Probability, the Second Law of Thermodynamics and Entropy

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Introduction

In this section, we are going to combine mechanics and quantum mechanics with the basic ideas of probability that we have developed.

We will need to be able to specify the state of physical systems. we will be using the method of ensembles because we do not have enough information about the initial states of systems to use deterministic methods. Even if we had enough information to use deterministic methods, we would not have the computational power to exploit it. The essence of the ensemble method is to consider a large number of replicas of the system, and to imagine that the experiment is repeated in each replica. We get the probabilities of interest by finding the fraction of replicas in some particular state.

The Basic Postulate

The *a-priori* probabilities of each specific outcome in an experiment are equal. By a-priori, we mean based on notions as yet unspecified by observation.

Macrostates and Microstates

In thermal physics, particular outcomes are called *microstates*, the outcome is called a *macrostate*. Thus, we can rephrase our basic postulate as: each microstate of a system occurs with equal probability. The question we need to address is: If particles (atoms, molecules, etc.) obey specific microscopic laws with specified interparticle interaction — what are the observable properties of a system containing large numbers of these particles.

Systems allowed to evolve to a single macroscopic state. Macroscopic states are described by macroscopic variables such as p, V, and T. Microstates are specified by the location and momentum of individual particles. Different numbers of microstates correspond to macrostates. The number of microstates corresponding to a macrostate is called the *multiplicity* of the macrostate. In many books, this multiplicity is called *the number of ways*

Specification of a State

Any system of particles can be described by quantum mechanics. A system is described by a wavefunction $\psi(q_1, q_2, ..., q_n)$ of some set of coordinates. The number of coordinates is equal to the number of degrees of freedom of the system. A particular state is then specified by giving the value of some set of quantum numbers. Such a description is complete – if ψ is specified at time t, quantum mechanics allows the prediction of ψ at any other time. (Recall that the set of quantum numbers n, l, m_l , m_s specify the state of hydrogen.)

Ensembles

The idea underlying the statistical approach is that if we wait long enough the system will flow through (or will be arbitrarily close to) all microscopic states consistent with the constraints imposed on the system. There are two ways of performing averages: time averaging and ensemble averaging. The method of ensemble averages is usually easier to implement.

Consider again a pair of dice, to get a statistical description, we could throw the same pair of dice *N* times or we could through *N* pairs of dice once. In either case, as $N \to \infty$, $P(\text{pair of sixes}) = \frac{N(\text{pair of sixes})}{N_{total}}$. The

probability of an event determined in this manner depends on the nature of the ensemble. The ensemble method is based on the frequency definition of probability. Under this definition it makes no sense to speak of the probability that a single seed would yield red flowers. It is meaningful to ask the probability that the seed will yield red flowers if it is regarded as a member of a group of similar seeds derived from a specific set of plants. The probability will obviously be different if the seed is a member of a collection of seeds known to yield red flowers, than if it is from a collection of seeds that yields pink flowers.

This method of ensembles is not the only method of calculating macroscopic properties, it is the method that our author uses although he doesn't describe the details. As we shall see later the method of maximum entropy yields identical results without need of ensembles.

In thermal physics we will be interested in the number of *accessible microstates*. An ensemble is simply a (mental) collection of systems, each a replica on the thermodynamic (macroscopic) level. Any of the replicas can represent the system.

The method of ensemble averaging is based on the idea that the equivalence of time averaging and ensemble averaging. It sounds reasonable, proving the equivalence is not easy. Dynamical systems that obey this equivalence are said to be *ergodic*. Mathematicians have devoted much time to the ergodic hypothesis. For physicists, this is time wasted, it is wasted for two reasons, all many body systems encountered in nature have been ergodic, and finally we are often interested in non-equilibrium systems where properties change with time.

Ensembles in Thermal Systems

The approach is to consider a large number of replicas of our system – with each replica subjected to the appropriate physical constraints. The replicas will in general be in different physical states and will be characterized by different macroscopic parameters. (T, P, V or U, V, N etc.) We will want to know the probability of some value of the parameter, in other words what fraction of the replicas assumes some particular value.

We usually have some partial knowledge of the system. The system can only be in one of the states compatible with the available information. It is these states that we call the accessible states of the system. Thus the systems in our ensembles will be distributed over the accessible states. We will now develop our first method of determining the probability of finding a system in one of its accessible states. Our first approach (which you won't find in your book, thought the pieces are there) is called the *microcanonical ensemble*.

