Statistical Physics

Xander Byrne

Lent 2022

1 Fondamentali

1.1 Microcanonical Ensemble

Consider a totally isolated system consisting of a large number of particles; the system's total energy $\mathbf{E}$ is therefore fixed. The quantum state of the overall system, $|\psi\rangle$, is therefore given by $\hat{H}|\psi\rangle = \mathbf{E}|\psi\rangle$ where $\hat{H}$ is the system's Hamiltonian. With $\mathbf{N} \sim 10^{23}$ particles, there will be enormous degeneracy, and a real system constantly transitions between degenerate states.

The *principle of equal a priori probabilities* ($\mathfrak{PEAP}$) says that for an isolated system in equilibrium, all accessible microstates are equally likely. There is no reason why this should *not* be true. For the ME, then, if $\mathbf{\Omega}(\mathbf{E})$ is the number of states $|n\rangle$ which have energy $\mathbf{E}$, then the probability that the system is in a particular state $|m\rangle$ is

$$p_m = \begin{cases} 1/\mathbf{\Omega}(\mathbf{E}) & \text{if } |m\rangle \text{ has energy } \mathbf{E} \\ 0 & \text{otherwise} \end{cases}$$

1.1.1 Entropy $\mathbf{S}$

$$\boxed{\mathbf{S} \equiv k_B \ln \mathbf{\Omega}}$$

If two non-interacting systems have $\mathbf{\Omega}_1(\mathbf{E}_1)$ and $\mathbf{\Omega}_2(\mathbf{E}_2)$, then because whichever of the $\mathbf{\Omega}_1$ states system 1 happens to be in, there are $\mathbf{\Omega}_2$ possible states for system 2, $\mathbf{\Omega}_t(\mathbf{E}_1, \mathbf{E}_2) = \mathbf{\Omega}_1(\mathbf{E}_1)\mathbf{\Omega}_2(\mathbf{E}_2)$, and so $\mathbf{S}_t(\mathbf{E}_1, \mathbf{E}_2) = \mathbf{S}_1(\mathbf{E}_1) + \mathbf{S}_2(\mathbf{E}_2)$.

Suppose we *do* allow the systems to interact, with a fixed total energy $\mathbf{E}_t = \mathbf{E}_1 + \mathbf{E}_2$; the systems might be two boxes of gas with a removable divider between them. There are a large number of initial states of the overall system, but the number of final states is outrageously larger, because every initial state remains possible when the divider is removed, but there are now *also* an enormous number of *new* states accessible which involve some gas on both sides. Thus $\mathbf{\Omega}_t(\mathbf{E}_t) \geq \mathbf{\Omega}_1(\mathbf{E}_1)\mathbf{\Omega}_2(\mathbf{E}_2)$ and $\mathbf{S}_t \geq \mathbf{S}_1 + \mathbf{S}_2$: a statement of $2\mathfrak{LT}$. There are so many new possibilities, and $\mathfrak{PEAP}$ says they are all equally likely, so there is only a vanishing probability that the system will return to its initial state.

Now $\mathbf{E}_1 \in [0, \mathbf{E}_t]$ and $\mathbf{E}_2 = \mathbf{E}_t - \mathbf{E}_1$, so

$$\mathbf{\Omega}_t(\mathbf{E}_t) = \sum_{\mathbf{E}_{1i}} \mathbf{\Omega}_1(\mathbf{E}_{1i})\mathbf{\Omega}_2(\mathbf{E}_t - \mathbf{E}_{1i}) = \sum_{\mathbf{E}_{1i}} \exp\left[\frac{\mathbf{S}_1(\mathbf{E}_{1i}) + \mathbf{S}_2(\mathbf{E}_t - \mathbf{E}_{1i})}{k_B}\right]$$

where $\mathbf{E}_{1i}$ are the possible energies of system 1, and we assume $\mathbf{E}_t - \mathbf{E}_{1i}$ are possible energies of system 2. The exponent in the sum peaks very strongly at some particular $\mathbf{E}_{1i} = \mathbf{E}^*$, and that term dominates the sum. This maximum value is found by:

$$\frac{\partial}{\partial \mathbf{E}_1}[\mathbf{S}_1(\mathbf{E}_1) + \mathbf{S}_2(\mathbf{E}_t - \mathbf{E}_1)]\bigg|_{\mathbf{E}_1=\mathbf{E}^*} = 0 \qquad \Rightarrow \qquad \frac{\partial \mathbf{S}_1}{\partial \mathbf{E}_1}\bigg|_{\mathbf{E}_1=\mathbf{E}^*} = \frac{\partial \mathbf{S}_2}{\partial \mathbf{E}_2}\bigg|_{\mathbf{E}_2=\mathbf{E}_t-\mathbf{E}^*}$$

where we have de-discretised $\mathbf{E}_{1i} \to \mathbf{E}_1$ (energy levels are usually very close together). Approximating the sum by its maximum summand,

$$\mathbf{\Omega}_t(\mathbf{E}_t) \approx \exp\left[\frac{\mathbf{S}_1(\mathbf{E}^*) + \mathbf{S}_2(\mathbf{E}_t - \mathbf{E}^*)}{k_B}\right] \qquad \Rightarrow \qquad \mathbf{S}_t(\mathbf{E}_t) \approx \mathbf{S}_1(\mathbf{E}^*) + \mathbf{S}_2(\mathbf{E}^*)$$

1.1.2 Temperature T

$$\boxed{\frac{1}{\mathbf{T}} \equiv \frac{\partial \mathbf{S}}{\partial \mathbf{E}}}$$

By this definition, the two systems above are most likely to be found in a state where they have the same $\mathbf{T}$. Bringing together two systems of *different* temperatures, and allowing $\delta\mathbf{E}_1$ to be transferred from 2 to 1,

$$\delta\mathbf{S}_t = \frac{\partial \mathbf{S}_1}{\partial \mathbf{E}_1}\delta\mathbf{E}_1 - \frac{\partial \mathbf{S}_2}{\partial \mathbf{E}_2}\delta\mathbf{E}_1 = \left(\frac{1}{\mathbf{T}_1} - \frac{1}{\mathbf{T}_2}\right)\delta\mathbf{E}_1$$

and so given that $\delta\mathbf{S}_t > 0$ from $2\mathfrak{LT}$, if we want $\delta\mathbf{E}_1 > 0$ we require $\mathbf{T}_2 > \mathbf{T}_1$. Hot to cold.

1.1.3 Heat Capacity C

$$\boxed{\mathbf{C} \equiv \frac{\partial \mathbf{E}}{\partial \mathbf{T}}} \qquad \Rightarrow \qquad \frac{\partial \mathbf{S}}{\partial \mathbf{T}} = \frac{\partial \mathbf{S}}{\partial \mathbf{E}}\frac{\partial \mathbf{E}}{\partial \mathbf{T}} = \frac{\mathbf{C}}{\mathbf{T}} \qquad \Rightarrow \qquad \Delta\mathbf{S} = \int \frac{\mathbf{C}(\mathbf{T})}{\mathbf{T}}\,\mathrm{d}\mathbf{T}$$

1.1.4 Volume V and Pressure p

The meaning of $\mathbf{V}$ is clear. We can now write $\mathbf{S} = \mathbf{S}(\mathbf{E}, \mathbf{V})$, and hence

$$\mathrm{d}\mathbf{S} = \frac{\partial \mathbf{S}}{\partial \mathbf{E}}\bigg|_{\mathbf{V}}\mathrm{d}\mathbf{E} + \frac{\partial \mathbf{S}}{\partial \mathbf{V}}\bigg|_{\mathbf{T}}\mathrm{d}\mathbf{V} = \frac{1}{\mathbf{T}}\mathrm{d}\mathbf{E} + \frac{\partial \mathbf{S}}{\partial \mathbf{V}}\bigg|_{\mathbf{E}}\mathrm{d}\mathbf{V}$$
$$\Rightarrow \mathrm{d}\mathbf{E} = \mathbf{T}\,\mathrm{d}\mathbf{S} - \mathbf{T}\,\frac{\partial \mathbf{S}}{\partial \mathbf{V}}\bigg|_{\mathbf{E}}\mathrm{d}\mathbf{V}$$

For now, take my word that the second coefficient is $\mathbf{p}$:

$$\mathbf{p} = \mathbf{T}\frac{\partial \mathbf{S}}{\partial \mathbf{V}} \qquad \Rightarrow \qquad \boxed{\mathrm{d}\mathbf{E} = \mathbf{T}\,\mathrm{d}\mathbf{S} - \mathbf{p}\,\mathrm{d}\mathbf{V}} \qquad (1\mathfrak{LT})$$

