CHAPTER 5 - SYSTEMS UNDER PRESSURE

5.1 Ideal gas law

The quantitative study of gases goes back more than three centuries. In 1662, Robert Boyle showed that at a fixed temperature T, the product of the pressure P and volume V of a specific sample of gas is a constant

$$PV = \text{const} \quad \text{(sample held at fixed } T\text{).} \tag{5.1}$$

By the words "specific sample", we mean that a certain amount of gas is placed in a sealed container, so that the amount of gas in the sample does not change during the experimental measurement. Eq. (5.1) reflects the fact that the volume occupied by a gas decreases when the pressure applied to the gas increases, under the constraints that both the amount of gas in the sample and its temperature are held constant. The situation is illustrated in Fig. 5.1, in which a sample of gas is placed in a sealed cylinder, one wall of which is a moveable piston:

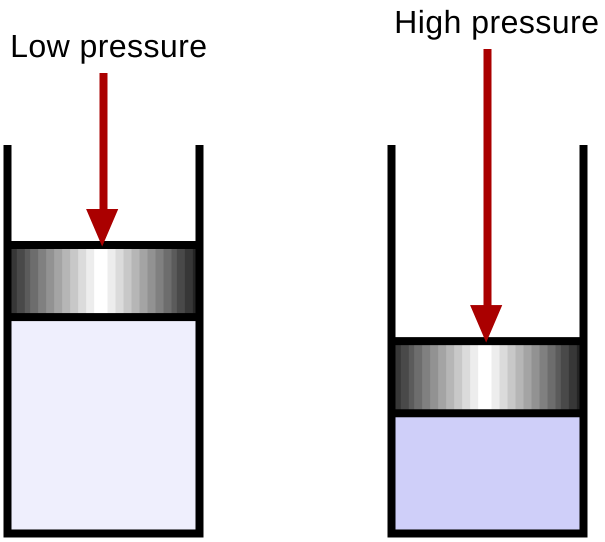


Fig. 5.1. Sample of gas in a sealed cylinder with a moveable piston.

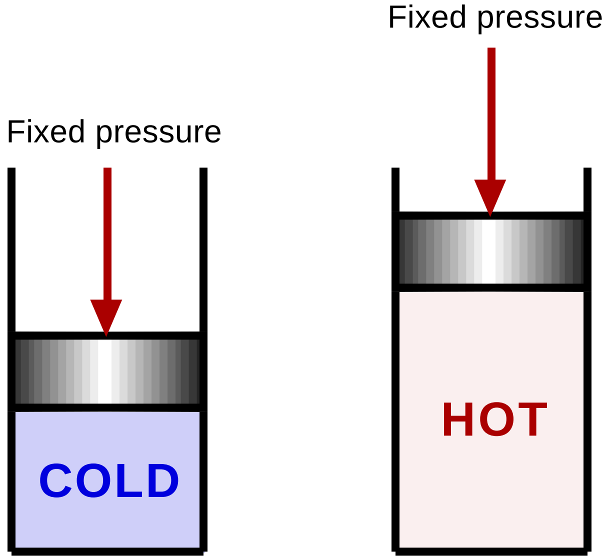


Fig. 5.2. Sample of gas under constant pressure expands when heated.

More than a century later, the temperature-dependence of the volume at fixed pressure was reported by a number of researchers: Charles (1787), Priestley (1790), Volta (1793), Dalton (1801) and Gay-Lussac (1802) (see Kauzmann, 1966):

$$V \quad T \qquad \text{(sample at fixed } P\text{).} \tag{5.2}$$

Eq. (5.2) tells us that a sample of gas held at a fixed pressure increases in volume as it is heated.

These two observations are combined into an expression known as the ideal gas law, which we will write in the form

$$PV = Nk_B T, \tag{5.3}$$

where N is the number of molecules in the gas sample, and k_B is Boltzmann's constant (see Chap. 4). It is more conventional to express the ideal gas law in terms of the number of moles, rather than the number of molecules, but the form we choose only requires notation from Chap. 4.