The Microcanonical Ensemble

The microcanonical ensemble represents isolated systems in equilibrium. An isolated system is a system that cannot exchange energy or particles with its surroundings. (That is, its total energy is conserved.)

When an isolated system is in equilibrium, the probability of finding the system in some state is independent of time. All macroscopic features of the system are also independent of time. Our fundamental requirement is the one that we have already stated: equal a-priori probabilities. An isolated system is equally likely to be in any of its accessible states. The corollary of this is: if an isolated system is not equally likely to be in any of its accessible states then it isn't in equilibrium. Equilibrium is a macroscopic concept.

Application to a Simple System

Consider *N* molecules of a one component system, the system is totally isolated. Thus *U*, *V*, and *N* are fixed. (*U*, *V*, *N*) will completely specify the macrostate of the system in equilibrium. When the system is not in equilibrium $\rho(\vec{r}, t)$, etc. need to be specified. let's say that in general, a macrostate can be specified by (*U*, *V*, *N*, α) where α denotes all additional variables. Then let $\Omega(U, V, N, \alpha)$ be the number of microstates specified by *V*, *N*, and α and with energy between *U* and $U + \delta U$. (Thus Ω is what we have called the multiplicity.) In this expression we need to use a range of energy because it is difficult to specify or measure the energy of a macroscopic system. (Looking ahead, quantum mechanics will not allow it $\delta U \delta t \geq \hbar$) If δU is chosen to be zero, Ω is a badly behaved function, its value is mostly zero, but at other times it jumps to the degeneracy to the level. Ω is insensitive to the size of δU , usually any choice of $\delta U \leq U$ works to make Ω a well behaved continuous function. While our author

calls Ω the multiplicity, I will often call it the *statistical weight* or the *thermo-dynamic probability* of the macrostate. An equilibrium state is characterized by $\Omega(U, V, N)$ since α is fixed for a particular equilibrium state.

Model System: Spin Magnets

Consider *N* separate and distinct sites on a line, at each site is a spin magnet that can point up or down. Up $+m \uparrow$

Down $-m \downarrow$

Recall for a dipole of moment \overrightarrow{m} in an external \overrightarrow{B} – field, the interaction energy of the dipole is $U = -\overrightarrow{m} \cdot \overrightarrow{B}$

Dipoles tend to orient in alignment with external fields. We're only allowing up or down. If the dipole is parallel to the field, U = -mB, if the dipole is antiparallel to the field U = mB. That is there are two possible states with an energy splitting of 2mB.

Consider *N* dipoles, *n* parallel to the field. Then,

$$U = \sum_{i} U_{i} = n(-mB) + (N-n)mB = (N-2n)mB$$

Thus, in this case we see that U = U(n) here since $U(\overrightarrow{B}, V, N, n)$. In this case we are keeping \overrightarrow{B} , N constant, volume has no effect, so $n \equiv \alpha$. n is completely determined by U (and vice-versa.)

If N = 9, n = 2, both arrangements below are possible.

 $\begin{array}{ccc} \uparrow \downarrow \downarrow & \downarrow \downarrow \downarrow \\ \uparrow \downarrow \downarrow & \uparrow \uparrow \downarrow \\ \downarrow \downarrow \downarrow & \downarrow \downarrow \downarrow \\ \end{array}$

These states are distinct, but cannot be distinguished macroscopically. The total number of microstates is 2^N , two possible orientations at N sites. The number of microstates with energy U(n) is given by C(N, n), n is the number of spin-up sites. Thus in this case

$$\Omega(n) = C(N,m) = \frac{N!}{(N-n)!n!}$$

This is the number of states with *n* spin-ups. By choosing $\delta U < 2mB$ the interval contains only one energy level, and $\Omega(n)$ is the statistical weight, degeneracy, or multiplicity.

If n = N, all spins are up, M = mn, U(n) = -mBN, $\Omega = 1$, this is the ground state.

If n = N/2, M = 0, U = 0, Ω is a maximum, and the system behaves as if there is zero field. (With a zero field the dipoles would be randomly oriented yielding a zero net magnetization.

