

Thermodynamics & Statistical Mechanics

Notes taken by J.Pearson, from a S4 course at the U.Manchester.
Lecture delivered by Prof.R.Bishop

July 29, 2007

Contents

1	Thermodynamics	3
1.1	The 1 st Law of Thermodynamics	3
1.1.1	Heat Capacities	3
1.2	Zeroth Law	3
1.3	Heat Engines	3
1.3.1	Otto Cycle	4
1.4	Kelvin-Planck Statement	4
1.4.1	Clausius' Statement	4
1.5	Carnot Cycles	4
1.6	The 2 nd Law of Thermodynamics	5
2	Thermodynamic Relations	5
2.1	Fundamental Thermodynamic Relation	5
2.2	Enthalpy	5
2.3	Helmholtz Free Energy	5
2.4	Gibbs Free Energy	6
3	Maxwell's Relations	6
4	Statistical Mechanics	7
4.1	Definitions	7
4.1.1	Microstate	7

4.1.2	Macrostate	7
4.1.3	Equal a priori Probabilities	7
4.1.4	Ensemble	7
4.1.5	Microcanonical Ensemble	7
4.1.6	Canonical Ensemble	7
4.2	Microcanonical Ensemble	7
4.3	Canonical Ensemble	10
4.4	Finding Partition Functions	12
4.4.1	Simple Systems	12
4.5	Energy States of Diatomic Molecules	13
4.5.1	Vibrational States	13
4.5.2	Rotational States	14
4.5.3	Translational States	15
4.6	Equipartition Theorem	15

1 Thermodynamics

A state variable is one that does not depend upon path taken, only start and end points.

1.1 The 1st Law of Thermodynamics

The change in internal energy of a system is equal to the sum of the heat added with the work done on the system:

$$\Delta E = \Delta Q + \Delta W \quad (1)$$

$$dE = DQ + DW \quad (2)$$

Here, a 'big D' - D - denotes an imperfect differential, as opposed to a perfect one denoted by d . The work W is positive for work being done on the system. If $\Delta Q = 0$, then the process is defined as *adiabatic*.

1.1.1 Heat Capacities

$$c_V \equiv \left(\frac{DQ}{dT} \right)_V \quad (3)$$

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V \quad (4)$$

$$c_p \equiv \left(\frac{DQ}{dT} \right)_p \quad (5)$$

$$(6)$$

For an ideal gas only, we can derive: $c_p - c_V = nR$.

For reversible, adiabatic, we can derive: $pV^\gamma = \text{const}$, where $\gamma \equiv \frac{c_p}{c_V}$. In a cycle, we have $\oint dE = 0$.

1.2 Zeroth Law

If two bodies are in thermal equilibrium with a third, then they are in thermal equilibrium with each other.

1.3 Heat Engines

See Fig(1a). These run in cycles, thus $\Delta E = 0$. Here, w = work done BY system, and W = work done ON system. ΔQ_H is absorbed from a hot source, with ΔQ_C emitted to a cooler reservoir. The engine does work, thus $w > 0$. Now, $w = Q_H - Q_C$, and, as efficiency η is defined as useful output over input, we have that $\eta = \frac{w}{Q_H} = 1 - \frac{Q_C}{Q_H}$

(b)
An
Otto
cy-
cle.

Figure 1: Schematic of both a heat engine & an Otto cycle.

1.3.1 Otto Cycle

See Fig(1b). Here, notice that Q_H goes into the system along $1 \rightarrow 2$, Q_C leaves the system on $3 \rightarrow 4$, and $4 \rightarrow 1, 2 \rightarrow 3$ are adiabats (i.e. $\Delta Q = 0$ along these). Now, from the heat capacity relations, we have that $c = \frac{\Delta Q}{\Delta T}$. Hence, $Q_H = c(T_2 - T_1)$ and $Q_C = -c(T_4 - T_3) = c(T_3 - T_4)$. Hence, we have an efficiency of $\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_3}{T_2}$.

