Statistical Physics I

Thomas Brosnan

Notes taken in Professor Manuela Kulaxizi's class, Michaelmas Term 2023

The [second] law that entropy always increases, holds, I think, the supreme position among the laws of Nature. … if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation."

- Sir Arthur Stanley Eddington

Contents

1 Thermodynamics **5**

1.1 System . . . 5
1.2 Static states . . . 5
1.3 Simple systems . . . 5
1.4 Thermodynamic parameters . . . 5
1.5 Postulate 1 . . . 5
1.6 Walls and Constraints/ Boundaries . . . 5
1.7 Types of Boundaries . . . 5
1.8 Postulate 2 . . . 6
1.9 Quasi state process . . . 6
1.10 1st Law of thermodynamics . . . 6
1.11 Exact differential . . . 6
1.12 Basic problem in thermodynamics . . . 7
1.13 2nd Law of thermodynamics . . . 7
1.14 Further restrictions on S . . . 7
1.15 Homogeneous degree k function . . . 7
1.16 3rd Law of thermodynamics . . . 7
1.17 Intensive parameters . . . 7
1.18 Gibbs Duhem relation . . . 8
1.19 Euler's theorem for homogeneous functions . . . 8
1.20 Solving the Gibbs-Duhem relation . . . 9
1.21 Thermodynamic configuration space . . . 9
1.22 Fundamental relation . . . 9
1.23 Free expansion . . . 9
1.24 Thermodynamic Potentials . . . 10
1.24.1 Helmholtz Free . . . 10
1.24.2 Gibbs free . . . 10
1.24.3 Grand canonical potential . . . 10
1.24.4 Enthalpy . . . 11
1.25 Maxwell's relations . . . 11
1.26 Concavity/Convexity . . . 11
1.27 Hessian matrix . . . 12
1.28 Physical properties . . . 12
1.28.1 Heat Capacities . . . 13
1.28.2 Coefficient of thermal expansion . . . 13
1.28.3 Coefficient of isothermal/isentropic compressability . . . 13
1.29 Consequences of stability . . . 14
1.30 Phase transitions . . . 14
1.31 First order phase transitions . . . 14
1.32 Second order phase transition . . . 14
1.33 Clausius-Clapeyron equation . . . 15
1.34 Gibbs phase rule . . . 16
1.35 Critical point of transition . . . 16

2 Mathematics of Statistical mechanics **18**

2.1 Gamma function . . . 18
2.2 Many variable Gaussian integral . . . 18
2.3 Sterling's approximation . . . 18

2.4 Area of a Hyper-sphere . . . 19
2.5 Volume of an n-ball . . . 21

3 Probability and statistics **22**
3.1 Sample space . . . 22
3.2 Probability . . . 22
3.3 Random variable . . . 22
3.4 Probability distribution . . . 22
3.5 Discrete variables . . . 22
3.6 Continuous variables . . . 22
3.7 Mean and variance . . . 23
3.8 Common distributions . . . 23
3.8.1 Binomial distribution . . . 23
3.8.2 Multinomial distribution . . . 23
3.8.3 Poisson distribution . . . 24
3.8.4 Gaussian distribution . . . 24
3.9 Central limit theorem . . . 24

4 Statistical mechanics **25**
4.1 Macro and microscopic description . . . 25
4.2 Ensemble . . . 25
4.3 Phase space . . . 25
4.4 Number of microstates . . . 26
4.5 Probability distribution . . . 27
4.5.1 Liouville's theorem . . . 27
4.5.2 Conservative system probability distribution . . . 28
4.6 Microcanonical ensemble . . . 28
4.7 Density of microstates . . . 29
4.8 Ideal Gas . . . 29

1 Thermodynamics

1.1 System

- In thermodynamics we usually deal with a macroscopic system, comprising of N constituents, where $1 >> \frac{1}{\sqrt{N}}$. The properties of these systems then arise as a result of symmetries and fundamental laws of physics.

1.2 Static states

- Macroscopic variables sense only coarse spatial averages of the coordinates describing the motion of the constituents.

  There are naturally two types of averaging, over time and over distance. These are implicit in macroscopic variables.

1.3 Simple systems

- Simple systems are microscopically homogeneous , isotropic, uncharged and large enough so that we need not take into account surface/boundary effects.

1.4 Thermodynamic parameters

- Volume $V = \sum_{j=1}^{m} V_j$ for j sub-systems.
- $\{N_i\}$, Chemical composition of the system, i denotes the type of constituent (i.e. different molecules).
- Internal Energy E, (or U), is the energy contained in the system excluding the center of mass motion and an external energy the system has as a whole due to external forces.

  These parameters are known as extensive parameters (meaning they scale with the system), otherwise they would be known as intensive parameters.

1.5 Postulate 1

- There exists states called **equilibrium states** of simple thermodynamic systems, that are completely characterised by the values of E, V and $\{N_1, N_2, ..., N_r\}$ for systems comprised of r different species of constituents.

1.6 Walls and Constraints/ Boundaries

- Walls/Boundaries separate the system from the environment and provide boundary conditions. Processes are initiated and the extensive parameters changed by the manipulation of the walls/boundaries.

1.7 Types of Boundaries

- A wall that is impermeable to the flow of heat is **adiabatic** , other wise it is **di-thermal**.
- A wall that does not allow mechanical work is **mechanically isolated**, (Volume preserved).
- A wall that does not allow chemical work is **chemically isolated**, ($\{N_i\}$ preserved).

1.8 Postulate 2

- There exists walls, adiabatic, with the property that the work done in taking an adibabatically enclosed system between two given states is determined entirely by the States and is independent of external conditions.

1.9 Quasi state process

- A quasi state process is a process that preserves the equilibrium of the system through out.

1.10 1st Law of thermodynamics

- The heat flux to a system in any process that leaves the number of constituents unchanged is simply the difference in the internal energies of the initial and final states.

  For simple systems and N = constant during the process, if we define positive work to be work done by the system, then:

$$đW = PdV \tag{1.1}$$

  Here P is the pressure and V is the volume. The $đ$ in the differential is there to note that this is not an exact differential.

  The first law then tells us that:

$$đQ = dE + đW = dE + PdV - \sum_{i=1}^{r} \mu_i dN_i \tag{1.2}$$

  Here the μ_i are the different chemical potentials of the constituents i.