Suppose we have two systems which can exchange volume (e.g. movable divider) and energy, but with fixed totals. The entropy of the system must be maximised at equilibrium, so if a small amount of energy and/or volume is exchanged the entropy will not change:

$$0 = \mathrm{d}\mathbf{S}_t = \mathrm{d}\mathbf{S}_1 + \mathrm{d}\mathbf{S}_2 = \frac{1}{\mathbf{T}_1}\mathrm{d}\mathbf{E}_1 + \frac{\mathbf{p}_1}{\mathbf{T}_1}\mathrm{d}\mathbf{V}_1 + \frac{1}{\mathbf{T}_2}\mathrm{d}\mathbf{E}_2 + \frac{\mathbf{p}_2}{\mathbf{T}_2}\mathrm{d}\mathbf{V}_2$$
$$= \left(\frac{1}{\mathbf{T}_1} - \frac{1}{\mathbf{T}_2}\right)\mathrm{d}\mathbf{E}_1 + \left(\frac{\mathbf{p}_1}{\mathbf{T}_1} - \frac{\mathbf{p}_2}{\mathbf{T}_2}\right)\mathrm{d}\mathbf{V}_1$$

To hold for any $\mathrm{d}\mathbf{E}_1$ and $\mathrm{d}\mathbf{V}_1$, we have that at equilibrium $\mathbf{T}_1 = \mathbf{T}_2$ and then $\mathbf{p}_1 = \mathbf{p}_2$.

1.2 Canonical Ensemble

Above we fixed a system's $\mathbf{E}$ and could find its $\mathbf{T}$. Alternatively, we may have a system with fixed $\mathbf{T}$ (like if the system is in contact with a large reservoir at $\mathbf{T}$), and then find its properties.

The total number of microstates of the whole system-reservoir situation is

$$\boldsymbol{\Omega}_t(\mathbf{E}_t) = \sum_{|n\rangle} \boldsymbol{\Omega}_r(\mathbf{E}_t - \mathbf{E}_n) = \sum_{|n\rangle} \exp\left(\frac{\mathbf{S}_r(\mathbf{E}_t - \mathbf{E}_n)}{k_B}\right)$$

where $\mathbf{E}_n \ll \mathbf{E}_t$ is the energy of the system's state $|n\rangle$ – note that we are summing over the *states*, not the energy levels: we may have $\mathbf{E}_m = \mathbf{E}_n$ but $m \neq n$. Note also that the number of microstates of the system in state $|n\rangle$ is 1: just $|n\rangle$. Expanding (and cutting down on ink),

$$\boldsymbol{\Omega}_t = \sum_n \exp\left(\frac{\mathbf{S}_r(\mathbf{E}_t) - \mathbf{E}_n\, \partial \mathbf{S}_r/\partial \mathbf{E}}{k_B}\right) = \boldsymbol{\Omega}_r(\mathbf{E}_t) \sum_n e^{-\mathbf{E}_n/k_B\mathbf{T}}$$

From $\mathfrak{PEAP}$, each of these $\boldsymbol{\Omega}_t$ states is equally likely. We can see that each system-state $|n\rangle$ contributes $\boldsymbol{\Omega}_r(\mathbf{E}_t)e^{-\mathbf{E}_n/k_B\mathbf{T}}$ of these, so the probability of the system being in state $|n\rangle$ is

$$p_n = \frac{1}{\mathbf{Z}} e^{-\mathbf{E}_n/k_B\mathbf{T}} \qquad \text{(Boltzmann)}$$

where $\mathbf{Z} \equiv \sum_m e^{-\mathbf{E}_m/k_B\mathbf{T}}$ is the *partition function*, summing over all microstates, is like a normalisation. Two independent systems at a common temperature with partition functions $\mathbf{Z}_1$ and $\mathbf{Z}_2$ can be assigned an overall partition function $\mathbf{Z}$:

$$\mathbf{Z} = \sum_m \sum_n e^{-(\mathbf{E}_m/k_B\mathbf{T})-(\mathbf{E}_n/k_B\mathbf{T})} = \sum_m e^{-(\mathbf{E}_m/k_B\mathbf{T})} \sum_n e^{-(\mathbf{E}_n/k_B\mathbf{T})} = \mathbf{Z}_1\mathbf{Z}_2$$

1.2.1 Energy Fluctuations

We define $\beta = (k_B\mathbf{T})^{-1}$, and hence $p_n = e^{-\beta\mathbf{E}_n}/\mathbf{Z}$ and $\mathbf{Z} = \sum e^{-\beta\mathbf{E}_m}$. The average energy of the system, which fluctuates in the canonical ensemble, is

$$\langle \mathbf{E} \rangle = \sum_n \mathbf{E}_n \frac{e^{-\beta\mathbf{E}_n}}{\mathbf{Z}} = -\frac{1}{\mathbf{Z}}\frac{\partial \mathbf{Z}}{\partial \beta} = -\frac{\partial \ln \mathbf{Z}}{\partial \beta}$$

$$\langle \mathbf{E}^2 \rangle = \sum_n \mathbf{E}_n^2 \frac{e^{-\beta\mathbf{E}_n}}{\mathbf{Z}} = \frac{1}{\mathbf{Z}}\frac{\partial^2 \mathbf{Z}}{\partial \beta^2}$$

$$\Rightarrow \Delta\mathbf{E}^2 \equiv \langle \mathbf{E}^2 \rangle - \langle \mathbf{E} \rangle^2 = \frac{1}{\mathbf{Z}}\frac{\partial^2 \mathbf{Z}}{\partial \beta^2} - \frac{1}{\mathbf{Z}^2}\frac{\partial \mathbf{Z}}{\partial \beta}\frac{\partial \mathbf{Z}}{\partial \beta} = \frac{\partial}{\partial \beta}\left[\frac{1}{\mathbf{Z}}\frac{\partial \mathbf{Z}}{\partial \beta}\right] = \frac{\partial^2 \ln \mathbf{Z}}{\partial \beta^2} = -\frac{\partial \langle \mathbf{E} \rangle}{\partial \beta}$$

The heat capacity $\mathbf{C}$ is defined slightly differently, as $\mathrm{d}\langle \mathbf{E} \rangle / \mathrm{d}\mathbf{T}$; hence $\Delta\mathbf{E}^2 = k_B\mathbf{T}^2\mathbf{C}$. Because both $\mathbf{E}$ and $\mathbf{C}$ are both proportional to $\mathbf{N}$, we have

$$\frac{\Delta \mathbf{E}}{\mathbf{E}} \propto \frac{\sqrt{\mathbf{C}}}{\mathbf{E}} \propto \frac{1}{\sqrt{\mathbf{N}}}$$

So in the thermodynamic limit $\mathbf{N} \to \infty$, the energy probability distribution is strongly peaked around $\langle \mathbf{E} \rangle$ and can be treated as fixed – the canonical ensemble then tends to the microcanonical ensemble with $\mathbf{E} = \langle \mathbf{E} \rangle$.

1.2.2 Entropy

The ensemble trick: consider a large ensemble of a large number W copies of whatever system is in question; suppose the probability distribution is p_n for each system to be in microstate $|n\rangle$, so $p_n W$ of the copies are in the microstate $|n\rangle$. The number of microstates of the whole ensemble is then:

$$\mathbf{\Omega} = \frac{W!}{\prod_n ([p_n W]!)} \qquad \Rightarrow \qquad \mathbf{S}_{\text{ens}} = k_B \ln(W!) - k_B \sum_n \ln([p_n W]!) = -k_B W \sum_n p_n \ln p_n$$

which we evaluate using Stirling's approximation and $\sum_n p_n = 1$. Now because $\mathbf{S}$ is extensive, we have that the entropy of a single system must then be

$$\boxed{\mathbf{S} = -k_B \sum_n p_n \ln p_n} \qquad \text{(Gibbs)}$$

Note that this was derived without assuming any particular probability distribution, so is general. For the microcanonical ensemble, we have

$$\mathbf{S}(\mathbf{E}) = -k_B \sum_{n|\mathbf{E}_n = \mathbf{E}} p_n \ln\left(\frac{1}{\mathbf{\Omega}(\mathbf{E})}\right) - k_B \sum_{m|\mathbf{E}_m \neq \mathbf{E}} 0 \ln 0 = k_B \ln \mathbf{\Omega}(\mathbf{E})$$

as before. For the canonical ensemble we instead have

$$\mathbf{S} = -k_B \sum_n p_n(-\beta \mathbf{E}_n - \ln \mathbf{Z}) = \frac{k_B \beta}{\mathbf{Z}} \sum_n e^{-\beta \mathbf{E}_n} \mathbf{E}_n + k_B \ln \mathbf{Z} = k_B \frac{\partial}{\partial \mathbf{T}}(\mathbf{T} \ln \mathbf{Z})$$

