Homework 21 (Due Tuesday, May 8th)

1. (a) Show that the probability of a fluctuation goes as

$$\mathcal{P} \propto \exp\left\{-\frac{1}{2kC_p}(\Delta S)^2 - \frac{\kappa_S V}{2kT}(\Delta P)^2\right\}$$

(see (15.1.15) in Pathria). (b) Using the above result and

$$\overline{\Delta V^2} = \left(\frac{\partial V}{\partial S}\right)_P^2 \overline{\Delta S^2} + \left(\frac{\partial V}{\partial P}\right)_S^2 \overline{\Delta P^2} + 2\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial V}{\partial P}\right)_S \overline{\Delta S \Delta P}$$

to show that $\overline{\Delta V^2} = kTV\kappa_T$ (Hint: From thermodynamics we have $\kappa_T = \kappa_S + TV\alpha^2/C_P$).

2. Write a program to simulate the motion of random walkers in one dimension. Call $x_i(t)$ the position of walker i at time t; initially all N walkers start at the origin ($x_i(0) = 0$ for $i = 1, \ldots, N$). At integer times the walkers flip a coin and take a unit step to the left or to the right with equal probability, so

$$x_i(t+1) = x_i(t) + \Re_i^{\pm}$$

where $\Re^{\pm}$ is $+1$ or -1 with equal probability. At each time step, after moving all the walkers, compute the variance of their positions,

$$\langle x^2 \rangle = \frac{1}{N}\sum_{i=1}^{N} x_i^2$$

Graph $\langle x^2 \rangle$ versus t; use at least $N = 1000$ walkers advancing to at least $t = 100$.

3. Experimental measurements (W. Pospisil, *Ann. Phys.*, vol. **83** pg. 735; 1927) of Brownian motion of soot particles (radius 4×10^{-5} cm) immersed in a water-glycerine solution (viscosity, 2.78×10^{-2} poise; temperature 18.8^o C) indicate that after a 10-second interval the variance of the horizontal displacement of the particles is $\langle x^2 \rangle = 3.3 \times 10^{-8}\text{cm}^2$. From this data, determine Boltzmann's constant; use Stoke's law to obtain the mobility from the viscosity.

4. In the Langevin theory, the velocity of a Brownian particle is given by

$$M\frac{d\mathbf{v}}{dt} = \mathcal{F}(t) = -\frac{\mathbf{v}}{B} + \mathbf{F}(t)$$

(a) Show that at equilibrium (i.e., as $t \to \infty$),

$$\langle \mathbf{v}(t) \cdot \mathbf{F}(t) \rangle = \frac{3kT}{MB} \qquad \text{and} \qquad \langle \mathbf{v}(t) \cdot \mathcal{F}(t) \rangle = 0$$

(b) Show that at equilibrium (i.e., as $t \to \infty$),

$$\langle \mathbf{r}(t) \cdot \mathcal{F}(t) \rangle = -3kT \qquad \text{and} \qquad \langle \mathbf{r}(t) \cdot \mathbf{F}(t) \rangle = 0$$