1.4 Kelvin-Planck Statement

It is impossible to construct an engine, operating in a cycle, which produces no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of heat.

1.4.1 Clausius' Statement

It is impossible to construct a refrigerator operating in a cycle, which produces no effect other than the transfer of heat from cooler to a warmer body.

1.5 Carnot Cycles

A Carnot cycle is defined as the most efficient reversible engine operating between two reservoirs. Thus, the process must be isothermal or adiabatic. We can derive $\frac{Q_C}{T_C} = \frac{Q_H}{T_H}$ for such engines.

1.6 The 2nd Law of Thermodynamics

We have Clausius' theorem, which says that $\oint \frac{DQ}{T} \leq 0$, with equality for reversible processes. Now, we define *entropy* thus:

$$S \equiv \frac{DQ^{rev}}{T} \quad (7)$$

Entropy S is a state variable, and in isolated systems has the property that $dS \geq 0$ - it can never decrease. $dS = 0$ for any reversible, adiabatic process. Spontaneous changes are always irreversible. It is more correct to say $\Delta S_{system} + \Delta S_{surroundings} = 0$, or $\Delta S_{universe} \geq 0$.

Now, as entropy is a state variable, it is path-independent; so, for an irreversible problem, we change the path so that it is reversible, so we can then use $\Delta S = \oint \frac{DQ}{T}$

2 Thermodynamic Relations

2.1 Fundamental Thermodynamic Relation

For hydrodynamic systems, we have $DW = -pdV$; we also have $DQ = TdS$; thus, inserting these into the 1st law $dE = DQ + DW$, we have:

$$dE = TdS - pdV \quad (8)$$

For magnetic systems we have $DW = -mdB$, and ‘string’ type systems $DW = \Gamma dl$.

2.2 Enthalpy

We define enthalpy to be:

$$H \equiv E + pV \quad (9)$$

And, after differentiating, and inserting other terms, we find that $H(S, P)$, and:

$$dH = TdS + VdP \quad (10)$$

2.3 Helmholtz Free Energy

We define Helmholtz free energy:

$$F \equiv E - TS \quad (11)$$

And, similarly, $F(V, T)$:

$$dF \equiv -pdV - SdT \quad (12)$$

2.4 Gibbs Free Energy

Again, $G(T, P)$:

$$G \equiv E - TS + pV \quad (13)$$

$$dG = -SdT + Vdp \quad (14)$$

3 Maxwell’s Relations

Fundamental thermodynamics relation:

$$dE = TdS - pdV \quad (15)$$

Hence, $E = E(S, V)$. Thus, its differential is:

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV \quad (16)$$

Which by comparison shows that:

$$\left(\frac{\partial E}{\partial S}\right)_V = T \quad (17)$$

$$\left(\frac{\partial E}{\partial V}\right)_S = -p \quad (18)$$

Now, we use commutivity of differential equations:

$$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial E}{\partial V}\right)_S \quad (19)$$

Hence, we easily derive Maxwell's first relation:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (20)$$

We can do the same from the enthalpy relation ($dH = TdS + VdP$) to get Maxwell's second relation:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (21)$$

From Helmholtz ($dF = -SdT - pdV$) we derive Maxwell's third relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (22)$$

And from Gibbs ($dG = -SdT + Vdp$) Maxwell's fourth:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad (23)$$

4 Statistical Mechanics

4.1 Definitions

4.1.1 Microstate

State of the system, as defined in terms of the behaviour of all constituent atoms.

4.1.2 Macrostate

State of the system, as defined in terms of macroscopic variables.

4.1.3 Equal a priori Probabilities

A set of events each has an equal probability of happening.

4.1.4 Ensemble

Collection of a large number of copies of the system, each in one of the allowed microstates.

4.1.5 Microcanonical Ensemble

The copies in the system are completely isolated from each other.