The most probable state is the most disordered, that is the one with the greatest multiplicity. In fact we can state a version of the second law of thermodynamics based on it.

The Second Law of Thermodynamics

If a system with many molecules is permitted to change, then — with overwhelming probability — the system will evolve to the macrostate of largest multiplicity and will subsequently remain in the macrostate.

In the preceding definition we are assuming that the system evolves in isolation, that is no energy transfers are made to or from the system.

The Equilibrium of an Isolated System and the Microcanonical Ensemble – Summary

Equilibrium states are fully specified by U, V, and, N – for non-equilibrium states we must specify additional variables, α . The basic idea of statistical mechanics is that during a measurement every microscopic state occurs – and the observed properties are averages over all microscopic states, to quantify this, me make the assumption of equal a-priori probabilities.

For an isolated system, with fixed total energy U, and fixed size, all microscopic states are equally likely at thermodynamics equilibrium. This allows us to write the probability of macrostates and microstates occurring.

$$P(\text{Macrostate}) = \frac{\text{Number of microstates corresponding to macrostate}}{\text{Total number of microstates}}$$
$$P(\text{Microstate}) = \frac{1}{Totalnumberof microstates} = \frac{1}{\Omega}$$

To this we add the equilibrium postulate: The equilibrium state corresponds to the value of α for which $\Omega(U, V, N, \alpha)$ attains its maximum value with (U, V, N) fixed. In other words, the equilibrium state is the state of maximum probability.

The microcanonical ensemble is an ensemble where all replicas have (almost) the same energy. The replicas do not exchange energy with each other, they can be thought of as separated by rigid, adiabatic, impermeable walls. *U*, *V*, and *N* are the natural variables of the microcanonical ensemble.

Entropy

The equilibrium state for a system corresponds to the value of α for which $\Omega(U, V, N, \alpha)$ attains its maximum value with U, V, N fixed. The equilibrium state is the state of maximum probability.

Instead of using Ω , we will now introduce the entropy *S* as a measure of the disorder of the system. The entropy of the system is given by

$$S = k \ln \Omega(U, V, N, \alpha).$$

During real (as distinct from idealized reversible processes) the entropy of an isolated system always increases. In the state of equilibrium, entropy attains its maximum value.

This is the Clausius statement of the second law of thermodynamics. At this time, I am going to use the maximization of Ω to derive the concepts of temperature, pressure, and chemical potential.

Thermal Equilibrium

U_1	U_2
V_1	V_2
N_1	N_2

Consider a system, that is isolated, and is divided into two parts by a wall s.t.

$$U_1 + U_2 = U$$
$$V_1 + V_2 = V$$

$$N_1 + N_2 = N$$

These equations are called the equations of constraint. We'll further assume that the sub-systems are not in equilibrium and that the wall separating them is rigid, impermeable and diathermal. That is, energy can pass through the wall, particles cannot, and the wall is fixed in place. For each division of U, V, and N between the sub-systems specified by the equations above, we can write

$$\Omega(U, V, N, \underbrace{U_1, V_1, N_1}_{\alpha}) = \Omega_1(U_1, V_1, N_1)\Omega_2(U_2, V_2, N_2)$$

where Ω_1 is the multiplicity of sub-system 1 in the macrostate specified by (U_1, V_1, N_1) , Ω_2 is the multiplicity of sub-system 1 in the macrostate specified by (U_2, V_2, N_2) , and Ω is the multiplicity of the composite system with this division of energy, volume, and particle number. Taking the product of Ω_1 and Ω_2 is justifed by the fundamental principle of counting. The contstraint equations limit U_1 , U_2 etc., we're choosing U_1 , V_1 , and N_1 as independent - in other words, they correspond to the α that we used earlier. But $S = k \ln \Omega$, so

$$S(U, V, N, U_1, V_1, N_1) = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2).$$

Now let the sub-systems come to equilibrium, at equilibrium, entropy is maximized, therefore

dS = 0,

and

$$0 = \mathrm{d}S_1 + \mathrm{d}S_2$$

we can rewrite this as

$$0 = \frac{\partial S_1}{\partial U_1} dU_1 + \frac{\partial S_1}{\partial V_1} dV_1 + \frac{\partial S_1}{\partial N_1} dN_1 + \frac{\partial S_2}{\partial U_2} dU_2 + \frac{\partial S_2}{\partial U_2} dU_2 + \frac{\partial S_2}{\partial V_2} dV_2 + \frac{\partial S_2}{\partial N_2} dN_2 + \frac{\partial S_2}{\partial V_2} dV_2 + \frac{\partial S_2}{\partial V_2}$$