1.11 Exact differential

- An exact differential of a function $f(a_1, a_2, ..., a_n)$ is given by:

$$df \equiv \sum_{i=1}^{n} (\frac{\partial f}{\partial a_i}) da_i \tag{1.3}$$

  This also means that:

$$\frac{\partial^2 f}{\partial a_i \partial a_j} = \frac{\partial^2 f}{\partial a_j \partial a_i}, \quad \forall\, i, j \tag{1.4}$$

  Anything of not of this form is inexact and denoted with a $đ$

1.12 Basic problem in thermodynamics

- The basic problem in thermodynamics is the determinism of the equilibrium state resulting after the removal of all internal constraints in a closed($\implies$ totally isolated) composite system.

1.13 2nd Law of thermodynamics

- There exists a function S (entropy) of the extensive parameters of any composite system defined for equilibrium states and has the property that it is maximised over the values assumed by the extensive parameters in the absence of internal constraints.
- This function $S(E, V, N)$ is called the fundamental equation or relation.

1.14 Further restrictions on S

- The entropy of any composite system is additive over its subsystems (i.e. S is extensive itself)
- Also S is continuous, differentiable and monotonically increasing function of the energy E. This means that for r subsystems:
- We can also find that if we scale our system by λ, then according to the above restrictions:

$$S(E, V, N) \to S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N) \tag{1.5}$$

This makes S a homogeneous degree 1 function.

1.15 Homogeneous degree k function

- A function $f(\lambda x_1, \lambda x_2, ..., \lambda x_n) = \lambda^k f(x_1, x_2, ..., x_n)$ is said to be homogeneous of degree k.

1.16 3rd Law of thermodynamics

-

$$\frac{\partial E}{\partial S} = 0 \implies S = 0 \tag{1.6}$$

Here the quantity $\frac{\partial E}{\partial S}$ is essentially temperature.

1.17 Intensive parameters

- From the fundamental equation we can theory solve $E = E(S, V, N_1, N_2, ..., N_r)$, E then must satisfy:

$$E(\lambda S, \lambda V, \lambda N_1, \lambda N_2, ..., \lambda N_r) = \lambda E(S, V, N_1, N_2, ..., N_r) \tag{1.7}$$

- Then taking the total derivative:

$$dE = \left(\frac{\partial E}{\partial S}\right) dS + \left(\frac{\partial E}{\partial V}\right) dV + \sum_{i=1}^{r} \left(\frac{\partial E}{\partial N_i}\right) dN_i \tag{1.8}$$

Then we define the intensive parameters:

$$T \equiv \left(\frac{\partial E}{\partial S}\right), \quad -P \equiv \left(\frac{\partial E}{\partial V}\right), \quad \mu_i \equiv \left(\frac{\partial E}{\partial N_i}\right) \tag{1.9}$$

These are intensive as they do not change under re-scaling of the system. Thus they can be consider homogeneous functions of degree 0 and are all functions of S, V, N. Then the total differential can be written as:

$$dE = TdS - PdV + \sum_{i=1}^{r} \mu_i dN_i \tag{1.10}$$

- This can be recognised as the first law of thermodynamics where $-PdV$ is the differential of the mechanical work and $\mu_i dN_i$ is the differential of the chemical work.

1.18 Gibbs Duhem relation

- Choosing $\lambda = \frac{1}{N_k}$, then $T \to T(\frac{E}{N_k}, \frac{V}{N_k}, \frac{N_1}{N_k}, \frac{N_2}{N_k}, ..., 1, ..., \frac{N_r}{N_k}) = T(E, V, N_1, N_2, .., N_r)$. Thus we can see the necessary independent parameters are $r + 1$ instead of $r + 2$. This implies there is a relation between them.

  This relation is the Gibbs-Duhem relation and to find this we need to use a property of homogeneous functions.

1.19 Euler's theorem for homogeneous functions

- If $f(\lambda x_1, \lambda x_2, ..., \lambda x_n) = \lambda^k f(x_1, x_2, ..., x_n)$, then:

$$k f(x_1, x_2, ..., x_n) = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\right) x_i \tag{1.11}$$

- Applying this theorem:

$$E(S, V, N_1, N_2, ..., N_r) = \left(\frac{\partial E}{\partial S}\right) S + \left(\frac{\partial E}{\partial V}\right) V + \sum_{i=1}^{r} \left(\frac{\partial E}{\partial N_i}\right) N_i \tag{1.12}$$

- Thus:

$$E = TS - PV + \sum_{i=1}^{r} \mu_i N_i \tag{1.13}$$

1.20 Solving the Gibbs-Duhem relation

- To do this we take the total differential of the above equation and see:

$$dE = TdS + SdT - PdV - VdP + \sum_i \mu dN_i + \sum_i N_i d\mu_i \tag{1.14}$$

  But by the first law this must be equal to 1.2. Thus we get:

$$SdT - VdP + \sum_i N_i d\mu_i = 0 \tag{1.15}$$

- This is our Gibb's-Duham relation.

1.21 Thermodynamic configuration space

- We define a thermodynamic configuration space.

  For a simple system such a space is spanned by co-ordinate axes that correspond to $S, E, V, N_1, N_2, ..., N_r$. Then $S(E, V, N_1, N_2, ..., N_r)$ defines a surface in this space that conforms to various requirements that S itself satisfies.

  Any system will proceed from a state A (point A on the surface of S) to state B, iff S is maximised at B compared to all other states.

  If we have $S_a < S_b$ then the process has a unique direction from lower to higher entropy and is irreversible.

  It is possible for the process to be reversible if $\Delta S = 0$.

1.22 Fundamental relation

- We can consider either $E(S, V, N_i)$ or $S(E, V, N_i)$ to be fundamental relations. But we cannot however, consider $E(T, V, N_i)$ or $S(T, V, N_i)$ to be fundamental as by the definition of T we must take a derivative and there we know we loose information relating to what is held constant.

1.23 Free expansion

- If a system changes by free expansion this means that $đW = 0$ through out this process.

1.24 Thermodynamic Potentials

- We can construct functions of intensive parameters that give as much information as S and E, i.e. they are fundamental relations. These potentials are Legendre transforms of either $E(S,V,N_i)$ or $S(E,V,N_i)$. Through examining their differentials one can find many partial derivative relations. These potentials are extensive functions. Just as in mechanics, the system will tend towards a lower value of a potential and at equilibrium, under the constraints as listed below, the potential will take the unchanging minimum value.