4.1.6 Canonical Ensemble

Copies of the system are in thermal contact

Figure 2: The whole system (in double lines) is an ensemble. Each dotted box is a macrostate (4 of these). Each group of 3 arrows is a microstate (8 of these).

4.2 Microcanonical Ensemble

Suppose we have equal a priori probabilities. That is, the probability of any microstate occurring is the same:

$$p_i = \frac{1}{\Omega} \quad (24)$$

Where Ω = statistical weight = number of microstates in a given macrostate. Notice that this must imply:

$$\sum_{i=0}^{\Omega} p_i = \Omega \frac{1}{\Omega} = 1 \quad (25)$$

An example of this is the standard combinatorial system: the number of ways to split N identical objects into two smaller groups n and $(N - n)$. This is given by:

$$\text{number of ways} = \frac{N!}{n!(N-n)!} = {}^N C_n \quad (26)$$

Thus, applying to some system where we want how many ways (i.e. how many microstates exist) we can arrange a system to have the same energy (i.e. in one macrostate:

$$\Omega = \frac{N!}{n!(N-n)!} \quad (27)$$

e.g. $\Omega(E, V, N)$ would be the number of ways to arrange a system so that all combinations, or copies of the system, have the same macroscopic variables E, V, N .

That is, the number of different microstates in a given macrostate. Ω is known as the statistical weight.

We can relate this statistical weight to the entropy S , via the Boltzmann Law:

$$S = k_B \ln \Omega \quad (28)$$

An example of such a system is that of the ‘spin $\frac{1}{2}$ paramagnet’:

Suppose we have N independent spin sites, each site contains a dipole which is parallel \uparrow , or anti-parallel \downarrow to an external magnetic field. Notice that the spins are independent, and each have an equal a priori probability of occurring. Thus, we may use the microcanonical ensemble.

If we want to count the number of microstates with the same energy, we may write $\Omega(N, n_\uparrow)$; Which will find the number of microstates with a given number of parallel spins (i.e. up-spins n_\uparrow). Thus:

$$\Omega(N, n_\uparrow) = \frac{N!}{n_\uparrow!(N - n_\uparrow)!} \quad (29)$$

Suppose we add up how many components (microstates) are in each macrostate, for all macrostates:

$$\sum_{n_\uparrow=0}^N \Omega(N, n_\uparrow) = 2^N \equiv \Omega(N) \quad (30)$$

Thus, counting the number of microstates yields 2^N .

A useful mathematical approximation is that of Stirling’s approximation:

$$\lim_{n \rightarrow \infty} \ln(n!) = n \ln n - n \quad (31)$$

Now, looking at the entropy of the paramagnetic system:

$$S = k_B \ln(\Omega(N, n_\uparrow)) \quad (32)$$

$$= k_B \ln \left(\frac{N!}{n_\uparrow!(N - n_\uparrow)!} \right) \quad (33)$$

$$= k_B [\ln(N!) - \ln(n_\uparrow!) - \ln(N - n_\uparrow)!] \quad (34)$$

$$= k_B [N \ln N - N - (n_\uparrow \ln n_\uparrow - n_\uparrow) - ((N - n_\uparrow) \ln(N - n_\uparrow) - (N - n_\uparrow))] \quad (35)$$

By using Stirling’s approximation. And, tidying up reveals:

$$S = k_B [N \ln N - n_\uparrow \ln n_\uparrow - (N - n_\uparrow) \ln(N - n_\uparrow)] \quad (36)$$

Now, from the fundamental thermodynamic relation for such a magnetic system:

$$dE = TdS - mdB \quad (37)$$

$$\Rightarrow dS = \frac{1}{T}dE + \frac{m}{T}dB \quad (38)$$

Thus, we may note that $S(E, B)$; and we can hence write its differential:

$$dS = \left(\frac{\partial S}{\partial E} \right)_B dE + \left(\frac{\partial S}{\partial B} \right)_E dB \quad (39)$$

