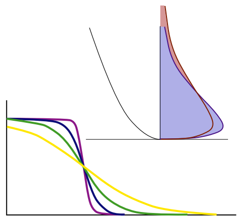
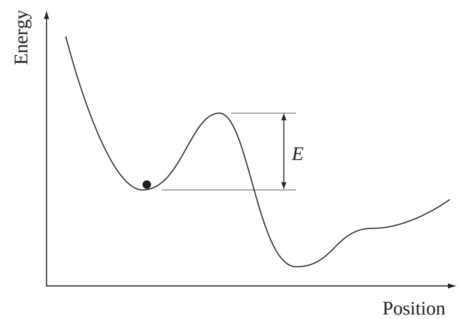


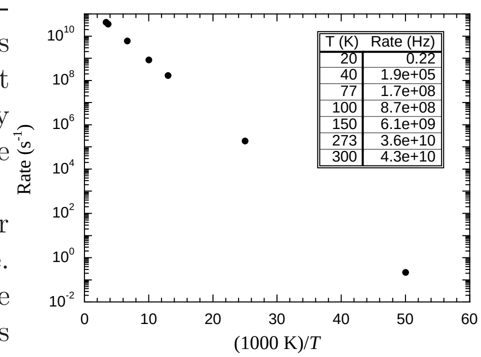
Statistical Mechanics

Homework Assignment 9

Due 20 November 2002

Problem 9.1 – Arrhenius Behavior





T (K)	Rate (Hz)
20	0.22
40	1.9e+05
77	1.7e+08
100	8.7e+08
150	6.1e+09
273	3.6e+10
300	4.3e+10

A system's energy is shown schematically in the upper figure at the right. The system is represented by the dot, which sits near the bottom of a local energy minimum. Over a peak in the energy lies a global energy minimum, which is where the system "wants" to be for maximum stability. To pass over the peak the system must raise its energy by E above the local minimum, after which it falls readily into the global minimum. The system might be an electron-hole pair in a semiconductor, in which case the low-energy state could correspond to the electron and hole recombining to emit a visible photon, although the situation is quite common and describes a great many important systems. We can learn about the energy function by measuring the dependence of the decay rate on the temperature of the surroundings.

Frequently there is a "characteristic time" τ over which the system's energy can be expected to change. If the system were an oscillator, this time would be approximately its period. In a solid or molecule, it is roughly the vibration period.

On a time scale short compared to τ the system's energy is approximately constant. Once each time interval τ, on average, the system's energy is "randomized." Equivalently, once each time interval τ the system tries to overcome the barrier, so that the attempt frequency is $\gamma = \tau^{-1}$.

(a) Assuming that the probability of finding the system at energy ϵ is proportional to the Boltzmann factor, and that the system attempts to overcome the barrier with frequency γ, show that the average transition rate may be expressed

$$W \propto \gamma \exp(-E/k_{\mathrm{B}}T)$$

(b) The lower figure plots the transition rate as a function of inverse temperature. From the plot and/or data shown, determine *approximately* the attempt frequency and the barrier height. You may use Kaleidagraph, Origin, or some other fitting software if you wish.

Problem 9.2 – Ideal Gas Averages (*Reif 7.19*)  A gas of molecules, each of mass m, is in thermal equilibrium at the absolute temperature T. Denote the velocity of a molecule by $\vec{\mathbf{v}}$, its three cartesian components by v_x, v_y, and v_z, and its speed by v. What are the following mean values:

(a) $\overline{v_x}$

(b) $\overline{v_x^2}$

(c) $\overline{v^2 v_x}$

(d) $\overline{v_x^3 v_y}$

(e) $\overline{(v_x + b v_y)^2}$ where b is a constant

(f) $\overline{v_x^2 v_y^2}$

Reif adds the following endearing remark: *If you need to calculate explicitly any integrals in this problem, you are the kind of person who likes to turn cranks but does not think.*

Problem 9.3 – Maxwellian Distribution

(a) What is the standard deviation (width) of the Maxwellian distribution of speeds of a classical gas in equilibrium at temperature T? That is, what is $\sqrt{\langle (v - \langle v \rangle)^2 \rangle}$?

(b) What is the width of the speed distribution of the atoms that emerge through a small hole in the wall of an oven maintained at T?

(c) In which of the two previous situations is the *relative* width of the distribution greater? The relative width is the ratio of the width to the average speed.