1.24.1 Helmholtz Free

- This is $\mathcal{F}(T,V,N_i)$ and is given by:

$$\boxed{\mathcal{F} = E - TS} \tag{1.16}$$

We use $\mathcal{F}$ in the case of an isothermal process along with there being chemical and mechanical isolation. $\mathcal{F}$ also has:

$$\boxed{-P = \left(\frac{\partial F}{\partial V}\right), \quad -S = \left(\frac{\partial F}{\partial T}\right), \quad \mu_i = \left(\frac{\partial F}{\partial N_i}\right)} \tag{1.17}$$

1.24.2 Gibbs free

- This is $\mathcal{G}(T,P,N_i)$ and is given by:

$$\boxed{\mathcal{G} = F + PV} \tag{1.18}$$

We use $\mathcal{G}$ in the case of an isothermal and Isobaric system along with chemical and mechanical isolation. $\mathcal{G}$ also has:

$$\boxed{V = \left(\frac{\partial G}{\partial P}\right), \quad -S = \left(\frac{\partial G}{\partial T}\right), \quad N_i = \left(\frac{\partial G}{\partial \mu_i}\right)} \tag{1.19}$$

1.24.3 Grand canonical potential

- This is $\mathcal{J}(T,V,\mu_i)$ and is given by:

$$\boxed{\mathcal{J} = E - TS - \sum_i \mu_i N_i} \tag{1.20}$$

We use $\mathcal{J}$ in the case of an isothermal process and fixed chemical potential, along with mechanical isolation. $\mathcal{J}$ also has:

$$-P = \left(\frac{\partial J}{\partial V}\right), \quad S = \left(\frac{\partial J}{\partial T}\right), \quad -N_i = \left(\frac{\partial J}{\partial \mu_i}\right) \tag{1.21}$$

1.24.4 Enthalpy

– This is $\mathcal{H}(S, P, N_i)$ and is given by:

$$\mathcal{H} = E + PV \tag{1.22}$$

We use $\mathcal{H}$ in the case of an Isobaric process along with thermal and chemical isolation. $\mathcal{H}$ also has:

$$P = \left(\frac{\partial H}{\partial V}\right), \quad S = \left(\frac{\partial H}{\partial T}\right), \quad \mu_i = \left(\frac{\partial H}{\partial N_i}\right) \tag{1.23}$$

1.25 Maxwell's relations

- In examining the different potentials above, one can use the fact that they are exact to derive extra partial derivative relations between the parameters. These relations come from the fact that it does not matter which order you take the derivatives. i.e. $\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}$. The relations discovered are:

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V, \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \\ \left(\frac{\partial V}{\partial T}\right)_P &= -\left(\frac{\partial S}{\partial P}\right)_T, \quad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \end{aligned} \tag{1.24}$$

- However it should be noted that if one comes to a problem where you can write down one of the thermodynamic potentials and solve the problem, then you will not need to use any of the Maxwell's relations through out that problem, provided the correct potential is chosen.

1.26 Concavity/Convexity

- A function $f(x_1, x_2, ..., x_n)$ with a parameter $t \in [0, 1]$, is concave iff:

$$f(tx_1 + (1-t)y_1, ..., tx_n + (1-t)y_n) \geq tf(x_1, ..., x_n) + (1-t)f(y_1, ..., y_n) \tag{1.25}$$

- f is instead convex iff:

$$f(tx_1 + (1-t)y_1, ..., tx_n + (1-t)y_n) \leq tf(x_1, ..., x_n) + (1-t)f(y_1, ..., y_n) \tag{1.26}$$

Concavity means all tangent lines are above the graph of the function, where as convexity means all tangent lines are below the graph of the function.

- For fixed N the thermodynamic potentials defined by the Legendre transform of $E(S, V, N_i)$ and $S(E, V, N_i)$ are convex functions of there extensive variables and concave functions of their intensive variables.

1.27 Hessian matrix

- For functions $f : \mathbb{R}^n \to \mathbb{R}$ of many variables which are at least twice differentiable the hessian matrix is defined as:

$$H = \begin{pmatrix} \frac{\partial^2 f}{\partial x_1^2} & \cdot & \cdot & \cdot & \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ \frac{\partial^2 f}{\partial x_m \partial x_1} & \cdot & \cdot & \cdot & \frac{\partial^2 f}{\partial x_1 \partial x_m} \end{pmatrix} \tag{1.27}$$

Then if the hessian matrix evaluated at a point $H(x_1^0, x_2^0, ..., x_n^0)$, is positive definite then it has positive eigenvalues and thus there is a local minimum at $\mathbf{x}_0$. Likewise if $H(x_1^0, x_2^0, ..., x_n^0)$ is negative definite there is a max at $\mathbf{x}_0$. If there are both positive and negative eigenvalues then $\mathbf{x}_0$ is a saddle point otherwise if $det(H) = 0$, then the test is inconclusive.

- For functions $f(x_1, x_2)$, twice differentiable, f is concave iff:

$$\frac{\partial^2 f}{\partial x_i^2} \leq 0, \ i = 1, 2, \ \text{ and } \frac{\partial^2 f}{\partial x_1^2}\frac{\partial^2 f}{\partial x_2^2} - \frac{\partial^2 f}{\partial x_1 \partial x_2} \geq 0 \tag{1.28}$$

And f is convex iff:

$$\frac{\partial^2 f}{\partial x_i^2} \geq 0, \ i = 1, 2, \ \text{ and } \frac{\partial^2 f}{\partial x_1^2}\frac{\partial^2 f}{\partial x_2^2} - \frac{\partial^2 f}{\partial x_1 \partial x_2} \geq 0 \tag{1.29}$$

1.28 Physical properties

- These are measurable properties of materials defined through the thermodynamic variables.