1.2.3 Free Energy $\boxed{\mathbf{F} = \mathbf{E} - \mathbf{T}\mathbf{S}}$

The Helmholtz free energy is a Legendre transform of $\mathbf{E}$, and is simply related to $\mathbf{Z}$:

$$\mathbf{F} = -\frac{\partial \ln \mathbf{Z}}{\partial \beta} - k_B \mathbf{T} \frac{\partial}{\partial \mathbf{T}}(\mathbf{T} \ln \mathbf{Z}) = k_B \mathbf{T}^2 \frac{\partial \ln \mathbf{Z}}{\partial \mathbf{T}} - k_B \mathbf{T} \frac{\partial}{\partial \mathbf{T}}(\mathbf{T} \ln \mathbf{Z}) = -k_B \mathbf{T} \ln \mathbf{Z}$$

1.3 Grand Canonical Ensemble

Consider a system whose numbers of particles $\mathbf{N}$ can change, so $\mathbf{S} = \mathbf{S}(\mathbf{E}, \mathbf{V}, \mathbf{N})$:

$$\mathrm{d}\mathbf{S} = \frac{1}{\mathbf{T}} \mathrm{d}\mathbf{E} + \frac{\mathbf{p}}{\mathbf{T}} \mathrm{d}\mathbf{V} - \frac{\boldsymbol{\mu}}{\mathbf{T}} \mathrm{d}\mathbf{N} \qquad \text{where} \qquad \boldsymbol{\mu} = -\mathbf{T} \left.\frac{\partial \mathbf{S}}{\partial \mathbf{N}}\right|_{\mathbf{E},\mathbf{V}}$$

Extending the argument in §1.1.4, but now allowing the systems to exchange particles too ($\mathbf{S}$ must now be stationary in another dimension, $\mathbf{N}$), we find that in equilibrium

$$0 = \left(\frac{1}{\mathbf{T}_1} - \frac{1}{\mathbf{T}_2}\right) \mathrm{d}\mathbf{E}_1 + \left(\frac{\mathbf{p}_1}{\mathbf{T}_1} - \frac{\mathbf{p}_2}{\mathbf{T}_2}\right) \mathrm{d}\mathbf{V}_1 + \left(-\frac{\boldsymbol{\mu}_1}{\mathbf{T}_1} + \frac{\boldsymbol{\mu}_2}{\mathbf{T}_2}\right) \mathrm{d}\mathbf{N}_1$$

so in equilibrium $\mathbf{T}_1 = \mathbf{T}_2$, then $\mathbf{p}_1 = \mathbf{p}_2$ and $\boldsymbol{\mu}_1 = \boldsymbol{\mu}_2$.

Rearranging for $\mathbf{E}$ gives an extension of the first law (and motivates the $-$ sign)

$$\mathrm{d}\mathbf{E} = \mathbf{T}\,\mathrm{d}\mathbf{S} - \mathbf{p}\,\mathrm{d}\mathbf{V} + \boldsymbol{\mu}\,\mathrm{d}\mathbf{N}$$

and hence $\boldsymbol{\mu} = \partial \mathbf{E}/\partial \mathbf{N}$, as could also be derived from its definition with some calculus.

In the Grand Canonical Ensemble, the system is connected to a reservoir of fixed $\mathbf{T}$ and $\boldsymbol{\mu}$ and large $\mathbf{E}$ and $\mathbf{N}$, and the system's $\mathbf{E}$ and $\mathbf{N}$ may both fluctuate; the system's microstates $|n\rangle$ each have their own energy $\mathbf{E}_n$ and a particle number $\mathbf{N}_n$. The total number of microstates of the system+reservoir is:

$$\begin{aligned}
\boldsymbol{\Omega}_t(\mathbf{E}_t, \mathbf{N}_t) &= \sum_n \boldsymbol{\Omega}_r(\mathbf{E}_t - \mathbf{E}_n, \mathbf{N}_t - \mathbf{N}_n) = \sum_n \exp\left(\frac{\mathbf{S}_r(\mathbf{E}_t - \mathbf{E}_n, \mathbf{N}_t - \mathbf{N}_n)}{k_B}\right) \\
&= \sum_n \exp\left(\frac{\mathbf{S}_r(\mathbf{E}_t, \mathbf{N}_t) - \mathbf{E}_n\, \partial \mathbf{S}_r/\partial \mathbf{E} - \mathbf{N}_n\, \partial \mathbf{S}_r/\partial \mathbf{N}}{k_B}\right) \\
&= \boldsymbol{\Omega}_r(\mathbf{E}_t, \mathbf{N}_t) \sum_n e^{-\mathbf{E}_n/k_B\mathbf{T} + \boldsymbol{\mu}\mathbf{N}_n/k_B\mathbf{T}} = \boldsymbol{\Omega}_r(\mathbf{E}_t, \mathbf{N}_t) \sum_n e^{-\beta(\mathbf{E}_n - \boldsymbol{\mu}\mathbf{N}_n)} \\
\Rightarrow p_n &= \frac{1}{\boldsymbol{\mathcal{Z}}} e^{-\beta(\mathbf{E}_n - \boldsymbol{\mu}\mathbf{N}_n)} \qquad \text{where} \qquad \boldsymbol{\mathcal{Z}} = \sum_m e^{-\beta(\mathbf{E}_m - \boldsymbol{\mu}\mathbf{N}_m)} = \sum_{\mathbf{N}=0}^{\infty} e^{\beta\boldsymbol{\mu}\mathbf{N}} \mathbf{Z}_{\mathbf{N}}
\end{aligned}$$

involving the grand canonical partition function; the last expression partitions the sum into terms with equal $\mathbf{N}$ and sums over those. We find

$$\begin{aligned}
\mathbf{S} &= k_B \frac{\partial}{\partial \mathbf{T}}(\mathbf{T} \ln \boldsymbol{\mathcal{Z}}) & \langle \mathbf{N} \rangle &= \frac{1}{\beta} \frac{\partial \ln \boldsymbol{\mathcal{Z}}}{\partial \boldsymbol{\mu}}\bigg|_{\mathbf{T}} \\
\langle \mathbf{E} \rangle - \boldsymbol{\mu} \langle \mathbf{N} \rangle &= -\frac{\partial \ln \boldsymbol{\mathcal{Z}}}{\partial \beta} & \Delta \mathbf{N}^2 &= \frac{1}{\beta^2} \frac{\partial^2 \ln \boldsymbol{\mathcal{Z}}}{\partial \boldsymbol{\mu}^2} = \frac{1}{\beta} \frac{\partial \langle \mathbf{N} \rangle}{\partial \boldsymbol{\mu}}\bigg|_{\mathbf{T}}
\end{aligned}$$

As with $\langle \mathbf{E} \rangle$ above, apparently $\Delta \mathbf{N}/\langle \mathbf{N} \rangle \propto \mathbf{N}^{-1/2}$, so in the thermodynamic limit $\langle \mathbf{N} \rangle \to \mathbf{N}$.

We define the *grand canonical potential* by

$$\boxed{\boldsymbol{\Phi} = \mathbf{F} - \boldsymbol{\mu}\mathbf{N}} = \mathbf{E} - \mathbf{T}\mathbf{S} - \boldsymbol{\mu}\mathbf{N} = -\frac{\partial \ln \boldsymbol{\mathcal{Z}}}{\partial \beta} - k_B \mathbf{T} \frac{\partial}{\partial \mathbf{T}}(\mathbf{T} \ln \boldsymbol{\mathcal{Z}}) = -k_B \mathbf{T} \ln \boldsymbol{\mathcal{Z}}$$

$$\Rightarrow \mathrm{d}\boldsymbol{\Phi} = -\mathbf{S}\mathrm{d}\mathbf{T} - \mathbf{p}\mathrm{d}\mathbf{V} - \mathbf{N}\mathrm{d}\boldsymbol{\mu} \qquad \Rightarrow \qquad \boldsymbol{\Phi} = \boldsymbol{\Phi}(\mathbf{T}, \mathbf{V}, \boldsymbol{\mu}) \qquad \text{and} \qquad \frac{\partial \boldsymbol{\Phi}}{\partial \mathbf{V}}\bigg|_{\mathbf{T},\boldsymbol{\mu}} = -\mathbf{p}$$

From its definition, $\boldsymbol{\Phi}$ is an extensive quantity, whereas the variables it depends on are all intensive except for $\mathbf{V}$. This implies that $\boldsymbol{\Phi}(\mathbf{T}, \mathbf{V}, \boldsymbol{\mu}) \propto \mathbf{V}$, and from its volume derivative we see that the proportionality constant must be $-\mathbf{p}(\mathbf{T}, \boldsymbol{\mu})$. Hence $\boldsymbol{\Phi}(\mathbf{T}, \mathbf{V}, \boldsymbol{\mu}) = -\mathbf{p}(\mathbf{T}, \boldsymbol{\mu})\mathbf{V}$.

