (defines pressure). Analogously, we can imagine letting the number of particles vary and expect that a maximal entropy with respect to N will define a new equilibrium and associated *thermodynamic potential*.

Consider a box divided into two sub-volumes V_A and V_B. The divider is a permeable membrane that allows particles to move from one side of the box to the other without changing the sub-volumes.

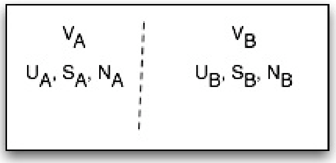

Figure 5: A system in which particles are allowed to cross a permeable membrane in order to maximize entropy

In equilibrium the total entropy S_{total} will be maximal:

$$\left(\frac{\partial S_{\text{total}}}{N_A}\right)_{U_A,V_A} = 0$$

Since $dN_A = -dN_B$, we can write

$$\frac{\partial S_A}{N_A} = \frac{\partial S_B}{N_B}.$$

Multiplying both sides by $-T$, we arrive at the definition of the chemical potential μ:

$$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}.$$

The equilibrium associated with μ is *diffusive equilibrium.* Think of μ as a potential or a force that tells us which way particle flow will occur. If $\mu_A < \mu_B$ then particles will flow from B to A. In general, particle flow occurs from the system with the higher chemical potential to the system with the lower chemical potential. The text works out some simple sample calculations for μ. For a small Einstein solid, we find $\mu = -\epsilon$ where ϵ is the level spacing of the harmonic oscillator.

So, collecting the thermodynamic potentials we've developed so far, we have:

$$\begin{aligned}\frac{1}{T} &= \left(\frac{\partial S}{U}\right)_{V,N}\\ P &= T\left(\frac{\partial S}{V}\right)_{U,N}\\ \mu &= -T\left(\frac{\partial S}{N}\right)_{U,V}\end{aligned}$$

13 Engines and Refrigerators

In class, we drew our basic engine energy diagrams: Heat Q_h enters our engine from a heat reservoir at temperature T_h. The engine does work W with the heat Q_h and expels waste heat Q_C to a cold reservoir at temperature T_c. A refrigerator operates the same way with all of the "arrows reversed. The efficiency of such an engine is the ratio of output work W to input energy Q_h.

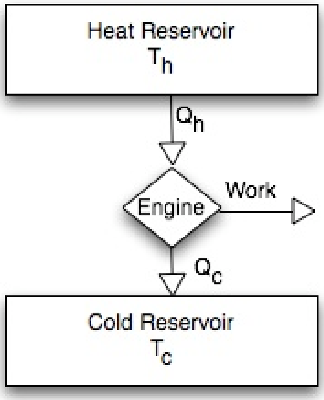

Figure 6: An engine operates by taking heat Q_h from a reservoir at temperature T_h, converting some of Q_h to work W, and expelling the rest of the heat $Q_c = Q_h - W$ to the waste reservoir at temperature T_c

$$\epsilon = \frac{W}{Q_h}.$$

The first law of thermodynamics, tells us that $Q_h = W + Q_c$, so that

$$\epsilon = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_C}{Q_h}.$$

The second law of thermodynamics relates the entropy generated at each step of the engine cycle. When heat Q_h is extracted from the hot reservoir, an amount of entropy Q_h/T_h is removed from the reservoir. When heat Q_c is expelled to the cold reservoir, an amount of entropy Q_c/T_c is generated and dumped into the cold reservoir. Since the net entropy production must be positive, we must have

$$\frac{Q_c}{T_c} \geq \frac{Q_h}{T_h}.$$

This can be read as

$$\frac{Q_c}{Q_h} \geq \frac{T_c}{T_h}$$

which allows us to express the efficiency of the engine as a bounded value:

$$\epsilon \leq 1 - \frac{T_c}{T_h}.$$

The upper limit of efficiency when $\epsilon = 1 - T_c/T_h$ is called the *Carnot efficiency* and represents the theoretical limit of any heat engine operating between reservoirs at temperatures T_h and T_c. All real engines have efficiencies considerably less than this upper limit.

Example: Power Plant The Pleasant Prairie Power Plant consists of two 612 MW units that operate with a hot reservoir (superheated steam) at 2000 F (1366 K) and a cold reservoir (evaporation towers) with temperature 955 F = 786 K. The Carnot efficiency of such an "engine" is $1 - T_c/T_h = 0.42$. Some 13,000 tons of coal arrive daily to feed the burners. If the power plant operated at its Carnot limit (impossible!), then it would still use only $0.42 \times 13,000 = 5460$ tons/day to generate useful work (electricity). The rest - 7540 tons of coal is waste energy.

Example: A Power Plant Uses a River for its Cold Reservoir Consider a power plant that produces 1 GW of electricity at an efficiency of 0.4. (a) What is the rate of waste heat expulsion to the environment?

