APPENDIX A

STATISTICAL MECHANICS OF THE MONATOMIC IDEAL GAS

NOTE: this appendix is taken unmodified from some older lecture notes I wrote for a different class. The notation may be a little different.

Consider a container of volume V which contains N atoms, which we will assume are "structureless" – that is, they contain no internal energy modes (vibration, rotation, or electronic excitation). Let us also assume that the potential energy due to interatomic forces is negligible compared to the kinetic energy of the atoms. These assumptions define the "monatomic ideal gas."

For simplicity, let the container be a cube of side length L, such that $V = L^3$. (The results we obtain will be independent of the assumed container geometry.)

The microstate of the system is specified by the positions and momenta of all atoms. If there are N atoms, then 3N coordinates (3 for each atom) must be specified, and 3N momenta, for a total of 6N degrees of freedom. The microstate of the gas is then fully specified by the 6N numbers $\{x_1, \ldots, x_{3N}, p_1, \ldots, p_{3N}\}$. We may represent the microstate geometrically as a point in a 6N-dimensional space, where the space is spanned by 3N orthogonal spatial coordinate axes x_i and 3N orthogonal momentum axes p_i . We call this 6N-dimensional space "phase space."

It is also useful to consider 2 subspaces of phase space. We will define "coordinate space" to be that space spanned by the 3N coordinate axes, and "momentum space" to be that space spanned by the 3N momentum axes.

In order keep the number of microstates finite, we divide up each coordinate axis into segments of length Δx , and each momentum axis into segments of length Δp . We can then construct a grid, or lattice, which divides phase space into small hypercubes of volume $\Delta W = (\Delta x \Delta p)^{3N}$. We will take all points within a given cube to correspond to one microstate. The number of microstates in a region of phase space with volume W is then simply

$$\Omega = W/\Delta W. \tag{A.1}$$

Therefore, rather than trying to count microstates directly (counting becomes

difficult when the numbers get very large!), we can find the volume of the region of phase space which satisfies some criteria, and then get Ω from Eq. (A.1).

Of course, the number of microstates will depend upon our choices of Δx and Δp . We'll see later that the only implication of this is that the entropy can only be determined to within some additive constant. But this was also true in thermodynamics – for the ideal gas, we integrated the Gibbs equation to get the entropy, which introduced an arbitrary integration constant s_0 . Recall that we introduced a postulate (the 3rd law of thermodynamics) which fixed the entropy at one temperature (T = 0) and removed the ambiguity. In statistical mechanics, no such postulate is needed – the problem is taken care of by a proper quantum-mechanical treatment of the problem.

Our objective is to count how many microstates (i.e., cubes in phase space) there are which are consistent with our macroscopic knowledge of the state of the system, for example the volume V and the internal energy U. Some of the microstates are consistent with our macroscopic specifications, but many are not (for example, those for which one or more atom lies outside the container).

There are two constraints on the system, which determine the region of phase space we are interested in. The first is that all atoms are located within the container:

$$0 < x_i < L, \quad i = 1, \dots, 3N.$$
 (A.2)

The second constraint is the specification of the total internal energy of the system. The total kinetic energy E of the gas is given by

$$E = \sum_{i=1}^{3N} \frac{1}{2}mv_i^2 = \sum_{i=1}^{3N} \frac{p_i^2}{2m},$$
(A.3)

where m is the mass of one atom. This equation shows that microstates with a given kinetic energy all lie on a sphere of radius $R = \sqrt{2mE}$ in momentum space.

Since we are assuming that translational kinetic energy is the only contribution to the total internal energy U of the gas (no potential energy or internal energy modes), the specification of the energy of the system is that E = U. Actually, we will assume that there is a very small, but non-zero, uncertainty in the energy. That is, the constraint on energy is

$$U - \delta U < E < U, \tag{A.4}$$

where $\delta U \ll U$. We'll assume that Δx and Δp are chosen to be small enough that there are very many microstates with kinetic energy in this range.