The ideal gas law is obeyed very well by dilute gases (V / N is large), and becomes less accurate as the gas becomes more dense (we pursue this non-ideal behavior in Chap. 6). It is important to note that Eq. (5.3) shows no dependence on the molecular species (H_2 *vs*. CCl_4) or mass (H_2 *vs*. I_2): all gases obey the same equation. Both the functional form of Eq. (5.3), and its universality, can be obtained by considering the motion of an ensemble of point particles at finite temperature. The molecular picture of gases was laid out by Bernoulli in 1738, then revised, rediscovered and completed over the following 150 years by Herapath (1821), Waterston (1845), Joule (1848), Rankin and Kronig (1856), Clausius (1857) and Maxwell and Boltzmann (see Kauzmann, 1966).

The basic form of the ideal gas equation is straightforward to obtain. Consider first, the one-dimensional motion of a point particle in a box bounded by two hard walls, as in Fig. 5.3. The particle travels at a constant speed u_x in the x-direction, and changes only its direction, not its speed, when it collides with a wall. It takes a time t for the particle to traverse the box, collide with one wall, traverse the box in the opposite direction, collide with the other wall, and return to its original position. If the distance between the walls is L_x, then

$$t = 2L_x / u_x. \tag{5.4}$$

When the particle collides with a wall, it reverses its velocity and its momentum; for example, when it hits the right-hand wall, its momentum changes from mu_x to $-mu_x$, where m is the mass of the particle. Hence, the magnitude of the *change* in momentum when it hits a wall is $mu_x - (-mu_x) = 2mu_x$.

The particle exerts a *force* on the wall during its collision. As you recall from first year mechanics, force is a rate of change of momentum, so that the average force exerted by the particle on the wall is

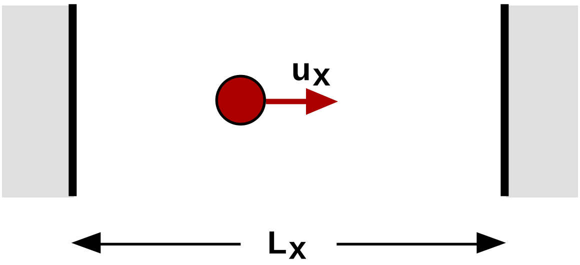


Fig. 5.3. Particle moving at constant speed between hard walls in one dimension.

$$
\begin{aligned}
[\textit{average force}] &= [\textit{change in momentum}] / [\textit{change in time}] \\
&= 2mu_x / (2L_x / u_x) \\
&= mu_x^2 / L_x. \qquad (5.5)
\end{aligned}
$$

Of course, the force exerted by the particle on the wall has the same magnitude as the force exerted by the wall on the particle.

Now place the particle in a three-dimensional box, with sides L_x, L_y, and L_z, although the particle still moves only in the *x*-direction with constant speed. The average force exerted by the particle on the end wall is still given by Eq. (5.5). The *pressure P* felt by the wall is just the average force divided by the area of the wall. Since the area of the wall at each end of the *x*-direction is $L_y \bullet L_z$, then

$$
\begin{aligned}
P &= [\textit{average force}] / [\textit{area of wall}] \\
&= (mu_x^2 / L_x) / (L_y L_z) \\
&= mu_x^2 / (L_x L_y L_z) \qquad (5.6)
\end{aligned}
$$

But the volume of the box is just

$$V = L_x L_y L_z, \qquad (5.7)$$

so that Eq. (6A.6) can be rewritten as

$$PV = mu_x^2. \qquad (5.8)$$

One can see that the specific values of L_x, L_y, and L_z do not enter into Eq. (5.8): what matters is the total volume *V*.

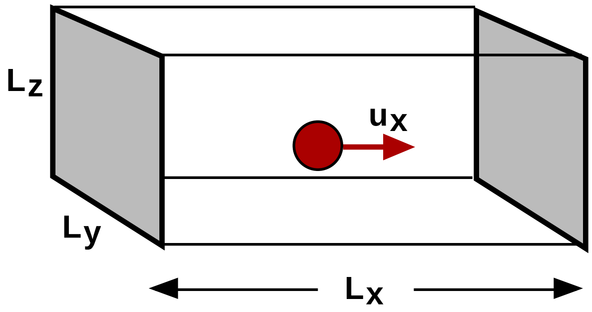


Fig. 5.4. Particle moving in a three-dimensional box.