The power delivered is $P = W/\Delta t = 1GW$. The work done is $W = \epsilon Q_h = \epsilon(W + Q_c)$. Therefore, $Q_c = (1-\epsilon)W/\epsilon$. So,

$$\frac{dQ_c}{dt} = \frac{1-0.4}{0.4}(1GW) = 1.5GW$$

(b) Assume that the cold reservoir is a river with a flow rate of $100m^3/s$. What is the downstream temperature of the river? 1.5 GJ goes into 100 m^3 of water each second. The heat delivered is $Q = mc\Delta T$. Therefore, the temperature rise of the river water is $\Delta T = Q/mc = Q/(\rho V c) = (1.5GJ)/[(1000kg/m^3)(100m^3)(4200J/kg-C)] = 3.6°C$. This is *thermal pollution.* One possible solution is to use river water to cool the plant as before, but allow the water to evaporate. This approach is pursued in the homework problems for this chapter.

Example: Thermal Gradient Power Generation One proposal for a green energy source is using the difference in temperature between the warmer surface layers of water and the deeper, colder layers of water in the ocean. What is the maximum possible efficiency of such an engine? The colder layers have an average temperature of 277 K, while the surface layers might be at 295 K. The Carnot efficiency of a thermal gradient engine is thus $\epsilon = 1 - 277/295 = 0.061 \approx 6\%$. In practice, the waste heat would increase the temperature of the cold bath, while reducing the temperature of the hot bath. Suppose we extract heat from the warmer water until its temperature drops by $0.5\Delta T = 9K$. We then expel the heat into the cold layers until its temperature increases by 9 K. The Carnot efficiency is then $\epsilon = 1 - (281.5/290.5) = 0.031 \approx 3\%$.

Suppose we wish to generate useful work at the rate of 1 GW. How many cubic meters of water would be required each second to accomplish this? The heat extracted from each kilogram of water is $C\Delta T = 9 \times 4186 = 38kJ$. At 3.1% efficiency, we can only get 1.2 kJ of work from this cycle. Therefore, we'd require about $10^9 J/1200J/kg = 8.6 \times 10^5 kg$ of water. This is about 900 m^3 of water each second.

13.1 Carnot Engine

In this section, we work out the total wok that can be done by an engine operating between two reservoirs at temperature T_h and T_c. The cycle that Carnot designed to produce the highest possible efficiency (Carnot efficiency) is a 4-step cycle that alternates isothermal and adiabatic expansions and compressions. For concreteness, we take a gas of N particles to be confined to a cylinder whose volume can be varied by the movement of a piston.

- **A: Isothermal Expansion from volume V_1 to volume V_2 at temperature T_h.** Here, the work done is
$$W_A = -\int_{V_1}^{V_2} PdV = -NkT_h \int_{V_1}^{V_2} \frac{dV}{V} = -NkT_h \log\left(\frac{V_2}{V_1}\right) < 0.$$
Since $W_A < 0$, the gas does work on the piston.

- **B: Adiabatic Expansion from volume V_2 to volume V_3.** During this process, the temperature of the gas drops from T_h to T_c. Since the expansion is adiabatic, the heat exchange with the environment is zero ($Q = 0$). By the first law, the work done is:
$$W_B = -\Delta U = -\frac{f}{2}Nk\Delta T = +\frac{f}{2}Nk(T_h - T_c) > 0.$$
Again, $W_B > 0$ so work is done by the gas on the piston.

- **C: Isothermal Compression from volume V_3 to volume V_4 at temperature T_c:** As in step A above, we have
$$W_C = -\int_{V_3}^{V_4} PdV = -NkT_c \int_{V_3}^{V_4} \frac{dV}{V} = -NkT_c \log\left(\frac{V_4}{V_3}\right) > 0.$$
Note that $V_4 < V_3$, so the work done in this step is greater than zero: piston does work on the gas.

- **D: Adiabatic Compression from volume V_4 to volume V_1.** During this process, the temperature of the gas increases from T_c back to T_h. Analogously to step B, we find the work done on this leg to be:

  $$W_D = -\Delta U = -\frac{f}{2}Nk(T_h - T_c) < 0.$$

  The gas does work on the piston.

The total work done in one cycle of the Carnot Engine's operation is the sum $W_A + W_B + W_C + W_D$. After a bit of algebra, you can find

$$W_T = -Nk\left[T_h \log\left(\frac{V_2}{V_1}\right) + T_c \log\left(\frac{V_4}{V_3}\right)\right]$$

. Now the adiabatic relations appropriate for steps B and D are:

$$\begin{aligned} T_h V_2^{\gamma-1} &= T_c V_3^{\gamma-1} \\ T_c V_4^{\gamma-1} &= T_h V_1^{\gamma-1} \end{aligned}$$

These imply the relation $(V_1/V_2) = (V_4/V_3)$ which allows us to simplify the total work expression:

$$W_T = -Nk \log\left(\frac{V_2}{V_1}\right)(T_h - T_c) < 0.$$

The gas does work on the piston!