2 Classical Gases

Everything can be derived from $\mathbf{Z}$, the sum over all states of $e^{-\beta\mathbf{E}}$. For a classical monatomic particle, its "state" is its position (q) and momentum (p), and hence for one particle:

$$\mathbf{Z}_1 = \frac{1}{h^3} \int \mathrm{d}^3 p \int \mathrm{d}^3 q\, e^{-\beta \mathbf{E}(p,q)}$$

where the h^3 (necessary for dimensional reasons) is descended from $\langle p|q \rangle = h^{-1/2} e^{-ipq/\hbar}$.

2.1 Ideal Gas

An ideal gas has $\mathbf{N}$ non-interacting particles, volume $\mathbf{V}$, and $\mathbf{E} = p^2/2m$ within $\mathbf{V}$ or $\mathbf{E} = \infty$ outside. Hence the canonical partition function for the whole gas is

$$\mathbf{Z} = \left(\frac{\mathbf{V}}{h^3}\int e^{-\beta|p|^2/2m}\mathrm{d}^3p\right)^{\mathbf{N}} = \left(\frac{\mathbf{V}}{h^3}\left(\sqrt{\frac{2m\pi}{\beta}}\right)^3\right)^{\mathbf{N}} = \left(\frac{\mathbf{V}}{\lambda^3}\right)^{\mathbf{N}} \qquad \text{where} \qquad \lambda = \frac{h}{\sqrt{2m\pi k_B\mathbf{T}}}$$

λ is the de Broglie wavelength of a particle with kinetic energy $\pi k_B\mathbf{T}$; note that thermodynamically its value depends only on $\mathbf{T}$; through λ, $\mathbf{Z} \propto \mathbf{T}^{3\mathbf{N}/2} \propto \beta^{-3\mathbf{N}/2}$. There should also be a factor of $\mathbf{N}!$ on the denominator to correct for the indistinguishability of the particles.

The free energy is $\mathbf{F} = -k_B\mathbf{T}\ln\mathbf{Z}$ and the pressure is $-\partial\mathbf{F}/\partial\mathbf{V}$, and hence

$$\mathbf{p} = k_B\mathbf{T}\frac{\partial}{\partial\mathbf{V}}\left[\mathbf{N}\ln\left(\frac{\mathbf{V}}{\lambda^3}\right) - \ln\mathbf{N}!\right] = \frac{\mathbf{N}k_B\mathbf{T}}{\mathbf{V}} \qquad \text{(Ideal Gas)}$$

The energy is given by

$$\mathbf{E} = -\frac{\partial}{\partial\beta}\ln\mathbf{Z} = -\frac{\partial}{\partial\beta}\left(-\frac{3\mathbf{N}}{2}\ln\beta + \mathbf{N}\ln\mathbf{V} + \text{ const.}\right) = \frac{3}{2}\mathbf{N}k_B\mathbf{T} \qquad \Rightarrow \qquad \mathbf{C_V} = \frac{3}{2}\mathbf{N}k_B$$

The entropy is:

$$\mathbf{S} = \frac{\partial}{\partial\mathbf{T}}(k_B\mathbf{T}\ln\mathbf{Z}) = k_B\ln\mathbf{Z} + k_B\mathbf{T}\frac{\partial\ln\mathbf{Z}}{\partial\mathbf{T}} = \mathbf{N}k_B\left[\frac{5}{2} + \ln\left(\frac{\mathbf{V}}{\mathbf{N}\lambda^3}\right)\right] \qquad (\mathfrak{ST})$$

Note that if the $\mathbf{N}!$ were not included we would have instead $\mathbf{S} = \mathbf{N}k_B[3/2 + \ln(\mathbf{V}/\lambda^3)]$, which is not extensive in its dependence on $\mathbf{V}$. $\mathfrak{ST}$ gives an extensive $\mathbf{S}$.

Alternatively, we can derive stuff using the grand canonical ensemble instead:

$$\boldsymbol{\mathcal{Z}} = \sum_{\mathbf{N}=0}^{\infty} e^{\beta\boldsymbol{\mu}\mathbf{N}}\mathbf{Z}_{\mathbf{N}} = \sum_{\mathbf{N}=0}^{\infty}\frac{1}{\mathbf{N}!}\left(\frac{e^{\beta\boldsymbol{\mu}}\mathbf{V}}{\lambda^3}\right)^{\mathbf{N}} = \exp\left(\frac{e^{\beta\boldsymbol{\mu}}\mathbf{V}}{\lambda^3}\right)$$

$$\Rightarrow \mathbf{N} \approx \langle\mathbf{N}\rangle = \frac{1}{\beta}\frac{\partial\ln\boldsymbol{\mathcal{Z}}}{\partial\boldsymbol{\mu}} = \frac{e^{\beta\boldsymbol{\mu}}\mathbf{V}}{\lambda^3} \qquad \Rightarrow \qquad \boldsymbol{\mu} = k_B\mathbf{T}\ln\left(\frac{\mathbf{N}\lambda^3}{\mathbf{V}}\right) < 0$$

$$\Rightarrow \mathbf{p}\mathbf{V} = -\boldsymbol{\Phi} = k_B\mathbf{T}\ln\boldsymbol{\mathcal{Z}} = k_B\mathbf{T}\frac{e^{\beta\boldsymbol{\mu}}\mathbf{V}}{\lambda^3} = \mathbf{N}k_B\mathbf{T}$$

2.1.1 Maxwell Distribution

Doing the partition integral for one particle and converting to velocity,

$$\mathbf{Z}_1 = \frac{1}{h^3}\int\mathrm{d}^3p\int\mathrm{d}^3q e^{-\beta|p|^2/2m} \propto \int\mathrm{d}^3v e^{-mv^2/2k_B\mathbf{T}} \propto \int_0^\infty v^2 e^{-mv^2/2k_B\mathbf{T}}\,\mathrm{d}v$$

As $\mathbf{Z}_1$ is proportional to the sum over states of the probabilities of occupation of those states, we deduce that the (normalised) velocity distribution of a gas particle is

$$f(v) = \left(\frac{m}{2\pi k_B\mathbf{T}}\right)^{3/2} 4\pi v^2 e^{-mv^2/2k_B\mathbf{T}}$$

From which we find that $\langle v^2\rangle = 3k_B\mathbf{T}/m$, and hence $\langle\mathbf{E}\rangle = m\langle v^2\rangle/2 = 3k_B\mathbf{T}/2$, as expected from the above result for the energy of an ideal gas.

2.1.2 Classical Diatomic Gases

Diatomic molecules have rotational and vibrational degrees of freedom which modify their (as yet solely translational) partition function. Assuming their translational, rotational, and vibrational motions are independent, we can write $\mathbf{Z}_1 = \mathbf{Z}_t\mathbf{Z}_r\mathbf{Z}_v$; we now deduce the latters.

Rotational. Modelling the molecule as a thin rigid rod of moment of inertia I,

$$\mathcal{L} = \frac{I}{2}\left(\dot\theta^2 + \sin^2\theta\dot\phi^2\right) \qquad \Rightarrow \qquad p_\theta = I\dot\theta; \qquad p_\phi = I\sin^2\theta\dot\phi$$

$$\Rightarrow \mathbf{E}(p_\theta, p_\phi, \theta, \phi) = p_\theta\dot\theta + p_\phi\dot\phi - \mathcal{L} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta}$$

$$\Rightarrow \mathbf{Z}_r = \frac{1}{h^2}\int \mathrm{d}\theta\mathrm{d}\phi \int \mathrm{d}p_\theta\,\mathrm{d}p_\phi\, e^{-\beta p_\theta^2/2I} e^{-\beta p_\phi^2/2I\sin^2\theta} = \frac{2\pi}{h^2}\int_0^\pi \mathrm{d}\theta \sqrt{\frac{2\pi I}{\beta}}\sqrt{\frac{2\pi I\sin^2\theta}{\beta}} = \frac{2Ik_B\mathbf{T}}{\hbar^2}$$

$$\Rightarrow \langle \mathbf{E}_r\rangle = -\frac{\partial \ln \mathbf{Z}_r}{\partial\beta} = k_B\mathbf{T}$$

as might be expected from equipartition since there are two DoF associated with rotation. Note the factor in front of the integral is $1/h^2$ as there are two dimensions of motion.