We can extend Eq. (5.8) by considering a system of N particles moving in the x-direction, such that each particle has a velocity ($u_{i,x}$, 0, 0), where each $u_{i,x}$ may be different. Then the total pressure exerted on the end walls by all N particles is

$$PV = m\sum_i u_{i,x}^2$$
$$= Nm \{(1/N)\sum_i u_{i,x}^2\}$$

or

$$PV = Nm <u_x^2> \qquad (5.9)$$

where

$$<u_x^2> = (1/N)\sum_i u_{i,x}^2 \qquad (5.10)$$

is the mean square velocity in the x-direction.

Finally, we allow the particles to move in the x, y, or z directions. Then Eq. (5.9) still holds except that the pressure is now experienced by all walls. Further, if the motion of the particles is equivalent in all directions, then

$$<u_x^2> = <u_y^2> = <u_z^2> \qquad (5.11)$$

and

$$<u^2> = <u_x^2 + u_y^2 + u_z^2> = <u_x^2> + <u_y^2> + <u_z^2>$$
$$= 3<u_x^2> = 3<u_y^2> = 3<u_z^2>. \qquad (5.12)$$

Thus, Eq. (5.9) has the general form

$$PV = Nm <u^2>/3. \qquad (5.13)$$

We have assumed no particular form for the distribution of particle velocities, except that they be equivalent in all three cartesian directions. Although we assumed that the particles travelled in straight lines without collisions, even that assumption can now be dropped without changing the form of Eq. (5.13).

Although there is no *explicit* temperature dependence to the right-hand side of Eq. (5.13), there is *implicit* temperature dependence, since the mean speed of the particles should increase with temperature. The dependence of $<u_x^2>$ on temperature at equilibrium can be obtained using the Boltzmann weight from Chap. 4. Since the system is an ensemble of point particles in a box of fixed geometry, the energy of a given particle is simply its kinetic energy

$$K = m(u_x^2 + u_y^2 + u_z^2) / 2. \qquad (5.14)$$

Thus, the mean square value of u_x^2 is, using the Boltzmann weight,

$$<u_x^2> = \frac{\int u_x^2 \exp\{-m(u_x^2 + u_y^2 + u_z^2) / (2k_BT)\} \, du_x \, du_y \, du_z}{\int \exp\{-m(u_x^2 + u_y^2 + u_z^2) / (2k_BT)\} \, du_x \, du_y \, du_z}$$

$$= \frac{\int u_x^2 \exp\{-mu_x^2 / (2k_BT)\} \, du_x}{\int \exp\{-mu_x^2 / (2k_BT)\} \, du_x}$$

$$= (2k_BT / m) \frac{\int z^2 \exp(-z^2) dz}{\int \exp(-z^2) dz}$$

According to Eq. (4.20), the ratio of the integrals is equal to 1/2. Thus,

$$<u_x^2> = k_BT / m,$$

or

$$m<u_x^2>/2 = k_BT / 2. \qquad (5.15)$$

Finally, Eq. (5.15) can be substituted into Eq. (5.9) to give

$$PV = Nk_BT. \qquad (5.16)$$

5.2 *NPT* and *NVT* ensembles

One can choose among many different ensembles for performing simulation studies. For example, in previous sections we presented algorithms for ensembles with fixed total energy *E* (MD) or fixed temperature *T* (MC). Only one member of the *E*, *T* pair can be held constant. In general, the ensembles are described by three fixed quantities:

•fixed particle number *N* *vs*. fixed chemical potential μ
•fixed energy *E* *vs.* fixed temperature *T*
•fixed volume *V* *vs.* fixed pressure *P*.

All of the systems that we investigate in this course have fixed particle number *N*. Further, all of the systems that we study with Monte Carlo methods have fixed temperature *T*. The two ensembles of interest to us are then *NVT* and *NPT*.

At fixed temperature, the energy of a system is not constant, as shown in Fig. 5.5. The Boltzmann factor exp(-β*E*) provides the correct weighting to generate an ensemble of configurations at constant temperature, refered to as an *isothermal* ensemble. Similarly, at fixed pressure, the volume of a system is not constant, as illustrated in Fig. 5.6. Depending on the system of interest, it may be more useful to work at fixed volume (called the *NVT*-ensemble if *N*, *V*, and *T* are all held constant) or at fixed pressure (called the *isobaric isothermal* ensemble, or *NPT*-ensemble if *N*, *P*, and *T* are all held constant).