Let us now find the volume W of the region of phase space satisfying eqs. (A.2) and (A.4). This volume may be expressed as a multidimensional integral:

$$W = \int_0^L dx_1 \int_0^L dx_2 \dots \int_0^L dx_{3N} W_{shell}$$
(A.5)

where W_{shell} is the volume of the spherical shell in momentum space defined by Eq. (A.4). Since the kinetic energy does not depend on the spatial coordinates (it only depends on the momentum coordinates), the integral in momentum space defining W_{shell} is independent of the coordinate values, and we may reverse the order of integration and do the coordinate integrals first. Each of these contributes a factor L, and therefore

$$W = L^{3N} W_{shell} = V^N W_{shell} \tag{A.6}$$

where $V = L^3$ is the container volume (in real 3D space).

To determine W_{shell} we may use a result from mathematics for the volume $W_n(R)$ of a sphere of radius R is n-dimensional space. It may be shown that

$$W_n(R) = \frac{\left(\pi R^2\right)^{n/2}}{\left(\frac{n}{2}\right)!}.$$
 (A.7)

Note that if n is odd we can evaluate (n/2)! in terms of the Gamma function: $z! = \Gamma(z+1)$ for any z. The Gamma function is defined by

$$\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt \tag{A.8}$$

and satisfies the recurrence formula $\Gamma(z+1) = z\Gamma(z)$. Therefore, $\Gamma(n/2)$ may be determined from this recurrence formula, given that $\Gamma(3/2) = \sqrt{\pi}/2$.

For the familiar cases of n = 2 and n = 3, Eq. (A.7) reduces to $W_2 = \pi R^2$ and $W_3 = (4/3)\pi R^3$, respectively, as expected.

 W_{shell} may be determined by the difference of two sphere volumes:

$$W_{shell} = W_{3N}(\sqrt{2mU}) - W_{3N}\left(\sqrt{2m(U-\delta U)}\right)$$
(A.9)

Or, using Eq. (A.7),

$$W_{shell} = W_{3N}(\sqrt{2mU}) \left[1 + \left(1 - \frac{\delta U}{U}\right)^{3N/2} \right].$$
(A.10)

Note that the term $(1 - \delta U/U)$ is very slightly less than one. Therefore, for any finite (but very small) δU , we have that

$$\lim_{N \to \infty} \left(1 - \frac{\delta U}{U} \right)^{3N/2} = 0 \tag{A.11}$$

and therefore

$$\lim_{N \to \infty} W_{shell} = W_{3N}(\sqrt{2mU}). \tag{A.12}$$

This seemingly-paradoxical result states that in the limit of large N, the shell volume equals the volume of the entire sphere! This is in fact the case: as the dimensionality of the space increases, the distribution of the volume of the sphere with radius becomes highly peaked near the surface of the sphere. For any small but finite shell width, if n is large enough then virtually all of the sphere volume is located within the shell.

This means that for large N, the number of microstates available to a gas which have kinetic energy very close to U is *overwhelmingly* larger than the number of microstates which have kinetic energy less than U. In the large Nlimit (which is what we are interested in), we have then that

$$\Omega = W_{3N}(\sqrt{2mU})/\Delta W \tag{A.13}$$

or

$$\Omega = \frac{(2\pi mU)^{3N/2}}{\Delta W\left(\frac{3N}{2}\right)!}.\tag{A.14}$$

Actually, there is one correction we need to make to Eq. (A.14). In counting microstates by integrating over phase space, we have implicitly assumed that the atoms are *distinguishable*. That is, suppose we interchange the position and momentum coordinates of particles 1 and 2. Then if the original microstate was

$$\{\underbrace{x_1, x_2, x_3}_{\text{atom 1}}, \underbrace{x_4, x_5, x_6}_{\text{atom 2}}, x_7, \dots, x_{3N}, \underbrace{p_1, p_2, p_3}_{\text{atom 1}}, \underbrace{p_4, p_5, p_6}_{\text{atom 2}}, p_7, \dots, p_{3N}\},\$$

the microstate with atoms 1 and 2 interchanged will be

$$\{\underbrace{x_4, x_5, x_6}_{\text{atom 2}}, \underbrace{x_1, x_2, x_3}_{\text{atom 3}}, x_7, \dots, x_{3N}, \underbrace{p_4, p_5, p_6}_{\text{atom 2}}, \underbrace{p_1, p_2, p_3}_{\text{atom 1}}, p_7, \dots, p_{3N}\}$$