Vibrational. Modelling the molecule as a spring of frequency ω whose atoms deviate from equilibrium by a distance ζ, we have

$$\mathbf{E}(\zeta, p_\zeta) = \frac{p_\zeta^2}{2m} + \frac{1}{2}m\omega^2\zeta^2$$

$$\Rightarrow \mathbf{Z}_v = \frac{1}{h}\int \mathrm{d}p_\zeta e^{-\beta p_\zeta^2/2m}\int \mathrm{d}\zeta e^{-\beta m\omega^2\zeta^2/2} = \frac{1}{h}\sqrt{\frac{2m\pi}{\beta}}\sqrt{\frac{2\pi}{\beta m\omega^2}} = \frac{k_B\mathbf{T}}{\hbar\omega}$$

$$\Rightarrow \langle \mathbf{E}_v\rangle = -\frac{\partial \ln \mathbf{Z}_v}{\partial\beta} = k_B\mathbf{T}$$

The unexpected degree of freedom comes from the potential energy of the spring.

The overall partition function for a diatomic molecule is thus

$$\mathbf{Z}_1 = \mathbf{Z}_t\mathbf{Z}_r\mathbf{Z}_v = \frac{\mathbf{V}}{\lambda^3}\frac{2Ik_B\mathbf{T}}{\hbar^2}k_B\mathbf{T} \propto \beta^{-7/2} \qquad \Rightarrow \qquad \mathbf{E} = -\frac{\partial\ln\mathbf{Z}}{\partial\beta} = \frac{7}{2\beta} = \frac{7}{2}k_B\mathbf{T}$$

For a gas of $\mathbf{N}$ diatomic molecules, the partition function again scales to the power of $\mathbf{N}$, hence the energy becomes $\frac{7}{2}\mathbf{N}k_B\mathbf{T}$ and the specific heat $\frac{7}{2}\mathbf{N}k_B$. However, at lower temperatures some degrees of freedom are "frozen out" and so do not contribute to this (see §3.1.3).

2.2 Interacting Gases

At low $\mathbf{N}/\mathbf{V}$, any gas behaves like an ideal gas; more generally

$$\frac{\mathbf{p}}{k_B\mathbf{T}} = \frac{\mathbf{N}}{\mathbf{V}} + B_2(\mathbf{T})\left(\frac{\mathbf{N}}{\mathbf{V}}\right)^2 + \dots$$

where $B_i(\mathbf{T})$ are "virial coefficients". The B_i can be computed from the potential $U(r)$ between two atoms separated by a distance r. The partition function is:

$$\mathbf{Z} = \frac{1}{\mathbf{N}!}\frac{1}{h^{3\mathbf{N}}}\int\left(\prod_{i=1}^{\mathbf{N}}\mathrm{d}^3p_i\,\mathrm{d}^3r_i\right)e^{-\beta\left(\sum_j p_j^2/2m + \sum_{j,k<j}U(r_{jk})\right)}$$

$$= \frac{1}{\mathbf{N}!}\frac{1}{h^{3\mathbf{N}}}\left[\prod_{i=1}^{\mathbf{N}}\int \mathrm{d}^3 p_i\, e^{-\beta p_i^2/2m}\right]\left[\int\left(\prod_{i=1}^{\mathbf{N}}\mathrm{d}^3 r_i\right) e^{-\beta\sum_{j,k<j}U(r_{jk})}\right]$$
$$= \frac{1}{\mathbf{N}!\lambda^{3\mathbf{N}}}\int\left(\prod_{i=1}^{\mathbf{N}}\mathrm{d}^3 r_i\right) e^{-\beta\sum_{j,k<j}U(r_{jk})}$$

which is a hard integral and doesn't separate. Defining the Mayer f function

$$f(r) \equiv e^{-\beta U(r)} - 1; \qquad\qquad f_{ij} \equiv f(r_{ij})$$

and noting that $f(\infty) \to 0$, we can approximate the integral:

$$\begin{aligned}
\mathbf{Z} &= \frac{1}{\mathbf{N}!\lambda^{3\mathbf{N}}}\int\left(\prod_{i=1}^{\mathbf{N}}\mathrm{d}^3 r_i\right)\prod_{j,k<j}^{\mathbf{N}}(1+f_{jk}) \approx \frac{1}{\mathbf{N}!\lambda^{3\mathbf{N}}}\int\left(\prod_{i=1}^{\mathbf{N}}\mathrm{d}^3 r_i\right)\left(1+\sum_{j,k<j}f_{jk}\right)\\
&= \frac{1}{\mathbf{N}!\lambda^{3\mathbf{N}}}\left[\mathbf{V}^{\mathbf{N}} + \sum_{j,k<j}\int\left(\prod_{i=1}^{\mathbf{N}}\mathrm{d}^3 r_i\right) f_{jk}\right]\\
&= \frac{1}{\mathbf{N}!\lambda^{3\mathbf{N}}}\left[\mathbf{V}^{\mathbf{N}} + \mathbf{V}^{\mathbf{N}-2}\sum_{j,k<j}\int \mathrm{d}^3 r_j\,\mathrm{d}^3 r_k\, f(r_{jk})\right] = \frac{1}{\mathbf{N}!\lambda^{3\mathbf{N}}}\left[\mathbf{V}^{\mathbf{N}} + \mathbf{V}^{\mathbf{N}-1}\overbrace{\sum_{j,k<j}}^{\approx\mathbf{N}^2/2}\overbrace{\int \mathrm{d}^3 r\, f(r)}^{I}\right]\\
&= \frac{1}{\mathbf{N}!\lambda^{3\mathbf{N}}}\left[\mathbf{V}^{\mathbf{N}} + \mathbf{V}^{\mathbf{N}-1}\frac{\mathbf{N}^2}{2}I\right] = \frac{\mathbf{V}^{\mathbf{N}}}{\mathbf{N}!\lambda^{3\mathbf{N}}}\left[1+\frac{\mathbf{N}^2}{2\mathbf{V}}I\right] \approx \frac{\mathbf{V}^{\mathbf{N}}}{\mathbf{N}!\lambda^{3\mathbf{N}}}\left(1+\frac{\mathbf{N}}{2\mathbf{V}}I\right)^{\mathbf{N}}
\end{aligned}$$

where the "massaging" at the end will make things properly extensive. To find the equation of state from this, note that $\mathbf{F} = -k_B\mathbf{T}\ln\mathbf{Z}$, and $\mathrm{d}\mathbf{F} = -\mathbf{p}\mathrm{d}\mathbf{V} - \mathbf{S}\mathrm{d}\mathbf{T}$ so

$$\mathbf{p} = -\left.\frac{\partial\mathbf{F}}{\partial\mathbf{V}}\right|_{\mathbf{T}} = k_B\mathbf{T}\frac{\partial\ln\mathbf{Z}}{\partial\mathbf{V}} = k_B\mathbf{T}\left[\frac{\mathbf{N}}{\mathbf{V}} - \frac{I}{2}\left(\frac{\mathbf{N}}{\mathbf{V}}\right)^2 + \mathcal{O}\left(\frac{\mathbf{N}}{\mathbf{V}}\right)^3\right]$$

Hence the second virial coefficient is $B_2(\mathbf{T}) = -\frac{1}{2}\int \mathrm{d}^3 r\left(e^{-\beta U(r)} - 1\right)$.

3 Quantum Gases

Back to non-interacting particles. A single particle has a partition function $\mathbf{Z}_1 = \sum_m e^{-\beta\mathbf{E}_m}$, where the sum is over all states of the system. It will be more convenient to approximate this sum as an integral over energy, so to do the sum over all states we need to know how many states have a given energy – the *density of states* $g(\mathbf{E})$.