The algorithm for the *NVT* ensemble requires nothing more than the Boltzmann weight for energy, since the volume and particle number are fixed at some user-defined values. Of course, a means must be developed for determining the pressure from the configurations. The *NPT* ensemble, on the other hand, has a fluctuating volume that must be sampled correctly. However, the expectations of *V* or V^2 are trivial to obtain from the *NPT* ensemble.

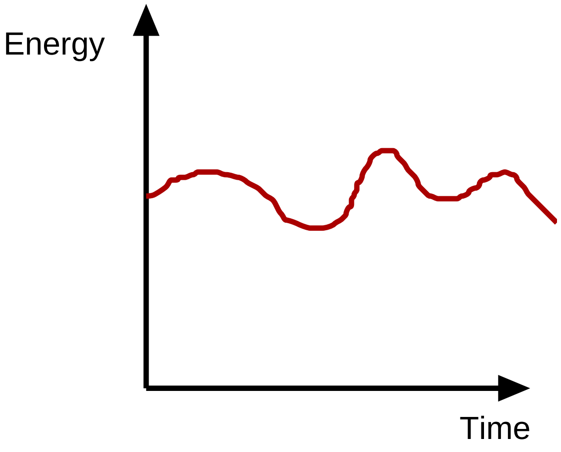


Fig. 5.5. The energy is not constant in a system at fixed temperature.

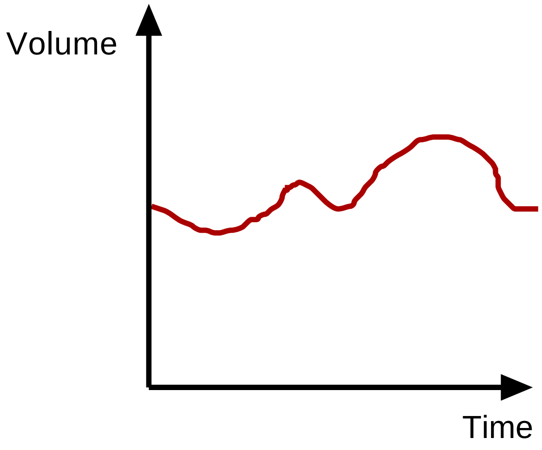


Fig. 5.6. The volume is not constant in a system at fixed pressure.

In the *NPT* ensemble, the Boltzmann weight must be generalized to include the work and change in entropy associated with a change in volume. Given the non-specific prerequisites for this course, we will not immediately invoke the Gibbs free energy as the relevant measure of energy. Rather, we reason our way through the behavior of the system to obtain the generalized algorithm.

Pressure term

When the system volume changes at constant pressure, work is done by/on the system. Consider a sample of gas held at constant temperature and pressure in a sealed cylinder. If the volume of the gas increases, then work is done on the piston, since the force applied to the piston has moved it through a distance. The situation is illustrated in Fig. 5.7. The force on the face of the piston is PA, where A is the area of the piston. This force acts through a distance D, resulting in a work of

$$\begin{aligned}[\mathit{work}] &= [\mathit{force}] \times [\mathit{distance}] \\ &= PA \bullet D \\ &= P\,\Delta V, \end{aligned} \qquad (5.17)$$