1.28.1 Heat Capacities

– There is the heat capacity at constant volume C_V:

$$C_V \equiv \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} \tag{1.30}$$

– And the heat capacity at constant pressure C_P:

$$C_P \equiv \left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial E}{\partial T}\right)_{P,N} + P\left(\frac{\partial V}{\partial T}\right)_{P,N} = \left(\frac{\partial H}{\partial T}\right)_{P,N} \tag{1.31}$$

1.28.2 Coefficient of thermal expansion

– This is α defined as:

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} \tag{1.32}$$

1.28.3 Coefficient of isothermal/isentropic compressability

– The coefficient of isothermal compressability is given by:

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \tag{1.33}$$

– And the coefficient of isentropic (though really here we mean adiabatic plus reversible but we assume everything is quasistatic so we can just say isentropic) compressability is:

$$\kappa_s \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,N} \tag{1.34}$$

- From these definitions the following properties can be shown:

$$\begin{gathered} C_P - C_V = TV\frac{\alpha^2}{\kappa_T} \\ \frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S} \\ C_V = TV\frac{\alpha^2\kappa_S}{\kappa_T(\kappa_T - \kappa_S)}, \quad C_P = TV\frac{\alpha}{\kappa_T - \kappa_S} \end{gathered} \tag{1.35}$$

1.29 Consequences of stability

- Due to convexity $\frac{\partial^2 S}{\partial E^2} < 0$, but $\frac{\partial S}{\partial E} = \frac{1}{T}$, This implies that:

$$\begin{gathered} \frac{1}{T^2}\left(\frac{\partial T}{\partial E}\right) = -\frac{1}{T^2 C_V} < 0 \\ \implies C_V > 0 \end{gathered} \tag{1.36}$$

  Then we can use relations 1.35 to get that $C_P > C_V > 0$.

  Similarly, $\frac{\partial^2 F}{\partial V^2} > 0$ implies that:

$$\kappa_S > 0 \tag{1.37}$$

  And then once again by relations 1.35, $\kappa_T > \kappa_S > 0$.

1.30 Phase transitions

- A phase is a state of matter with uniform properties such that at thermodynamic equilibrium a characteristic state equation for the state exists.

  We will consider phase transitions as the failure of equilibrium/stability conditions .

  There are two large classes of phase transitions.

1.31 First order phase transitions

- Also known as discontinuous, here the different phases are at different regions in the thermodynamic configuration space. In these transitions the derivative of the thermodynamic potential describing the system is not continuous.

1.32 Second order phase transition

- Also known as continuous phase transition, here the two phases are continuous in the thermodynamic equilibrium space.

1.33 Clausius-Clapeyron equation

- At a first order transition the Gibbs free energy at the point of transition is $\mathcal{G} = \mathcal{G}^{(1)} + \mathcal{G}^{(2)}$, where $\mathcal{G}^{(1)}$ and $\mathcal{G}^{(2)}$, are the Gibbs free energy of phase 1 and 2, respectively. Then we have that

$$\boxed{\begin{aligned}\left(\frac{\partial G}{\partial T}\right) &= -S_{(1)} \neq S_{(2)} \\ \left(\frac{\partial G}{\partial P}\right) &= -V_{(1)} \neq V_{(2)}\end{aligned}} \tag{1.38}$$

For a first order phase transition the pressure remains the same while the volume increases from $V \to V'$ because the two phases have different densities.

At the boundary where phases coexist, so $d\mathcal{G} = 0_{tot}$, this is due to the fact that $\mathcal{G}$ wants to be at a minima at equilibrium for the conditions of constant pressure and temperature. So if T and V are fixed as we cross the phase boundary then we get that:

$$\boxed{d\mathcal{G}_{tot} = 0 = \mu_1 dN_1 + \mu_2 dN_2} \tag{1.39}$$

But since we are dealing with an isolated system $dN_1 = -dN_2$. Here N_i is the number of particles in phase i. These two equations tell us that $\mu_1 = \mu_2$. Also here we can use the Gibbs Duhem relation 1.15, to use the fact that $\mu_1 = \mu_2$ to write down:

$$\boxed{\begin{aligned} &-\frac{S_1}{N_1}dT + \frac{V_1}{N_1}dP = -\frac{S_2}{N_2}dT + \frac{V_2}{N_2}dP \\ &\implies dP(\frac{V_1}{N_1} - \frac{V_2}{N_2}) = dT(\frac{S_1}{N_1} - \frac{S_2}{N_2}) \\ &\implies \left.\frac{dP}{dT}\right|_{across\ boundary} = \frac{\Delta s}{\Delta v}\end{aligned}} \tag{1.40}$$

Where the final term is in terms of specific volume v and entropy s. If we then define the latent heat per particle as $l \equiv T\Delta S$, which we can consider constant as this phase change we are discussing is at constant temperature. Thus the Clausius–Clapeyron equation is:

$$\boxed{\frac{dP}{dT} = \frac{l}{T\Delta v}} \tag{1.41}$$

This latent heat is always specified with a name that tells you which phase transition it is from and to, eg. the latent heat of vaporisation,sublimation, etc... There is no latent heat in second order phase transitions.

1.34 Gibbs phase rule

- This gives us an expression for the number of thermodynamic degrees of freedom, If a system can exist in M possible phases and has r constituents, this means we have $2 + M(r-1)$ independent variables. The 2 comes from temperature and pressure and the $M(r-1)$ comes from the r constituents, which have a Gibbs-Duhem relationship for each phase. Then if the phases of each constituent are in equilibrium with each other we must have that $\forall\ i = 1, 2, ..., r,\ \ \mu_i^{(1)} = \mu_i^{(2)} = ... = \mu_i^{(M)}$. Thus there are an extra $r(M-1)$ equations. Thus the total number of degrees of freedom are $f = 2 + M(r-1) - r(M-1)$, thus:

$$\boxed{f = r + 2 - M} \tag{1.42}$$

1.35 Critical point of transition

- If we have a region in the phase space where $\frac{\partial P}{\partial V} > 0$, the this implies that $\kappa_T < 0$, which is a violation of stability. So phase transition must take place at the point where this begins to happen and where there is a point of inflection so that convex shape of the graph also changes to concave at this point too. So:

$$\boxed{\frac{\partial P}{\partial V} = \frac{\partial^2 P}{\partial V^2} = 0} \tag{1.43}$$

This idea I think is best motivated from the below figure taken from Concepts in thermal physics by Blundell and Blundell.