Thus, comparing the two, we get expressions for the temperature T and magnetic moment m , in terms of differentials of the entropy:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_B \quad (40)$$

$$\frac{m}{T} = \left(\frac{\partial S}{\partial B} \right)_E \quad (41)$$

Now, we notice that the energy of the system may be written in terms of the number of up- and down-spins, multiplied by the product of the magnetic dipole moment with the magnetic field B . Note that $N = n_\uparrow + n_\downarrow$:

$$E = n_\uparrow(-\mu B) + n_\downarrow(\mu B) \quad (42)$$

$$= (N - 2n_\uparrow)\mu B \quad (43)$$

Hence, doing the differentiation & rearranging:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_B \quad (44)$$

$$= \left(\frac{\partial S}{\partial n_\uparrow} \right) \left(\frac{\partial n_\uparrow}{\partial E} \right) \quad (45)$$

$$= \frac{k_B}{2\mu B} \ln \left[\frac{n_\uparrow}{n_\downarrow} \right] \quad (46)$$

Similarly:

$$\frac{m}{T} = -\frac{k_B T}{2\mu B^2} \ln \left[\frac{n_\uparrow}{n_\downarrow} \right] \quad (47)$$

This example illustrates how properties of the system can be found, once the statistical weight has been calculated, and the fundamental thermodynamic relation for the system written.

4.3 Canonical Ensemble

Suppose we have a system in a heat bath, where the system has a constant energy E_0 . Now, if we want to find the probability that we will find the system in a state p_i , with energy ϵ_i , where $\epsilon_i \ll E_0$. Now, there will be $\Omega(E_0 - \epsilon_i)$ microstates with this energy.

Thus, we may write:

$$p_i \propto \Omega(E_0 - \epsilon_i) \quad (48)$$

Or, writing a properly normalised probability:

$$p_i = \frac{\Omega(E_0 - \epsilon_i)}{\sum_i \Omega(E_0 - \epsilon_i)} \quad (49)$$

Now, by the Boltzmann law $S = k_B \ln \Omega$:

$$\Omega(E_0 - \epsilon_i) = e^{\frac{S(E_0 - \epsilon_i)}{k_B}} \quad (50)$$

Now, when we expand the argument of the exponential by a Taylor series:

$$S(E_0 - \epsilon_i) = S(E_0) - \epsilon_i \left(\frac{\partial S}{\partial E} \right)_{E=E_0} + \dots \quad (51)$$

Also, by the fundamental thermodynamic relation we have that $\frac{\partial S}{\partial E} = \frac{1}{T}$. Hence:

$$p_i = \frac{e^{\frac{S(E_0) - \epsilon_i}{k_B T}}}{\sum_i e^{\frac{S(E_0) - \epsilon_i}{k_B T}}} \quad (52)$$

$$= \frac{e^{-\epsilon_i \beta}}{\sum_i e^{-\epsilon_i \beta}} \quad (53)$$

$$\beta \equiv \frac{1}{k_B T} \quad (54)$$

Hence, we may write that the probability p_i of finding the system in an energy state ϵ_i , in terms of its partition function Z ; which arises as a normalisation constant:

$$p_i = \frac{1}{Z} e^{\epsilon_i \beta} \quad (55)$$

$$Z \equiv \sum_i e^{\epsilon_i \beta} \quad (56)$$

Where the sum in the partition function is over all distinguishable states; which was implied in the derivation using the statistical weight. This is called the Boltzmann distribution.