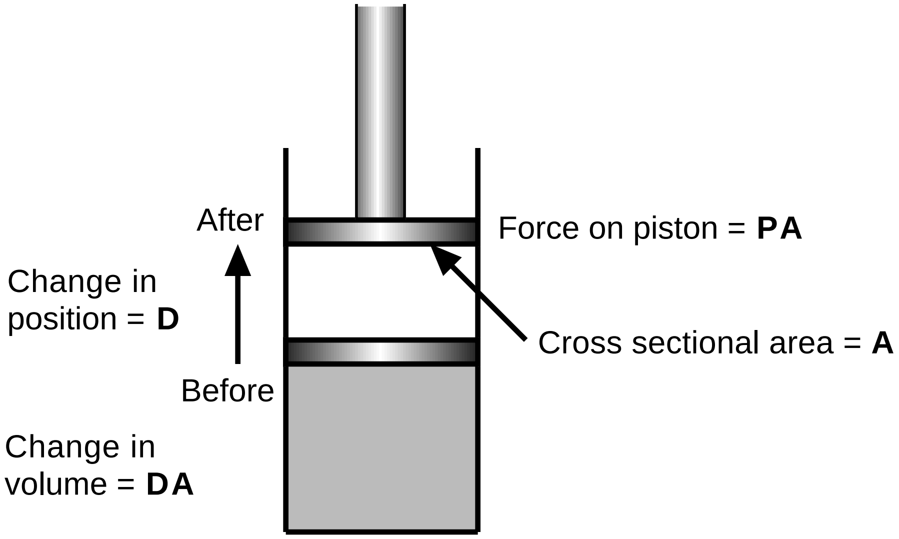


Fig. 5.7. Work associated with the change in volume changes the (free) energy of the system at constant pressure.

where ΔV is the change in volume. Thus, the total energy of the system is not just the interaction energy E between particles, but also includes $P \Delta V$, the work done by the gas. The quantity $E + PV$ represents *part of* what is called the free energy of the system. But clearly $E + PV$ cannot be the whole story, or else any small pressure applied to a system of non-interacting particles would drive the system to zero volume, which is the minimum value of $E + PV$ for $P > 0$ and $E = 0$.

Entropy term

The reason why a gas of non-interacting particles does not collapse under pressure is because of its entropy S

$$S = k_B \ln\Omega, \tag{5.18}$$

where k_B is the inevitable Boltzmann's constant and Ω is the number of configurations available to the system. As the volume of a gas decreases, so does the number of positions that a particle can occupy in that volume. Hence, if the number of configurations that a particle can assume decreases, then so too must S according to Eq. (5.18). The entropic contribution enters into the total free energy, G, as

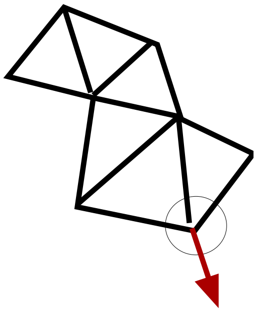
$$G = E + PV - TS. \tag{5.19}$$

Hence, a *decrease* in the entropy results in an *increase* in the free energy. While small volumes may be favored by the PV term in the free energy, they are opposed by the entropic term TS which favors large S.

How do we evaluate the free energy in an algorithm? One can consider many situations, of which two are:

Algorithm: single particle moves

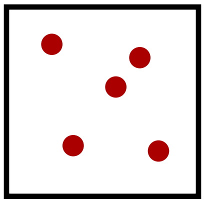
Suppose that one has an enclosed surface (*i.e.*, a bag), subject to pressure:



First, discretize the surface of the bag by creating a connected surface of plaquettes (*e.g.*, triangles). In turn, move each vertex that defines the plaquettes, and at each move of a single vertex, evaluate $\Delta(E + PV)$.

Algorithm: system rescaling

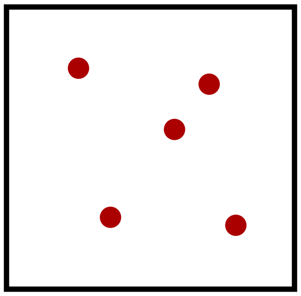
This method, developed by Wood (1968), is very useful for systems with periodic boundary conditions (see Chap. 6 and also Allen and Tildesley, 1987). Consider a system of particles placed in a box:



We denote the positions by x and the length scale of the box by L. If the positions of all of the particles and the boundaries of the box are rescaled *simultaneously* to new values

$$x \rightarrow Rx \qquad (5.20)$$
$$L \rightarrow RL$$

where R represents a common scale factor, then there is a change in volume ΔV and a change in entropy ΔS.



The change in volume and its contribution to ΔG through $P\Delta V$ is obvious. The change in the entropy is more subtle, and is best obtained through partition functions, which are not covered in the prerequisites for this course. The following rudimentary derivation will have to suffice.