Now using our equations of constraint $dV_1 = dV_2 = dN_1 = dN_2$ and dU = 0, so $dU_1 = -dU_2$, we can simplify this expression to

$$0 = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1, N_1} dU_1 + \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2, N_2} dU_2$$

and using $dU_1 = -dU_2$, this becomes

$$\left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} = \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2}$$

This is the condition for thermal equilibrium (i.e. no heat transfer). We already know a condition for the equilibrium of two systems in thermal contact:

$$T_1 = T_2$$
.

We use this to define absolute temperature,

$$\frac{1}{T_i} = \left(\frac{\partial S_i}{\partial U_i}\right)_{V_i, N_i}.$$

The choice is not unique, but it this choice makes the absolute temperature scale identical to the ideal gas temperature scale.

Thermal and Mechanical Equilibrium

We will now consider two subsystems not in equilibrium separated by moveable, diathermal, impermeable walls. In such a system, energy and volume will flow until equilibrium is achieved.

U_1	U_2
V_1	V_2
N_1	N_2

The equations of constraint are

$$U_1 + U_2 = U,$$

 $V_1 + V_2 = V,$
 $N_1 + N_2 = N.$

These yield $dU_1 = -dU_2$, $dV_1 = -dV_2$, and $dN_1 = dN_2 = 0$. Again we use entropy maximization at equilibrium, dS = 0 yielding

$$0 = \left(\frac{\partial S_1}{\partial U_1}\right) dU_1 + \left(\frac{\partial S_1}{\partial V_1}\right) dV_1 + \left(\frac{\partial S_2}{\partial U_2}\right) dU_2 + \left(\frac{\partial S_2}{\partial V_2}\right) dV_2$$

At equilibrium, we would expect temperature and pressure to be equal in this case.

$$0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left[\left(\frac{\partial S_1}{\partial V_1}\right) - \left(\frac{\partial S_2}{\partial V_2}\right)\right] dV_1$$

Thus at equilibrium, $T_1 = T_2$, and $\left(\frac{\partial S_1}{\partial V_1}\right)_{U_1,N_1} = \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2,N_2}$. Now the partial derivatives in this case must describe the equality of pressure. We define pressure for each subsystem as

$$\frac{p_i}{T_i} = \left(\frac{\partial S_i}{\partial V_i}\right)_{U_i, N_i}$$

This definition reduces to pV = NkT when applied to an ideal gas.

Thermal and Diffusive Equilibrium

We can continue this analysis in a similar vein by considering the wall to be diathermal, rigid and permeable. The analysis leads to an expression for the equilibrium of matter flow. This leads to the definition of chemical potential μ_i of the ith chemical species through

$$\left(\frac{\partial S_i}{\partial N_i}\right) = -\frac{\mu_i}{T_i}.$$

Chemical potential controls matter equilibrium.

The Fundamental Thermodynamic Relation

S = S(U, V, N) contains complete thermodynamic information. We could equivalently write U = U(S, V, N), U is minimized at equilibrium, if we start from U, and consider the same systems and walls we get the following definitions:

$$T_{i} = \left(\frac{\partial U_{i}}{\partial S_{i}}\right)_{V_{i},N_{i}}$$
$$p_{i} = -\left(\frac{\partial U_{i}}{\partial V_{i}}\right)_{U_{i},N_{i}}$$

$$\mu_i = \left(\frac{\partial U_i}{\partial N_i}\right)_{S_i, V_i}$$

Thus if U = U(S, V, N), then

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

and

$$dU = TdS - pdV + \mu dN$$

This is called the fundamental thermodynamic relation or the fundamental thermodynamic identity. Note: T = T(S, V, N), p = p(U, V, N), and $\mu = \mu(N, S, V)$. The fundamental thermodynamic relation can be used to recover the definitions of T, p, μ . We can also solve the relationship for entropy

$$dS = rac{dU}{T} + rac{p}{T}dV - rac{\mu}{T}$$

this allows us to recover the equivalent definitions in the entropy representation.