Take a cubic volume $\mathbf{V} = L^3$; the states are something like $\psi_{\mathbf{k}} \propto \exp(i\mathbf{k}\cdot\mathbf{r})$, where $\mathbf{k}$ takes the values $2\pi\mathbf{n}/L$ with $\mathbf{n} \in \mathbb{N}^3$, and hence every state takes up a volume $(2\pi)^3/\mathbf{V}$ in $\mathbf{k}$-space. The number of states with $k = |\mathbf{k}| \in [k, k+\mathrm{d}k]$ is then

$$g_k(k)\,\mathrm{d}k = \frac{4\pi k^2\,\mathrm{d}k}{8\pi^3/\mathbf{V}} = \frac{\mathbf{V}}{2\pi^2}k^2\,\mathrm{d}k \qquad \Rightarrow \qquad g_k(k) = \frac{\mathbf{V}}{2\pi^2}k^2$$

For non-relativistic systems, we have $\mathbf{E} = (\hbar^2/2m)k^2 \Rightarrow k = \sqrt{2m\mathbf{E}/\hbar^2}$. Hence

$$g(\mathbf{E}) = g_k(k)\frac{\mathrm{d}k}{\mathrm{d}\mathbf{E}} = \frac{\mathbf{V}}{2\pi^2}\left(\frac{2m\mathbf{E}}{\hbar^2}\right)\frac{1}{2}\sqrt{\frac{2m}{\mathbf{E}\hbar^2}} = \frac{\mathbf{V}}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mathbf{E}^{1/2}$$

For relativistic systems, we instead have $\mathbf{E} = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4} \Rightarrow k = \frac{1}{\hbar c}\sqrt{\mathbf{E}^2 - m^2 c^4}$, so

$$g(\mathbf{E}) = \frac{\mathbf{V}}{2\pi^2}\left(\frac{\mathbf{E}^2 - m^2c^4}{\hbar^2 c^2}\right)\frac{1}{\hbar c}\frac{\mathbf{E}}{\sqrt{\mathbf{E}^2 - m^2c^4}} = \frac{\mathbf{V}}{2\pi^2\hbar^3 c^3}\mathbf{E}\sqrt{\mathbf{E}^2 - m^2c^4} \to \frac{\mathbf{V}}{2\pi^2\hbar^3 c^3}\mathbf{E}^2$$

where the limit at the end is that of zero mass.

3.1 Warmup Systems

3.1.1 Photons AKA Blackbody Radiation

Traditionally we work with $\omega = \mathbf{E}/\hbar$ rather than $\mathbf{E}$. A state can have any number of photons, so consider the partial canonical partition function for one particular pair of ω and $\mathbf{k}$:

$$\mathbf{Z}_{\omega,\mathbf{k}} = \sum_{N=0}^{\infty} e^{-\beta N\hbar\omega} = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

For a given ω, there are $g_\omega(\omega)\,\mathrm{d}\omega = 2g(\mathbf{E})\,\mathrm{d}\mathbf{E}$ different possible values of $\mathbf{k}$ and polarisation (there are 2 transverse polarisation states in each $\mathbf{k}$-state), each of which have the same $\mathbf{Z}_{\omega,\mathbf{k}}$, so the partition function for the frequency ω is then

$$\mathbf{Z}_\omega = (\mathbf{Z}_{\omega,\mathbf{k}})^{g_\omega(\omega)\mathrm{d}\omega}$$

which looks less silly when lned. The overall partition function $\mathbf{Z}$ would be a product of all the $\mathbf{Z}_\omega$ (assuming photons of different frequencies don't interact), but that would involve a product integral (which is apparently a thing). Instead, consider

$$\ln \mathbf{Z} = \int_{\omega=0}^{\infty} \ln \mathbf{Z}_\omega = -\int_0^\infty \ln\left(1 - e^{-\beta\hbar\omega}\right) g_\omega(\omega)\,\mathrm{d}\omega$$

Substituting for $g(\omega)\mathrm{d}\omega = 2g(\mathbf{E})\mathrm{d}\mathbf{E}$ in the massless relativistic case,

$$\ln \mathbf{Z} = -\int_0^\infty \ln\left(1 - e^{-\beta\hbar\omega}\right)\frac{2\mathbf{V}}{2\pi^2\hbar^3c^3}(\hbar\omega)^2\mathrm{d}(\hbar\omega) = -\frac{\mathbf{V}}{\pi^2c^3}\int_0^\infty \omega^2 \ln\left(1 - e^{-\beta\hbar\omega}\right)\mathrm{d}\omega$$

With this, we can calculate stuff like the energy

$$\mathbf{E} = -\frac{\partial \ln \mathbf{Z}}{\partial\beta} = \frac{\mathbf{V}}{\pi^2c^3}\int_0^\infty \frac{\omega^2\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}\,\mathrm{d}\omega = \int_0^\infty \frac{\mathbf{V}\hbar}{\pi^2c^3}\frac{\omega^3\,\mathrm{d}\omega}{e^{\beta\hbar\omega} - 1} = \mathbf{V}\overbrace{\frac{\pi^2k_B^4}{15c^3\hbar^3}}^{a}\mathbf{T}^4 = \mathbf{V}a\mathbf{T}^4$$

Hence the heat capacity $\mathbf{C_V} \equiv \mathrm{d}\mathbf{E}/\mathrm{d}\mathbf{T}\,\big|_{\mathbf{V}} = 4\mathbf{V}a\mathbf{T}^3$. From an intermediate stage above we can identify the spectral energy density $\mathbf{E}_\omega(\omega)$:

$$\boxed{\mathbf{E}_\omega(\omega) = \frac{\mathbf{V}\hbar}{\pi^2c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}} \qquad \text{(Planck)}$$

We can also calculate the free energy by integrating by parts:

$$\mathbf{F} = -k_B\mathbf{T}\ln\mathbf{Z} = k_B\mathbf{T}\frac{\mathbf{V}}{\pi^2c^3}\int_0^\infty \omega^2\ln\left(1 - e^{-\beta\hbar\omega}\right)\mathrm{d}\omega = -\frac{\mathbf{E}}{3}$$

from which we can calculate the pressure and entropy, as $\mathrm{d}\mathbf{F} = -\mathbf{p}\mathrm{d}\mathbf{V} - \mathbf{S}\mathrm{d}\mathbf{T}$, so:

$$\mathbf{p} = -\left.\frac{\partial\mathbf{F}}{\partial\mathbf{V}}\right|_{\mathbf{T}} = \frac{a\mathbf{T}^4}{3} = \frac{\mathbf{E}}{3\mathbf{V}} \qquad \mathbf{S} = -\left.\frac{\partial\mathbf{F}}{\partial\mathbf{T}}\right|_{\mathbf{V}} = \frac{4\mathbf{V}}{3}a\mathbf{T}^3 = \frac{4\mathbf{E}}{3\mathbf{T}}$$

3.1.2 Phonons

Sound waves propagating through solids can be treated as massless gas particles with energy $\hbar\omega$. The density of states is the same as photons except with c replaced by c (the speed of sound in the material) and the 2 polarisation states replaced by 3 (longitudinal too):

$$g_\omega(\omega) = \frac{3\mathbf{V}}{2\pi^2 c^3}\omega^2$$

Also, there is a maximum frequency ω_D. The total number of phonons is apparently equal to the number of degrees of freedom of the system, which is $3\mathbf{N}$, so

$$3\mathbf{N} = \int_0^{\omega_D} \frac{3\mathbf{V}}{2\pi^2 c^3}\omega^2 \,\mathrm{d}\omega = \frac{\mathbf{V}}{2\pi^2 c^3}\omega_D^3 \qquad \Rightarrow \qquad \omega_D = \left(\frac{6\pi^2\mathbf{N}}{\mathbf{V}}\right)^{1/3} c$$

As with photons, the number of phonons in one state is unlimited, so we can modify the photon expressions with something like $c^3 \to 2c^3/3$ and changing the integrals' upper bounds:

$$\mathbf{E} = \frac{3\mathbf{V}\hbar}{2\pi^2 c^3}\int_0^{\omega_D} \frac{\omega^3\,\mathrm{d}\omega}{e^{\beta\hbar\omega}-1} = \frac{3\mathbf{V}\hbar}{2\pi^2 c^3}\left(\frac{1}{\beta\hbar}\right)^4 \int_0^{\hbar\omega_D/k_B\mathbf{T}} \frac{x^3\,\mathrm{d}x}{e^x-1} = \mathbf{V}\frac{3k_B^4\mathbf{T}^4}{2\pi^2 c^3\hbar^3}\int_0^{\mathbf{T}_D/\mathbf{T}} \frac{x^3\,\mathrm{d}x}{e^x-1}$$

where we have substituted the Debye temperature $\mathbf{T}_D = \hbar\omega_D/k_B$. The proper integral has no analytic solution, but the limits of high and low temperature are analytic.