The number of configurations available to a single particle is proportional to the volume occupied by the particle: the larger the volume, the larger the number of positions that the particle can occupy. For particle #1, let's write the number of configurations as

$$\Omega_1 = CV, \qquad (5.21)$$

where C is a proportionality constant. Eq. (5.21) applies to each particle in the system on an individual level. We now introduce a second particle into the system, and count the available configurations. The number of configurations in the *system* of particles #1 and #2, is proportional to the product of Ω_1 and Ω_2: that is, for each configuration of particle #1 there are Ω_2 possible configurations of particle #2, and hence there are $\Omega_1 \bullet \Omega_2$ configurations in total for the two particles. Repeating this argument, the total number of configurations for the entire system of N particles is then

$$\Omega_{tot} = \Omega_1 \bullet \Omega_2 \bullet \Omega_3 \bullet \ldots \bullet \Omega_N$$

$$V \bullet V \bullet V \ldots \bullet V = V^N. \qquad (5.22)$$

Since $S = k_B \ln\Omega$, then

$$\Delta S = k_B \ln V_{new}^N - k_B \ln V_{old}^N = k_B N (\ln V_{new} - \ln V_{old}).$$

The constant C has disappeared from ΔS because of the logarithms. Hence

$$T\Delta S = k_B TN \ln(V_{new} / V_{old}) \quad (5.23a)$$

$$\beta T\Delta S = N \ln(V_{new} / V_{old}). \quad (5.23b)$$

The procedure for the rescaling algorithm is then the following:

1. Make trial moves on the particle positions as usual; evaluate $\beta\Delta E$ for each move; accept or reject the move according to $\exp(-\beta\Delta E)$.

2. Make a trial rescale of the particle positions and box size; evaluate $\beta\Delta E$ for the system associated with the rescaling, $\beta T\Delta S$ from Eq. (5.23b) and $\beta P\Delta V$; then accept or reject the rescaling according to $\exp(-\beta\Delta E + \beta T\Delta S - \beta P\Delta V)$.

3. Note that each Cartesian direction should be scaled by a different factor.

The interested reader may wish to derive the ideal gas equation by minimizing the free energy $E + PV - Tk_B \ln\Omega$ with respect to volume using Eq. (5.22) for Ω_{tot}.

References

M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids* (Oxford, 1987).

W. Kauzmann, 1966. *Kinetic Theory of Gases* (Benjamin, New York) Chaps. 1 and 2.

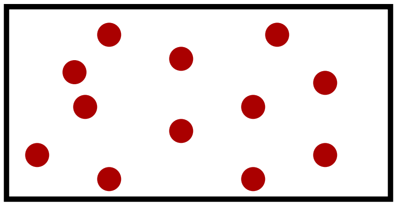
W. W. Wood, *J. Chem. Phys.* 48: 415-434 (1968).

5.3 Project 5 - Ideal gas at constant pressure

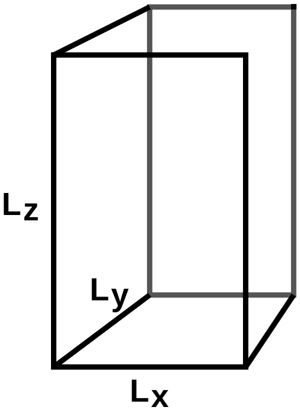
A system of non-interacting particles in a box has a simple computational description. In fact, it is not even necessary to include particles in the simulation in order to obtain the equation of state (*volume as a function of pressure*) of the system: all that is needed is the box rescaling algorithm. However, to make life easier for writing Project 6, point-like particles are included in Project 5.

Physical system

A system of point-like, non-interacting particles are placed in a rectangular prism (opposite faces are identical rectangles) in three-dimensional space. The particles are allowed to move within the prism



The system is held at fixed pressure, not fixed volume, so the box sides fluctuate in length.



Simulation parameters

A rectangular prism has three sides of inequivalent length, which we define as L_x, L_y and L_z. In this project, no length scale is provided by the particles, since they are point-like. Similarly, no energy scale is provided by the interparticle potential energy, since there isn't one. But we know from the ideal gas law that

$$PV = Nk_BT, \tag{5.24}$$

so that

$$[density] = N / V = P / k_BT = \beta P. \tag{5.25}$$

In other words, the length scale for the volume is provided by $(\beta P)^{-1/3}$.