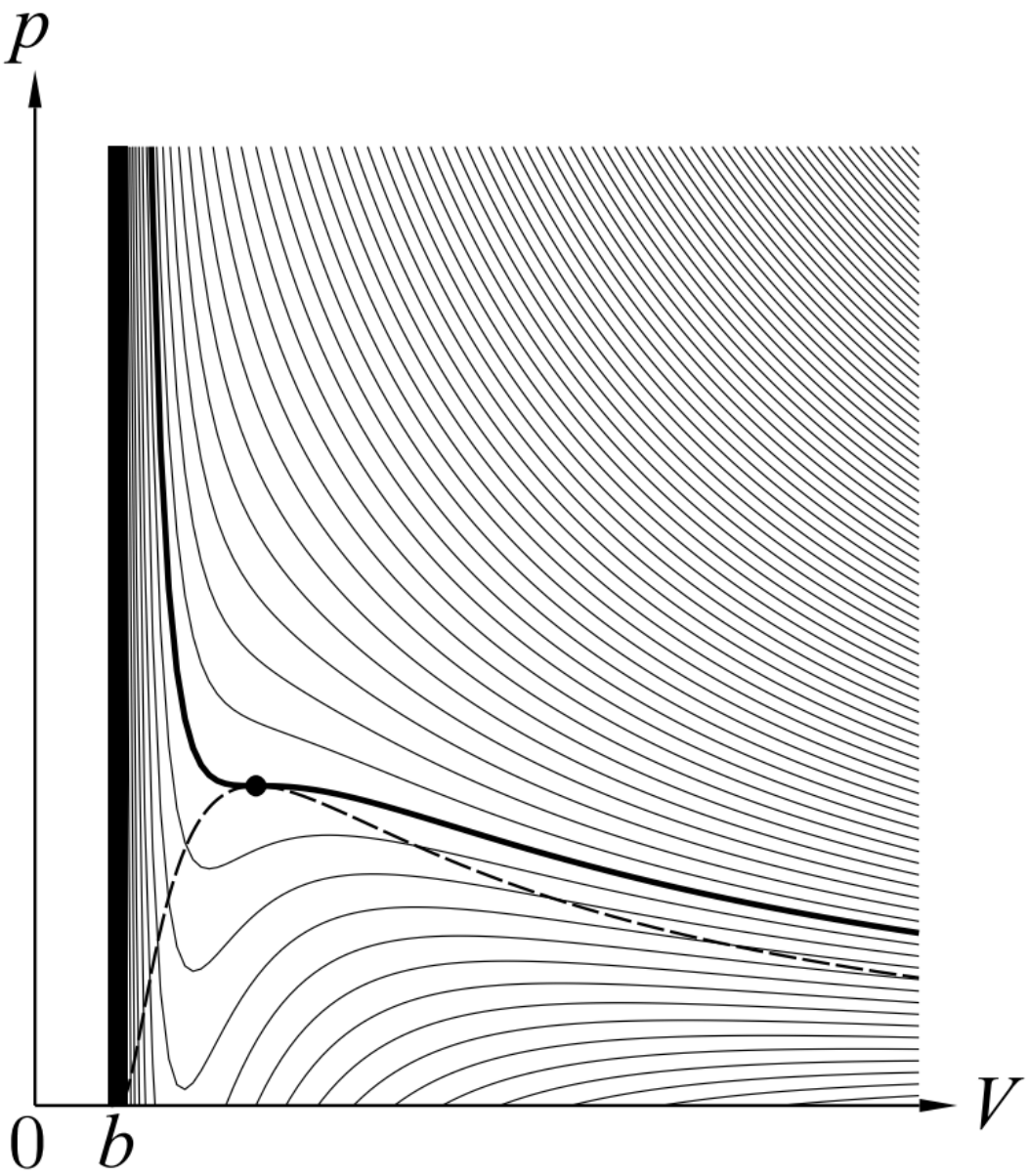

Figure 1: *Isotherms of the van der Waals gas. Isotherms towards to the top right of the graph correspond to higher temperatures. The dashed line shows the region in which liquid and vapour are in equilibrium. The thick line is the critical isotherm and the dot marks the critical point.*

2 Mathematics of Statistical mechanics

2.1 Gamma function

- The Gamma function is the generalisation of the factorial function to non integers ($\Gamma(n+1) = n!$ if n is an integer). It is expressed in the form of an integral and many problems reduce to turning an integral into the gamma function. It is defined as follows:

$$\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt \tag{2.1}$$

Also has the usefull property that $\Gamma(z+1) = z\Gamma(z)$.

2.2 Many variable Gaussian integral

- The Gaussian integral is well known, $\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$. This can then be generalised to have any sort of multi-variable quadratic powers. If we have have n variables, $x_1, x_2, ..., x_n$, then any quadratic combination of these can be written as:

$$a_{11}x_1^2 + a_{12}x_1x_2 + ... = \sum_{i,j=1}^{n} x_i A_{ij} x_j = \mathbf{x}^T A \mathbf{x} \tag{2.2}$$

Where here we have introduced the symmetric matrix $A^T = A$ to account for the coefficients a_{ij}. We can use this generalisation via the means of eigenvalues to prove the following integral:

$$\int_{-\infty}^{\infty} dx_1 dx_2 ... dx_n e^{-\frac{1}{2}\mathbf{x}^T A \mathbf{x}} = \frac{(2\pi)^{\frac{n}{2}}}{\sqrt{det(A)}} \tag{2.3}$$

- And if we add any linear term:

$$\int_{-\infty}^{\infty} dx_1 dx_2 ... dx_n e^{-\frac{1}{2}\mathbf{x}^T A \mathbf{x} + B^T \mathbf{x}} = \frac{(2\pi)^{\frac{n}{2}}}{\sqrt{det(A)}} e^{\frac{1}{2}B^T A^{-1} B} \tag{2.4}$$

2.3 Sterling's approximation

- This approximation is said to only work for large N, but has an error of less than 1% for $N > 100$ so its pretty good, this comes from Hyper physics. See also the graph below as visual proof. The approximation

is as follows:

$$\ln(N!) = \sum_{k=1}^{N} ln(k) \approx \int_{1}^{N} ln(k)dk = N\ln(N) - N \tag{2.5}$$

This can be extended to the gamma function:

$$\ln(\Gamma(N+1)) \approx N\ln(N) - N \tag{2.6}$$

- This approximation is could be slightly better if instead $\ln(N!) \approx N\ln(N) - N + \frac{1}{2}\ln(2\pi N)$. Both of these are shown below.