Now, if there is a degeneracy of the energy levels $g(\epsilon_i)$, the partition function may be written more completely as:

$$Z = \sum_i g(\epsilon_i) e^{-\epsilon_i \beta} \quad (57)$$

We may write the average energy of the system:

$$\langle E \rangle = \sum_i \epsilon_i p_i \quad (58)$$

$$= \sum_i \frac{\epsilon_i e^{-\epsilon_i \beta}}{e^{-\epsilon_i \beta}} \quad (59)$$

$$= -\frac{\partial}{\partial \beta} \ln Z \quad (60)$$

Similarly for the heat capacity:

$$\langle c_V \rangle = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V \quad (61)$$

$$= k_B \beta^2 \left(\frac{\partial^2}{\partial \beta^2} \ln Z \right)_V \quad (62)$$

Now, the general form of the system entropy is given by:

$$\langle S \rangle = -k_B \sum_i p_i \ln p_i \quad (63)$$

So, for this case, with the appropriate expression for the probability:

$$\langle S \rangle = -k_B \sum_i p_i \ln \frac{e^{-\epsilon_i \beta}}{Z} \quad (64)$$

$$= -k_B \sum_i p_i (-\beta \epsilon_i - \ln Z) \quad (65)$$

$$= k_B \beta \sum_i p_i \epsilon_i + k_B \ln Z \sum_i p_i \quad (66)$$

$$= \frac{\langle E \rangle}{T} + k_B \ln Z \quad (67)$$

Now, Helmholtz free energy is defined as $F \equiv E - TS$. Thus, we can write:

$$F = -k_B T \ln Z \quad (68)$$

Now, for a hydrostatic system:

$$F = E - TS \quad (69)$$

$$\Rightarrow dF = -pdV - SdT \quad (70)$$

Hence, we see that $F(V, T)$; and we can write its differential:

$$dF = \left(\frac{\partial F}{\partial V} \right)_T dV + \left(\frac{\partial F}{\partial T} \right)_V dT \quad (71)$$

Which, upon comparison, yields:

$$p = - \left(\frac{\partial F}{\partial V} \right)_T \quad (72)$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_V \quad (73)$$

Or, analogously for a magnetic system; we replace the pressure with magnetic moment, to find $m = - \left(\frac{\partial F}{\partial B} \right)_T$.

Thus, once the partition function has been found, all other properties of the system may be calculated. This is the analogy to the statistical weight in the microcanonical ensemble.

4.4 Finding Partition Functions

4.4.1 Simple Systems

Suppose we have a single dipole in a magnetic field. The possible energies of the system are given by:

$$\epsilon_{\uparrow} = -\mu B \quad (74)$$

$$\epsilon_{\downarrow} = \mu B \quad (75)$$

Hence, the partition function for a single dipole:

$$Z_1 = \sum_i e^{-\epsilon_i \beta} = e^{\mu B \beta} + e^{-\mu B \beta} = 2 \cosh(\mu B \beta) \quad (76)$$

Another example is that of a quantum mechanical energy level system: one particle with two possible energy levels ϵ_1 & ϵ_2 . Now, the partition function for a single particle can be written:

$$Z_1 = \sum_i e^{-\epsilon_i \beta} = e^{-\epsilon_1 \beta} + e^{-\epsilon_2 \beta} \quad (77)$$

Now, suppose we have a similar system, but with two distinguishable particles. The partition

Figure 3: The possible configurations of a system with one particle & two energy levels.

Figure 4: The possible configurations of a system with two distinguishable particles & two energy levels.

function for the 2-particle system may be written:

$$Z_2^{dist} = e^{-2\epsilon_1 \beta} + 2e^{-(\epsilon_1 + \epsilon_2) \beta} + e^{-2\epsilon_2 \beta} \quad (78)$$

Notice that $Z_2^{dist} = Z_1^2$.