The second microstate is different from the first unless atoms 1 and 2 happen to have the *same* position and momentum vectors, such that $x_1 = x_4$, etc. For a low-density gas, this is extremely unlikely, so in general exchanging atoms 1 and 2 produces a different microstate of the gas, which corresponds to a different point in phase space. Since this microstate satisfies the macroscopic constraints [eqs. Eq. (A.2) and Eq. (A.4)], both of the above microstates are in the accessible region of phase space, and therefore we have counted both of them in Ω .

This is correct if atoms 1 and 2 are distinguishable, so that exchanging them really does produce a new microstate of the gas. However, it turns out that atoms which are identical (i.e., the same isotope of the same element) are actually *indistinguishable* in nature. That is, exchanging them *does not* produce a new microstate of the system.

Since we have in effect treated the atoms as distinguishable when counting microstates, we have overcounted the number of microstates, and need to correct our expression for Ω . Let us assume that the gas density is low enough that we can neglect the possibility that any 2 atoms are at the same position (to within Δx) and have the same momentum (to within Δp). Then we simply need to divide Ω by the number of ways to permute the atom labels among the N atoms, which is N!. Therefore, the correct expression for Ω is

$$\Omega = \frac{(2\pi mU)^{3N/2}}{\Delta WN! \left(\frac{3N}{2}\right)!}.$$
(A.15)

Using Stirling's formula to approximate the factorial terms $(n! \approx n^n e^{-n})$, we have

$$\Omega = \left(\frac{eV}{N}\right)^N \left[\frac{4\pi emU}{3N}\right]^{3N/2} \frac{1}{(\Delta x \Delta p)^{3N}}$$
(A.16)

Let us take the product $\Delta x \Delta p$ to be some constant a. Then the entropy is

$$S = k \ln \Omega \tag{A.17}$$

$$= Nk \left[\ln \hat{v} + \frac{3}{2} \ln \left(\frac{4\pi m \hat{u}}{3a^2} \right) + \frac{5}{2} \right]$$
(A.18)

where $\hat{v} = V/N$ and $\hat{u} = U/N$. Since this expresses S as a function of U, V, and N, we have succeeded in deriving a fundamental relation for the ideal gas.

The only uncertainty remaining is the additive constant resulting from the unknown value of a. If we had analyzed this problem from the point of view of quantum mechanics (rather than classical mechanics), we would have found the same result for S as in Eq. (A.18), but with the constant a replaced by *Planck's constant* h, which is a fundamental constant, given by

$$h = 6.626 \times 10^{-34}$$
 J-s. (A.19)

With the substitution a = h, we then have

$$\hat{s} = k \left[\ln \hat{v} + \frac{3}{2} \ln \left(\frac{4\pi m \hat{u}}{3h^2} \right) + \frac{5}{2} \right].$$
 (A.20)

(Note that the units of \hat{s} are J/molecule/K. If we would rather work with moles, we only need replace k by \hat{R} .)

APPENDIX A. STATISTICAL MECHANICS OF THE MONATOMIC IDEAL GAS162

Evaluating the temperature from $1/T = (\partial \hat{s}/\partial \hat{u})_{\hat{v}}$ we find

$$\hat{u} = \frac{3}{2}kT.\tag{A.21}$$

Therefore, Eq. (A.20) may also be expressed as

$$\hat{s} = k \left[\ln \hat{v} + \frac{3}{2} \ln \left(\frac{2\pi m k T}{h^2} \right) + \frac{5}{2} \right].$$
 (A.22)