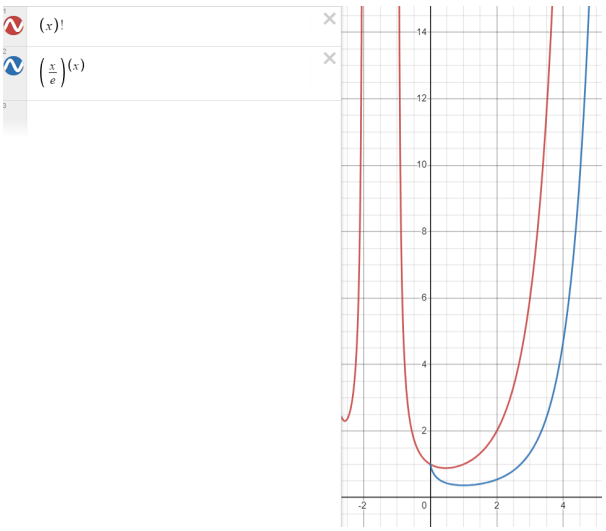

Figure 2: Sterling approximation vs $\Gamma(x-1)$

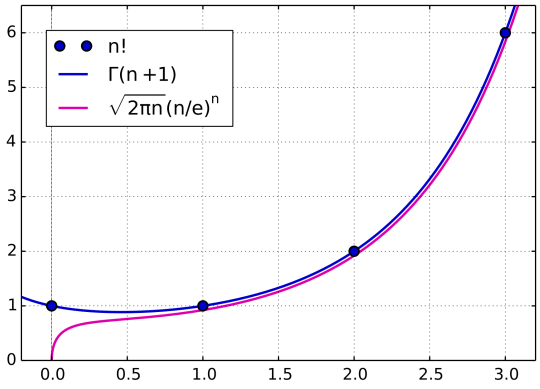

Figure 3: Slightly better Sterling approximation vs $\Gamma(x-1)$

2.4 Area of a Hyper-sphere

- We denote $S^{n-1}(R)$ as the $n-1$ sphere of radius R, That is the following set of points:

$$S^{n-1}(R) = \left\{ x \in \mathbb{R}^n \middle| \sum_{i=1}^{n} x_i^2 = R^2 \right\} \tag{2.7}$$

Then we denote $S_{n-1}(R)$ the area of this sphere. The formula for this can be motivated by considering how one would extend spherical co-ordinates to higher dimensions. For $n-1$ dimensions the co-ordinates would extend as follows

Cartesian	Spherical
x_1	$r\cos\phi_1$
x_2	$r\sin\phi_1\cos\phi_2$
x_3	$r\sin\phi_1\sin\phi_2\cos\phi_3$
.	.
.	.
.	.
x_{n-2}	$r\sin\phi_1\sin\phi_2...\sin\phi_{n-2}\cos\phi_{n-1}$
x_{n-1}	$r\sin\phi_1\sin\phi_2...\sin\phi_{n-2}\sin\phi_{n-1}$

Table 1: Extension of spherical co-ords to $n-1$ dimensions

Where here $\phi_1, \phi_2, ..., \phi_{n-1} \in [0, \pi]$ and $\phi_{n-1} \in [0, 2\pi]$. One can then see that the Jacobian, i.e. the determinant of the Jacobian matrix when changing from $n-1$ Cartesian co-ords to $n-1$ spherical is as follows:

$$\begin{gathered} J = r^{n-1}\sin^{n-2}\phi_1\sin^{n-3}\phi_2...\sin\phi_{n-2} \\ \implies dx_1dx_2...dx_{n-1} = r^{n-1}d\Omega_{n-1}dr = r^{n-1}dS_{n-1}(1)dr \end{gathered} \tag{2.8}$$

The last step here is given as the definition of Ω_n is $\Omega_n = S_{n-1}/r^{n-1} \implies d\Omega_{n-1} = dS_{n-1}(1)$. Finally to find the area, we consider the following integral two which we know the result:

$$I_n = \int_{-\infty}^{\infty}\prod_{i=1}^{n} dx_i e^{-x_i^2} = \pi^{\frac{n}{2}} \tag{2.9}$$

And converting to spherical co-ords:

$$\begin{gathered} I_n = \int_0^{\infty} r^{n-1}dS_{n-1}(1)dre^{-r^2}, \quad u = r^2 \\ \implies I_n = \frac{1}{2}S_{n-1}(1)\int_0^{\infty} u^{\frac{n}{2}-1}e^{-u}du = \frac{1}{2}\Gamma(\frac{n}{2})S_{n-1}(1) \end{gathered} \tag{2.10}$$

Re-arranging:

$$\begin{gathered} S_{n-1}(1) = \frac{2\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2})} \\ \implies S_{n-1}(R) = \frac{2\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2})}R^{n-1} \end{gathered} \tag{2.11}$$

Where the last jump is from dimensional analysis.

2.5 Volume of an n-ball

- An n-ball is denoted $V^n(R)$ and the volume of this ball $V_n(R)$. The value of this can be found from considering:

$$V_n(R) = \int_{constraints} \prod_{i=1}^{n} dx_i = \int_0^R r^{n-1} dr \int dS_{n-1}$$
$$\implies V_n(R) = \frac{2\pi^{\frac{n}{2}}}{n\Gamma(\frac{n}{2})} R^n \tag{2.12}$$

3 Probability and statistics

3.1 Sample space

- Space of all possible outcomes of an experiment or observed random phenomena.

3.2 Probability

- If we perform the experiment N times and obtain n positive results, then the probability of a positive result is:

$$Pr = \lim_{N\to\infty} \frac{n}{N} \tag{3.1}$$

3.3 Random variable

- A function which takes real values and is defined on the sample space.

3.4 Probability distribution

- Describes the relationship between the random variables and the probabilities that the random variable X will obtain a certain value.

3.5 Discrete variables

- If the possible values of a random variable are discrete, i.e. $X \in \{x_1, x_2, ..., x_n\}$, then:

$$Pr[X = x_i] = P_i, \qquad \sum_{i=1}^{n} P_i = 1 \tag{3.2}$$

3.6 Continuous variables

- If the random variable takes on continuous values, i.e. $X \in [a, b] \in \mathbb{R}$, then:

$$Pr[x \leq X \leq x + dx] = \rho(x)dx, \qquad \int_a^b \rho(x)dx = 1 \tag{3.3}$$

Here $\rho(x)$ is a probability distribution/density.