Let us belabor the issue of units, since it is a source of some confusion for those new to computer simulations. Perhaps because a computer deals with numbers, it is tempting, but wrong, to assume that the computer knows what units are being used in a code. One might say: I'll put the temperature equal to 6, the pressure equal to 2, and measure the volume of the system. Of course the code will generate a number, but with what units? For the ideal gas problem, we see that the only combination of physical observables that generates a length unit is $(\beta P)^{-1/3}$. Thus, in the ideal gas problem, the computer does not use MKSA or cgs or imperial length units, but rather $(\beta P)^{-1/3}$. If there were a hard core interaction between the particles, the situation would be different, and the hard core radius would provide a length unit.

The physical behavior of the point-particle system does not depend upon the numerical value of βP. All that one does in changing the value of βP, is change the units. For a fixed N, your code need be run at only one value of βP. But just to make sure it's working properly, run it at several values and confirm that the density is always equal to βP.

Code

1. Choose a value of N equal to 216.

2. Choose three values of βP within the range 1 to 10, even though you know that all values are really the same value.

3. Set up the rectangular prism with sides L_x, L_y and L_z. For computational convenience, place the center of the prism at the origin.

4. Make trial moves on the particle positions; do not accept moves in which a particle passes outside of the prism. Neglect particle interactions. The P-V relation doesn't depend upon the particles being present in this case, so you can turn off the particle

movement part of your code to speed things up. But getting the particle movement section of your code working now will shorten the time needed to write the code for project 6.

5. Rescale the box lengths L_x, L_y and L_z independently. On each trial move for the box lengths, the volume changes by an amount ΔV. Accept the move according to the Boltzmann weight associated with $\beta P \Delta V$ and the entropic term, Eq. (5.23b).

6. Rescale the box for every sweep over the particle positions. Perform N sweeps between each configuration that you keep for data analysis. Use at least 300 configurations to construct the ensemble averages.

Analysis

1. Allow the system to relax before taking data, then calculate the ensemble averages $<V>$ and $<V^2>$.

2. Find the density, and compare it with βP.

3. The volume compression modulus at constant temperature is

$$K_V^{-1} = - (\partial V / \partial P) / V. \qquad (5.26)$$

That is, the more rapidly V changes with P, the more "compressible" the system is and the smaller K_V is. For an ideal gas, clearly

$$\beta K_V = \beta P. \qquad (5.27)$$

Verify this analytically. Compare it with the computational determination of K_V from the slope of a ln$V$ *vs.* P plot:

$$K_V^{-1} = - \partial \ln V / \partial P. \qquad (5.28)$$

and the fluctuation-dissipation theorem

$$(\beta K_V)^{-1} = [<V^2> - <V>^2] / <V>. \qquad (5.29)$$

Report

Your report should incude the following items:

- a statement of the ideal gas equation and its compression modulus
- a (page or more) description of the *NPT* ensemble and the basis of the algorithm that you use for it
- a written outline of your code
- your data analysis
- an estimate of the uncertainties in your results (*e.g.*, break up your data set into two parts and see how the results change); estimate the error in K_V from Eq. (5.27).
- a copy of your code

Demonstration code

The demonstration code for this project is a two-dimensional gas. This just means that the pressure is an energy per unit area (Π), rather than an energy per unit volume (P). A system of point particles in two dimensions obeys the same form of ideal gas law as particles in three dimensions,

$$\Pi A = N / k_B T \qquad \text{or} \qquad \beta \Pi A = N \tag{5.30}$$

where Π is the surface pressure, and A is the area.

The demonstration code displays the length scale

$$[length] = (N / \beta\Pi)^{1/2}, \tag{5.31}$$

indicated by the red bar near the top of the window. This length scale is fixed at a certain number of pixels in the demo, and does not change with N. If you try running the code at different N, you will see that, although both the size and the shape of the box vary in the ensemble, the ensemble averages show no particular N - dependence.

Particles number 1 and N are given special colors in the demo code, so that their diffusion rate through the system can be seen visually.