For $\mathbf{T} \gg \mathbf{T}_D$, the integral is between 0 and a small number, so x is never very big and $e^x - 1 \approx 1 + x - 1 = x$. Thus the integral is of x^2 and we have

$$\mathbf{E}(\mathbf{T} \gg \mathbf{T}_D) \approx \mathbf{V}\frac{k_B^4\mathbf{T}^4}{2\pi^2 c^3\hbar^3}\left(\frac{\mathbf{T}_D}{\mathbf{T}}\right)^3 \qquad \Rightarrow \qquad \mathbf{C_V} \approx \mathbf{V}\frac{k_B^4}{2\pi^2 c^3\hbar^3}\mathbf{T}_D^3 = 3\mathbf{N}k_B$$

For $\mathbf{T} \ll \mathbf{T}_D$, the integral tends to the improper value of $\pi^4/15$, so

$$\mathbf{E}(\mathbf{T} \ll \mathbf{T}_D) \approx \mathbf{V}\frac{\pi^2 k_B^4\mathbf{T}^4}{10c^3\hbar^3} \qquad \Rightarrow \qquad \mathbf{C_V} \approx \mathbf{V}\frac{2\pi^2 k_B^4\mathbf{T}^3}{5c^3\hbar^3} = \frac{12\pi^4}{5}\mathbf{N}k_B\left(\frac{\mathbf{T}}{\mathbf{T}_D}\right)^3$$

3.1.3 Quantum Diatomic Gases

The Classical analysis of diatomic gases, where the molecule was modelled as a classical vibrating rod, gave a heat capacity of $\frac{7}{2}\mathbf{N}k_B$, but this is only observed at high $\mathbf{T}$.

Rotational. Rather than modelling the molecule as a rigid rod, we note that the energy levels are quantised like

$$\mathbf{E}_j = \frac{\hbar^2}{2I}j(j+1) \qquad j = 0, 1, 2, \ldots \qquad g_j = 2j+1$$

and so the rotational partition function is actually

$$\mathbf{Z}_r = \sum_{j=0}^{\infty}(2j+1)e^{-\beta\hbar^2 j(j+1)/2I}$$

At high temperatures $\beta \ll \hbar^2/2I$, this can be approximated by an integral

$$\mathbf{Z}_r(\beta \ll \hbar^2/2I) \to \int_0^{\infty}(2j+1)e^{-\beta\hbar^2 j(j+1)/2I}\,\mathrm{d}j = \frac{2I}{\beta\hbar^2}$$

in agreement with the Classical result. However, at low temperatures the contributions to the partition function of all but the $j = 0$ states will be exponentially suppressed, and so $\mathbf{Z}_r \to 1$, $\mathbf{E}_r \to 0$, and $\mathbf{C}_{\mathbf{V},r} \to 0$. We also see that modes with low I are also exponentially suppressed, justifying the neglect of axial rotation modes.

Vibrational. $\mathbf{E}_n = \hbar\omega(n + 1/2)$, so

$$\mathbf{Z}_v = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2\sinh(\beta\hbar\omega/2)}$$

The high-$\mathbf{T}$ limit gives $\mathbf{Z}_v \to 1/\beta\hbar\omega = k_B\mathbf{T}/\hbar\omega$, but the low temperature limit gives $\mathbf{Z}_v \approx e^{-\beta\hbar\omega/2}$, $\mathbf{E}_v \approx \frac{1}{2}\hbar\omega e^{-\beta\hbar\omega/2} \approx \frac{1}{2}\hbar\omega$ (the energy of the ground state), and hence $\mathbf{C}_{\mathbf{V},v} \to 0$.

In both cases, we see that the degrees of freedom "freeze out" at lower temperatures, as they relax into their ground states and stop contributing to $\mathbf{C}_{\mathbf{V}}$.

3.2 Non-Relativistic Bosons

Any number of bosons can fit into a state $|r\rangle$, so for a given state the GCPF is

$$\mathcal{Z}_{|r\rangle} = \sum_{\mathbf{N}_r=0}^{\infty} e^{-\beta\mathbf{N}_r(\mathbf{E}_r - \boldsymbol{\mu})} = \frac{1}{1 - e^{-\beta(\mathbf{E}_r - \boldsymbol{\mu})}}$$

where we have assumed $\mathbf{E}_r > \boldsymbol{\mu} \forall |r\rangle$, and hence that $\boldsymbol{\mu} < 0$. The overall GCPF is then:

$$\mathcal{Z} = \prod_{|r\rangle} \frac{1}{1 - e^{-\beta(\mathbf{E}_r - \boldsymbol{\mu})}}$$

from which we can calculate the average number of particles in total, from which the number in each state:

$$\langle \mathbf{N} \rangle = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \boldsymbol{\mu}} = -\frac{1}{\beta}\frac{\partial}{\partial \boldsymbol{\mu}} \sum_{|r\rangle} \ln\left(1 - e^{-\beta(\mathbf{E}_r - \boldsymbol{\mu})}\right) = \sum_{|r\rangle} \frac{e^{-\beta(\mathbf{E}_r - \boldsymbol{\mu})}}{1 - e^{-\beta(\mathbf{E}_r - \boldsymbol{\mu})}} = \sum_{|r\rangle} \frac{1}{e^{\beta(\mathbf{E}_r - \boldsymbol{\mu})} - 1}$$

$$\Rightarrow \qquad \boxed{\left\langle \mathbf{N}_{|r\rangle} \right\rangle = \frac{1}{e^{\beta(\mathbf{E}_r - \boldsymbol{\mu})} - 1}} \qquad (\mathfrak{BE})$$

where we note that this distribution allows any number of particles in a given state. Note also that the degeneracy of the state $|r\rangle$ has not been mentioned; there could be many states with energy $\mathbf{E}_r$ besides $|r\rangle$. Hence the total number of particles and total energy are

$$\mathbf{N} = \int_0^\infty \mathrm{d}\mathbf{E}\, g(\mathbf{E}) \frac{1}{z^{-1}e^{\beta\mathbf{E}} - 1} = \frac{\mathbf{V}}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\mathbf{E}^{1/2}}{z^{-1}e^{\beta\mathbf{E}} - 1}\,\mathrm{d}\mathbf{E}$$

$$= \mathbf{V} \underbrace{\left(\frac{2m\pi k_B\mathbf{T}}{h^2}\right)^{3/2}}_{1/\lambda^3} \underbrace{\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}}{z^{-1}e^{x} - 1}\,\mathrm{d}x}_{\mathrm{Li}_{3/2}(z)} \qquad \Rightarrow \qquad \frac{\mathbf{N}}{\mathbf{V}} = \frac{1}{\lambda^3}\mathrm{Li}_{3/2}(z)$$

$$\mathbf{E} = \int_0^\infty \mathrm{d}\mathbf{E}'\, g(\mathbf{E}') \frac{\mathbf{E}'}{z^{-1}e^{\beta\mathbf{E}'} - 1} = \frac{\mathbf{V}}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\mathbf{E}'^{3/2}}{z^{-1}e^{\beta\mathbf{E}'} - 1}\,\mathrm{d}\mathbf{E}'$$

$$= \mathbf{V} \underbrace{\left(\frac{2m\pi k_B \mathbf{T}}{h^2}\right)^{3/2}}_{1/\lambda^3} \frac{3}{2\beta} \underbrace{\frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}}{z^{-1}e^x - 1}\,\mathrm{d}x}_{\mathrm{Li}_{5/2}(z)} \qquad \Rightarrow \qquad \frac{\mathbf{E}}{\mathbf{V}} = \frac{3}{2\beta}\frac{1}{\lambda^3}\mathrm{Li}_{5/2}(z)$$

where the *fugacity* $z \equiv e^{\beta\boldsymbol{\mu}} \in [0,1]$ (as $\boldsymbol{\mu} < 0$), and the *polylogarithm functions* $\mathrm{Li}_n(z)$ are:

$$\mathrm{Li}_n(z) \equiv \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}}{z^{-1}e^x - 1}\,\mathrm{d}x = \sum_{m=1}^{\infty} \frac{z^m}{m^n}$$

Hence $\mathrm{Li}_n(z)$ are monotonically increasing functions, and $\mathrm{Li}_n(1) = \zeta(n)$. Recall also that

$$\begin{aligned}\mathbf{p}\mathbf{V} = -\boldsymbol{\Phi} = \frac{1}{\beta}\ln \boldsymbol{\mathcal{Z}} = -\frac{1}{\beta}\sum_{|r\rangle} \ln\left(1 - ze^{-\beta \mathbf{E}_r}\right) = -\frac{1}{\beta}\int_0^\infty \mathrm{d}\mathbf{E}\, g(\mathbf{E}) \ln\left(1 - ze^{-\beta\mathbf{E}}\right) \\ = \frac{2}{3}\int_0^\infty \mathrm{d}\mathbf{E}\, g(\mathbf{E}) \frac{\mathbf{E} z e^{-\beta\mathbf{E}}}{1 - ze^{-\beta\mathbf{E}}} = \frac{2}{3}\mathbf{E}\end{aligned}$$

where to go from the first line to the second we have used the fact that $g(\mathbf{E}) \propto \mathbf{E}^{1/2}$.