In general there is more than a single chemical species in out thermal system. The general form of the fundamental thermodynamic relation is:

$$dU = TdS - pdV + \sum_{j} \mu^{j} dN^{j}$$

where μ^{j} is the chemical potential of the j^{th} chemical species. In this expression $\mu^{j} = (\partial U^{j} / \partial N^{j})_{S,V,\mu^{i}}$, and the equilibrium condition is $\mu_{1}^{j} = \mu_{2}^{j}$. μ is a potential for matter flow. At this point, we are in a good position to explore entropy and equilibrium.

Entropy and Equilibrium

S = S(U, V, N) is a fundamental relation in that it contains complete thermodynamic information about the system. At equilibrium *S* is a maximum. The properties of *S* are that $S = \Sigma S_i$ is a continuous, differentiable, monotonic function of *U* that is homogeneous of degree one in *U*, *V*, and *N*. For now we will also assert that at T = 0, S = 0. This latter statement assumes the strong form of the third law of thermodynamics. We will explore the strong and weak forms of the third law of thermodynamics at a later date.

Equilibrium in the Entropy Representation

Consider again two subsystems separated by rigid, impermeable, diathermal walls.

$$S = S_1 + S_2$$
$$dS = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1, N_1} dU_1 + \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2, N_2} dU_2$$
$$dS = \frac{1}{T_1} dU_1 + \frac{1}{T_2} dU_2$$

Now, at equilibrium dU = 0 and dS = 0, and $T_1 = T_2$. Close to equilibrium we can write

$$dS \approx \underbrace{\left(rac{1}{T_1} - rac{1}{T_2}
ight)}_{(-)ve} dU_1.$$

Assuming $T_1 > T_2$ by a small amount we can see that since dS must be positive, dU_1 must be negative. In other words if $T_1 > T_2$, U_1 will decrease, U_2 will increase as energy flows from subsystem one to subsystem two. Thus our new formulation agrees with our intuitive understanding of the situation.

Now if we change the wall to having a moveable, impermeable diathermal wall, we have

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1.$$

Now, *U* and *V* are independent, so the coefficients must separately equal 0. Thus, as we have noted, at equilibrium $T_1 = T_2$ and $p_1 = p_2$. Infinitesimally close to 0, we can write

$$\underbrace{\frac{dS}{(+)\mathbf{v}\mathbf{e}}}_{(+)\mathbf{v}\mathbf{e}} \approx \underbrace{\frac{p_1 - p_2}{T}}_{(+)\mathbf{v}\mathbf{e}} \underbrace{\frac{dV_1}{(+)\mathbf{v}\mathbf{e}}}_{(+)\mathbf{v}\mathbf{e}}$$

where I have assumed that $p_1 > p_2$. This again agrees with our intuitive understanding of the situation — the region at higher pressure will grow. We could similarly analyze the situation of a rigid, permeable, diathermal

wall. Infinitesimally close to equilibrium we would find that

$$\underbrace{\frac{dS}{(+)\mathrm{ve}}}_{(+)\mathrm{ve}} \approx \underbrace{\frac{\mu_2 - \mu_1}{T}}_{(-)\mathrm{ve} \text{ if } \mu_1 > \mu_2} \underbrace{\frac{dV_1}{(-)\mathrm{ve}}}_{(-)\mathrm{ve}}$$

matter flows from high μ to low μ .

Entropy and the Energy Transfer by Heating

Entropy increases can also be related to the energy transfer by heating. We could for instance (as our author does, and you should read) examine entropy changes as energy is transferred to an ideal gas by heating. Other examples are to be found in you university physics text. In general, we find that

$$\triangle S_{\text{system}} \geq \frac{\text{Energy transfer by heating}}{T}.$$

The equality holds for a *quasistatic* process — in other words for a slow process where the system remains arbitrarily close to equilibrium. For fast processes, the entropy change is greater. We have to be careful to use the appropriate temperature, for slow processes, there is no problem, the system and the heating source will have the same temperature. For fast processes the system is far from equilibrium, the system temperature could change drastically. For fast processes, the appropriate temperature of the heating source.