3.7 Mean and variance

- The mean μ is the same as the expectation value of the random variable $\langle X \rangle$. This takes the following form for the discrete case:

$$\mu = \langle X \rangle \equiv \sum_{i=1}^{n} P_i x_i \tag{3.4}$$

And in the continuous case:

$$\mu = \langle X \rangle \equiv \int_a^b \rho(x) x dx \tag{3.5}$$

Providing both of these are convergent.

- In both cases the variance is defined as $\sigma^2 \equiv \langle X^2 \rangle - \langle X \rangle^2$.

3.8 Common distributions

3.8.1 Binomial distribution

- Here there are two outcomes B and W with probabilities p and $q = 1 - p$. Suppose in N trials we observe n times B and $N - n$ times W. To compute the probability in N independent trials to observe n positive results is:

$$Pr(N, n, p) = \binom{N}{n} p^n (1-p)^{N-n}, \quad \binom{N}{n} = \frac{N!}{n!(N-n)!} \tag{3.6}$$

This prefactor can be motivated from the following. The number of ways to arrange n distinct objects in N distinct boxes, with $N > n$, is $N(N-1)...(N-n+1) = \frac{N!}{(M-n)!}$. This just comes from the fact that there are N boxes to put the first object in, $N-1$ to put the second in... repeated until there are no more objects left to place. Then seeing as all the n objects are identical we have to divide by $n!$ to avoid over counting. leaving us with the above prefactor.

- For this distribution $\mu = Np$ and $\sigma = Np(1-p)$.

3.8.2 Multinomial distribution

- Generalisation of binomial, for when there are k possible outcomes, with $k > 2$ and so P_i, $i = 1, 2, ..., k$. Then we we can write:

$$Pr[X_1 = n_1, X_2 = n_2, ..., X_k = n_k,] = \frac{N!}{n_1! n_2! ... n_k!} P_1^{n_1} P_2^{n_2} ... P_k^{n_k} \tag{3.7}$$

Where the total number of trials is $\sum_{i=1}^{k} n_i = N$. As well as $\sum_{i=1}^{k} P_i = 1$.

3.8.3 Poisson distribution

- This distribution that gives us the probability of k events to occur in a fixed time or space interval given that we know that these events occur at a constant rate r in a fixed time interval t:

$$Pr[X = k] = e^{-rt}\frac{(rt)^k}{k!} \tag{3.8}$$

  Or if we know that the average number of events in this given interval is λ:

$$Pr[X = k] = e^{-\lambda}\frac{\lambda^k}{k!} \tag{3.9}$$

- For this distribution both $\mu = \sigma = \lambda$.

3.8.4 Gaussian distribution

- Is the most common important continuous distribution. Applies to most random phenomena with given average μ and standard deviation σ. The distribution takes the form:

$$\rho(x) = \frac{1}{\sqrt{2\pi\sigma}}e^{-\frac{(x-\mu)^2}{2\sigma^2}} \tag{3.10}$$

3.9 Central limit theorem

- Suppose that X_i, $i = 1, 2, ..., N$ are random independent variables with the same probability distribution $\rho(x)$. If we define a new random variable $Y = X_1 + X_2 + ... + X_N$, then in the limit as $N \to \infty$ (In practise we have $N >> 1$). Then the probability distribution $Pr[y \leq Y \leq y + dy] = \rho(y)dy$, is a Gaussian distribution.

4 Statistical mechanics

- Thermodynamic Laws are an essential consequence of statistics and fundamental laws of nature (here mechanics) i.e. fundamental physics governing the behaviour of the constituents of the system.

4.1 Macro and microscopic description

- The goal of statistical mechanics is to relate thermodynamic quantities E, V and N with the set $\{p_i, q_i\}, i = 1, 2, ..., 3N$. The set $\{p_i, q_i\}$ defines the microstate of the system, where as E, V, N characterise the macrostate.
- Each particle in a system has energy $E_k = E_k(x_i, p_i)$, this implies the total energy E is:

$$E = \sum_k n_k E_k \tag{4.1}$$

Where n_k is the occupation number, i.e. the number of constituents with a given energy E_k. In general many micro states will "realise" a given macrostate. Here "realise" is the word Manuela uses, as an alternate definition of realise is "cause to happen".

4.2 Ensemble

- Is a collection of a very large number of identical systems differing only in initial conditions, expected to realise all the possible micro-states of a given macrostate.

4.3 Phase space

- The appropriate formalism for classical systems requires considering the phase space. The phase space is defined by the aforementioned mentioned set $\{p_i, q_i\}$, which has dimensionality $6N$, (q_i, p_i) defines a point in the phase space. The Energy is determined by the Hamiltonian of the system $\mathcal{H}(q_i, p_i)$. The Hamiltonian has the property:

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}, \quad i = 1, 2, ..., 3N \tag{4.2}$$

For isolated systems we have that:

$$\frac{d\mathcal{H}}{dt} = \frac{\partial \mathcal{H}}{\partial t} = 0 \implies \mathcal{H} = E = \text{preserved} \tag{4.3}$$

- The possible micro-states realising a given macrostate belong to a subspace of the total phase space which satisfy $\mathcal{H}(q_i, p_i) = E$. The dimensionality of this subspace is $6N - 1$, always one less then the full phase space dimension.

Any easy example of this is the harmonic oscillator. In 1-D we know the particle traces out an ellipse in the phase space, with the size of the ellipse being related to the energy of the particle. Here the particles path is in a 1-D subspace (the ellipse) of the 2-D plane of the phase space.

In practise E being a continuous variable, makes sense to ask or expect that $E - \frac{1}{2}\Delta E \leq \mathcal{H} \leq E + \frac{1}{2}\Delta E$ or equivalently:

$$E \leq \mathcal{H} \leq E + \Delta E, \qquad \frac{\Delta E}{E} << 1 \tag{4.4}$$

In this case the space available to the system is not a hypersurface, but the volume of a thin shell included between the hypersurfaces defined by E and $E + \Delta E$.

4.4 Number of microstates

- The number of microstates ($\{q_i, p_i\}$) realising an energy E is denoted Ω. In general we would expect that the infinitesimal of this quantity is related to the infinitesimal of the phase space volume, i.e. $\delta\Omega \sim \delta V$. This is just saying that if there are more possible values for the position and momentum then there should be more possible configurations with the same energy. More precisely we write:

$$\delta\Omega = \rho(q, p, t)\delta q \delta p \tag{4.5}$$

Here q and p represent all the momenta and all the positions, this means: $q = \{q_i\}$ and $p = \{p_i\}$. The quantity $\rho(q, p, t)$ is the density of microstates. We can consider this as the number of microstates divided by the phase space volume.