Infact, it is true that for distinguishable particles, the N -body partition function can be related to the single-body partition function by:

$$Z_N^{dist} = Z_1^N \quad (79)$$

Suppose that the two particles are now indistinguishable. Writing the two-particle partition func-

Figure 5: The possible configurations of a system with two indistinguishable particles & two energy levels.

tion:

$$Z_2^{indist} = e^{-2\epsilon_1\beta} + e^{-(\epsilon_1+\epsilon_2)\beta} + e^{-2\epsilon_2\beta} \quad (80)$$

Notice that $Z_N^{indist} \neq Z_1^N$. The only way to do this is in the ‘classical limit’, where there are many more accessible energy states than particles. Only in the case of the classical limit, we may write:

$$Z_N^{indist} = \frac{Z_1^N}{N!} \quad (81)$$

4.5 Energy States of Diatomic Molecules

4.5.1 Vibrational States

From quantum mechanics, we know that the energy states of a 1D SHO can be written:

$$\epsilon_i = \left(n + \frac{1}{2}\right) \hbar\omega \quad (82)$$

Once the algebra is done, you find that the one body partition function is:

$$Z_1 = \frac{1}{2 \sinh \frac{1}{2} \hbar\omega\beta} \quad (83)$$

And the average energy calculated:

$$\langle E \rangle = - \left(\frac{\partial}{\partial \beta} \ln Z \right) \quad (84)$$

$$= \frac{1}{2} \hbar\omega \coth\left(\frac{1}{2} \hbar\omega\beta\right) \quad (85)$$

Looking at high ($\hbar\omega \ll \beta$) and low ($\hbar\omega \gg \beta$) temperature limits:

$$\lim_{T \rightarrow 0} \langle E \rangle = \frac{1}{2} \hbar\omega \quad (86)$$

$$\lim_{T \rightarrow \infty} \langle E \rangle = k_B T \quad (87)$$

4.5.2 Rotational States

Again, from QM, we know that the energy states of a rigid-rotor can be expressed as:

$$\epsilon_\ell = \frac{\ell(\ell+1)\hbar^2}{2I} \quad (88)$$

Rememebering that there is a degeneracy of $(2\ell+1)$ per state. Thus, the partition function is:

$$Z_1 = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\frac{\ell(\ell+1)\hbar^2}{2I}\beta} \quad (89)$$

In the high temperature limit ($k_B T \gg \frac{\hbar^2}{2I}$), the discrete sum is very well approximated by the integral:

$$\lim_{T \rightarrow \infty} Z_1 = \int_0^\infty (2\ell + 1) e^{-\frac{\ell(\ell+1)\hbar^2}{2I}\beta} d\ell \quad (90)$$

Which may be evaluated with the substitution $x = \ell(\ell + 1)$:

$$\lim_{T \rightarrow \infty} Z_1 = \frac{2I}{\hbar^2 \beta} = \frac{2Ik_B T}{\hbar^2} \quad (91)$$

And the corresponding high-temperature limit of the internal energy:

$$\lim_{T \rightarrow \infty} \langle E \rangle = k_B T \quad (92)$$

4.5.3 Translational States

Suppose a single particle is in a spherical system. We can define the density of states to be the number of states in a spherical shell $k \rightarrow k + dk$ as:

$$D(k)dk = \frac{V k^2}{2\pi^2} dk \quad (93)$$

And the partition function is found to be:

$$Z_1 = \int_0^\infty D(k) e^{-\beta \epsilon(k)} dk \quad (94)$$

Where $\epsilon(k) = \frac{\hbar^2 k^2}{2m}$.

In the evaluation of the integral, we will end up defining the ‘quantum concentration’:

$$n_Q \equiv \left(\frac{m}{2\pi\hbar\beta} \right)^{\frac{3}{2}} \quad (95)$$

Thus, the single particle partition function can be found to be:

$$Z_1 = V n_Q \quad (96)$$

And the average internal energy due to translational motion, with 3 degrees of freedom being $\langle E \rangle = \frac{3}{2} k_B T$.

This leads quite nicely onto the equipartition theorem:

4.6 Equipartition Theorem

For each degree of freedom of a system with an energy which is quadratic in either position or momentum, the average energy is $\frac{3}{2} k_B T$, in the corresponding high-temperature limit.