Before looking at some examples, lets remind ourselves of a few basic facts. Recall the first law, we have written it in the form $\triangle U = Q + W$, where W, and Q are not functions of state. We can write this for infinitesimals as dU = dQ + dW where the d denotes an inexact differential. We will frequently integrate such forms, but should remember that they are not true differentials. If you look at the examples, you will see that we are integrating well defined functions or the expressions will contain an integrating factor. As an example $\frac{1}{T}$ is an integrating factor for dQ. In other words dS = dQ/T is a perfect differential if dQ is added reversibly. We have also defined W to be positive when work is done on the system.

Examples

It's now time to use some of our tools to examine some specific situations.

Melting Ice

If ice melts slowly at 0°C, by how much does its multiplicity change?

$$\triangle S = S_{liquid} - S_{ice} = k \ln \Omega_{liquid} - k \ln \Omega_{ice} = k \ln \frac{\Omega_{liquid}}{\Omega_{ice}}$$

Now, examining this, we can see that we will need to calculate $\triangle S$. If we consider the ice to melt slowly (and there is no reason not to make this assumption, the number of accessible microstates is not going to depend on the rate of melting!) So we can write

$$\triangle S = \frac{Q}{T}$$

Since my calculators were all at the office, we'll use our authors numbers, we take 18 g of ice, at 273 K, with $L_{f_{ice}} = 3.34 \times 10^5$ J/Kg, we get

$$\Delta S = \frac{(3.34 \times 10^5 \text{ J/Kg})(18 \times ^{-3} \text{ Kg})}{273 \text{ K}} = 22 \text{ J/K}.$$

We can now combine our calculations to yield

$$\ln \frac{\Omega_{liquid}}{\Omega_{ice}} = \frac{1}{k} \frac{Q}{T} = \frac{22 \text{ J/K}}{1.4 \times 10^{-23} \text{ J/K}} = 1.6 \times 10^{24}$$

then

$$rac{\Omega_{liquid}}{\Omega_{ice}} = e^{1.6 imes 10^{24}} = 10^{6.9 imes 10^{23}}$$

There are many more microstates available to the liquid than there were to the solid.

Object thrown into the sea

An object of mass m, mass specific heat c_p and temperature T_1 is thrown into the sea which has temperature T_0 . Calculate the total change in entropy. Assume the process is slow.

$$\triangle S_{total} = \triangle S_{mass} + \triangle S_{sea}$$

$$\Delta S_{total} = \int_{\text{mass}} \frac{dQ}{T} + \int_{\text{sea}} \frac{dQ}{T}$$
$$\Delta S_{total} = \int_{T_1}^{T_0} \frac{mcpdT}{T} + \int \frac{dQ}{T_0}$$
$$\Delta S_{total} = mc_p \ln\left(\frac{T_0}{T_1}\right) + \frac{Q}{T_0}$$
heat lost by mass = heat gained by sea
$$\Delta S_{total} = mc_p \ln\left(\frac{T_0}{T_1}\right) + \frac{mc_p(T_1 - T_0)}{T_0}$$
$$\Delta S_{total} = mc_p \left(\frac{T_1}{T_0} - 1 - \ln\frac{T_1}{T_0}\right)$$

Isothermal Compression of an Ideal Gas

For an ideal gas, we have noted that U = U(T) only. Now, recall the first law $\triangle U = Q + W$, or in differential form dU = dQ + dW. In this case if we consider compression from V_1 to V_2 , at fixed temperature dU = 0, and dW = -pdV, thus

$$dU = \mathbf{d}Q - pdV.$$

In this case however, since the process is isothermal dU = 0 and so dQ = pdV, then

$$\triangle S = \int_{1}^{2} \frac{\mathrm{d}Q}{T} = \int_{1}^{2} \frac{pdV}{T} = \frac{1}{T} \int_{1}^{2} pdV$$

now, recall pV = NkT, so

$$\triangle S = \int_{1}^{2} \frac{NkdV}{V} = Nk \ln \frac{V_2}{V_1} = -Nk \ln \frac{V_1}{V_2}.$$

Entropy and Disorder

We have defined entropy in terms of the logarithm of the multiplicity. Sometimes entropy is described as a measure of disorder, the greater the disorder, the greater the entropy. This works well if we are only considering solids, liquids, and gases. You should be aware that it is not always a good description and should be used with caution.