The quantity $\delta q \delta p$ is the phase space available to a given microstate. This can be written as:

$$\delta q \delta p = \frac{dq dp}{\gamma_0} \tag{4.6}$$

Here γ_0 is the volume associated to a single microstate, to be related to Heisenberg's uncertainty principle. dq and dp are the regular differentials for momentum and position defined as:

$$dq = \prod_{i=1}^{3N} dq_i, \quad dp = \prod_{i=1}^{3N} dp_i \tag{4.7}$$

In general classical physics is valid so long as $\frac{dqdp}{\gamma_0} >> 1 \implies \delta\Omega >> 1$. Now we can then integrate the

above expression for $\delta\Omega$, equation 4.5:

$$\Omega(E \leq \mathcal{H} \leq E + \Delta E, V, N) = \int \frac{dqdp}{\gamma_0}\rho(q,p,t)$$
$$\implies \Omega(E,V,N) = \int_\Gamma \frac{dqdp}{\gamma_0}\rho(q,p,t) \tag{4.8}$$

Where Γ = phase space constraints. Equivalent to saying integrating over all the available phase space.

4.5 Probability distribution

- The probability distribution Pr is defined as:

$$Pr(q,p,t) \equiv \frac{\rho(q,p,t)}{\Omega} = \frac{\text{number of microstates in } \delta V}{\text{total number of microstates}} \tag{4.9}$$

Then the average of any physical quantity $f(q,p)$ can be found from:

$$\langle f \rangle = \int_\Gamma \frac{dqdp}{\gamma_0} f(q,p) Pr(q,p,t) \tag{4.10}$$

Where Γ is once again the phase space available to the system.

4.5.1 Liouville's theorem

- Tells us that the distribution function (for us $Pr(q,p,t)$) is constant along any trajectory in phase space. Mathematically this means:

$$\frac{dPr}{dt} = 0 \tag{4.11}$$

This can be restated in terms of the Poisson bracket, which for two functions $f(p_i, q_i, t)$ and $g(p_i, q_i, t)$, is defined as:

$$\{f,g\} = \sum_i^N \left(\frac{\partial f}{\partial q_i}\frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial q_i} \right) \tag{4.12}$$

the Poisson bracket also has that for $f(p_i, q_i, t)$:

$$\frac{df}{dt} = \{f, H\} + \frac{\partial f}{\partial t} \tag{4.13}$$

So we can re-write 4.11 as:

$$\frac{\partial Pr}{\partial t} = -\{Pr, H\} \tag{4.14}$$

4.5.2 Conservative system probability distribution

- For conservative systems we have that $\frac{\partial Pr}{\partial t} = 0$. So using the above equation 4.14 this can be written as

$$\begin{aligned} 0 = \sum_i^N \left(\frac{\partial Pr}{\partial f}\frac{\partial f}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial Pr}{\partial f}\frac{\partial f}{\partial p_i}\frac{\partial H}{\partial q_i} \right) = \frac{\partial Pr}{\partial f}\{f, H\} \\ \implies \{f, H\} = 0 \end{aligned} \tag{4.15}$$

  Where the last step is due to f being arbitrary and we want $Pr(f)$ so $\frac{\partial Pr}{\partial f} \neq 0$. This allows us to write $Pr = Pr(f(q, p))$. So no time dependence as long as $\{f, H\} = 0$.

- We can choose the simplest form for $f(q, p)$, $f = H$. This means that for isolated systems:

$$Pr(\mathcal{H}) = \begin{cases} \text{constant}, & E \leq \mathcal{H} \leq E + \Delta E \\ 0, & \text{otherwise} \end{cases} \tag{4.16}$$

  This is the case as for isolated systems $\mathcal{H}$ is a constant and we also know Pr must vanish when not very near the value of the energy of the system E.

4.6 Microcanonical ensemble

- Ensemble (large number) of isolated identical systems (in terms of structure & Hamilton dynamics) which differ in initial conditions. All possible microstates are then expected to be observed within the ensemble (all microstates which realise a given energy).
- The average of a quantity over a microcanonical ensemble is the same as a time average of that quantity over one ensemble.

$$\langle f \rangle_{ensemble} = \langle f \rangle_{time} \tag{4.17}$$

4.7 Density of microstates

- We know that the probability over the phase space available to the system Γ must be 1 so:

$$\int_\Gamma Pr \frac{dqdp}{\gamma_0} = 1 \implies Pr = \frac{1}{\Gamma} \tag{4.18}$$

We also assume that all states have equal probabilities, so the probability distribution Pr can also be written as:

$$Pr = \frac{1}{\Omega} \implies \rho(q,p) = 1 \tag{4.19}$$

This result makes sense as we would expect the number of microstates to be contingent on how we can change the positions of particles in the phase space and it wouldn't make any sense if the density of microstates was any different to the density of phase space points. This all means we can write Ω as:

$$\Omega = \int_\Gamma \frac{dqdp}{\gamma_0} = \Gamma \tag{4.20}$$

- We are interested in the number of microstates with energies $E \leq \mathcal{H} \leq E + \Delta E$. For this we introduce a new quantity $W(E,V,N)$, the density of microstates of given $\{E,V,N\}$, such that:

$$\delta\Omega = W\delta E \tag{4.21}$$

This can be expressed as:

$$\delta\Omega = \int_{(\delta E)} \frac{dqdp}{\gamma_0} = \int_{H\leq E+\delta E} \frac{dqdp}{\gamma_0} - \int_{H\leq E} \frac{dqdp}{\gamma_0} \tag{4.22}$$

So in the limit as $\delta E \to \infty$

$$W(E,V,N) = \frac{\partial}{\partial E} \int_{H\leq E} \frac{dqdp}{\gamma_0} \tag{4.23}$$

4.8 Ideal Gas

- For an ideal gas it is assumed that all the particles are identical with mass m and non-interacting, so for N particles enclosed in a volume V in 3D space the Hamiltonian takes the form $\mathcal{H} = \sum_i^{3N} \frac{p_i^2}{2m}$.