3.2.1 High T

In the limit of small z, using the sum form of $\mathrm{Li}_{3/2}(z)$ we have

$$\frac{\mathbf{N}}{\mathbf{V}} = \frac{1}{\lambda^3}\left(z + \frac{z^2}{2\sqrt{2}} + \mathcal{O}(z^3)\right)$$

from which we see that for fixed $\mathbf{N}$ and $\mathbf{V}$, the limit of small z means small λ and hence high $\mathbf{T}$. One might have thought that small $z = e^{\beta\boldsymbol{\mu}}$ would mean *low* $\mathbf{T}$, but $\boldsymbol{\mu}$ depends on $\mathbf{T}$ too.

We also have

$$\frac{\mathbf{E}}{\mathbf{V}} = \frac{3}{2\beta}\frac{1}{\lambda^3}\left(z + \frac{z^2}{4\sqrt{2}} + \mathcal{O}(z^3)\right) = \frac{3}{2\beta}\frac{1}{\lambda^3} z\left(1 + \frac{z}{4\sqrt{2}} + \mathcal{O}(z^2)\right)$$

and $\mathbf{p}\mathbf{V} = \frac{2}{3}\mathbf{E}$. To obtain the equation of state we require $\mathbf{E}$ in terms of $\mathbf{N}$, so we must eliminate z. Taking the expression for $\mathbf{N}/\mathbf{V}$, we can sort of invert it:

$$z = \frac{\mathbf{N}\lambda^3}{\mathbf{V}} - \frac{z^2}{2\sqrt{2}} + \cdots = \frac{\mathbf{N}\lambda^3}{\mathbf{V}} - \frac{1}{2\sqrt{2}}\left(\frac{\mathbf{N}\lambda^3}{\mathbf{V}} - \frac{z^2}{2\sqrt{2}}\right)^2 + \cdots \approx \frac{\mathbf{N}\lambda^3}{\mathbf{V}}\left[1 - \frac{1}{2\sqrt{2}}\frac{\mathbf{N}\lambda^3}{\mathbf{V}} + \ldots\right]$$

where in the second equality we have substituted in for z using the first equality, Matryoshka-ing it until we get terms to the right order in $\mathbf{N}\lambda^3/\mathbf{V}$ and high enough order in z to be able to ignore. Using $\mathbf{p}\mathbf{V} = \frac{2}{3}\mathbf{E}$ and substituting z, we find

$$\begin{aligned}\mathbf{p}\mathbf{V} = \frac{2}{3}\frac{3}{2\beta}\frac{\mathbf{V}}{\lambda^3}\underbrace{\frac{\mathbf{N}\lambda^3}{\mathbf{V}}\left[1 - \frac{1}{2\sqrt{2}}\frac{\mathbf{N}\lambda^3}{\mathbf{V}} + \ldots\right]}_{z}\left(1 + \frac{1}{4\sqrt{2}}\underbrace{\frac{\mathbf{N}\lambda^3}{\mathbf{V}}\left[1 - \frac{1}{2\sqrt{2}}\frac{\mathbf{N}\lambda^3}{\mathbf{V}} + \ldots\right]}_{z} + \ldots\right) \\ = \mathbf{N}k_B\mathbf{T}\left(1 - \frac{1}{4\sqrt{2}}\frac{\mathbf{N}\lambda^3}{\mathbf{V}} + \ldots\right)\end{aligned}$$

which as expected for a high-temperature gas, is the ideal gas law plus a second virial coefficient, which in this case reduces the pressure.

3.2.2 Low T & Bose-Einstein Condensates

Recall that $\mathbf{N}/\mathbf{V} = \mathrm{Li}_{3/2}(z)/\lambda^3$, and $\boldsymbol{\mu} < 0$ so $z \in [0,1]$. Suppose we decrease $\mathbf{T}$ towards 0, at fixed $\mathbf{N}$ and $\mathbf{V}$. z then increases from its small value up towards its maximum value of 1. $\mathrm{Li}_{3/2}(z)$ is monotonically increasing and hence does not exceed $\mathrm{Li}_{3/2}(1) = \zeta(3/2)$. Suppose z reaches 1 at a temperature $\mathbf{T}_c$ (typically $\sim 10^{-6}$K), so that

$$\frac{\mathbf{N}}{\mathbf{V}} = \frac{1}{\lambda^3}\zeta\left(\frac{3}{2}\right) = \left(\frac{2m\pi k_B \mathbf{T}_c}{h^2}\right)^{3/2}\zeta\left(\frac{3}{2}\right) \qquad \Rightarrow \qquad \mathbf{T}_c = \frac{h^2}{2m\pi k_B}\left(\frac{1}{\zeta(3/2)}\frac{\mathbf{N}}{\mathbf{V}}\right)^{2/3}$$

Decreasing the temperature below $\mathbf{T}_c$ appears to reduce $\mathbf{N}$, as $\mathrm{Li}_{3/2}$ has "saturated" and can no longer compensate. In fact this is because the density of states, proportional to $\mathbf{E}^{1/2}$ accidentally excludes the ground state, which has $\mathbf{E}_0 = 0$ and hence $\langle \mathbf{N}_0 \rangle = \frac{z}{1-z}$. Unless z is *really* close to 1, $\mathbf{N}_0$ is only a few; for $z = 0.9$, $\mathbf{N}_0 = 9$, which is not much compared to the $\sim 10^{23}$ particles in other states! However as z approaches 1, $\mathbf{N}_0$ can reach macroscopic values and hence its exclusion becomes irresponsible. The ground state was the only state not included in the earlier calculation of $\mathbf{N}/\mathbf{V}$, so we should modify it to

$$\mathbf{N} = \frac{\mathbf{V}}{\lambda^3}\mathrm{Li}_{3/2}(z) + \frac{z}{1-z}$$

$\mathbf{T}$ can now get low without there being changes in $\mathbf{N}$ or $\mathbf{V}$, as although reducing $\mathbf{T}$ increases λ (decreasing the first term which is bounded by $\mathbf{V}\zeta(3/2)/\lambda^3$), it also pushes z arbitrarily close to 1 so the second term can pick up the slack to keep $\mathbf{N}$ constant. What is happening is that as $\mathbf{T}$ falls, the bosons all start piling into the ground state, giving $\sim 10^{23}$ particles in a single quantum state! The fraction of particles in the ground state for $\mathbf{T} < \mathbf{T}_c$ is

$$\frac{\mathbf{N}_0}{\mathbf{N}} = \frac{1}{\mathbf{N}}\frac{z}{1-z} = 1 - \frac{\mathbf{V}}{\mathbf{N}\lambda^3}\mathrm{Li}_{3/2}(z) = 1 - \frac{\mathbf{V}}{\mathbf{N}\lambda^3}\zeta\left(\frac{3}{2}\right) = 1 - \left(\frac{\mathbf{T}}{\mathbf{T}_c}\right)^{3/2}$$

which gets closer and closer to 1 on lowering the temperature. For $\mathbf{T} > \mathbf{T}_c$ this is invalid as in this regime $\mathrm{Li}_{3/2}(z) \neq \zeta\left(\frac{3}{2}\right)$.

The equation of state can now be updated to include the ground state at $z \lesssim 1$:

$$\mathbf{p} = \frac{2}{3}\frac{\mathbf{E}}{\mathbf{V}} - \frac{1}{\beta}\ln(1-z) \approx \frac{2}{3}\frac{\mathbf{E}}{\mathbf{V}} \approx \frac{k_B\mathbf{T}}{\lambda^3}\zeta\left(\frac{5}{2}\right)$$

where the first approximation derives from the second term being much smaller than the first ($\ln(1-z)$ does blow up, but only when *really* close to $z = 1$), and the second comes from the fact that $\mathrm{Li}_{5/2}(z)$ is about $\zeta(5/2)$ when z is *quite* close to 1. We see that $\mathbf{p} \propto \mathbf{T}^{5/2}$ and is independent of $\mathbf{N}/\mathbf{V}$.

3.2.3 Phase Transition at $\mathbf{T} = \mathbf{T}_c$

A phase transition is a discontinuity in a physical observable. Consider the energy again, neglecting the ground state as above:

$$\frac{\mathbf{E}}{\mathbf{V}} = \frac{3}{2}\frac{k_B\mathbf{T}}{\lambda^3}\mathrm{Li}_{5/2}(z) \qquad \Rightarrow \qquad \frac{\mathbf{C_V}}{\mathbf{V}} = \frac{15}{4}\frac{k_B}{\lambda^3}\mathrm{Li}_{5/2}(z) + \frac{3}{2}\frac{k_B\mathbf{T}}{\lambda^3}\frac{\mathrm{dLi}_{5/2}}{\mathrm{d}z}\frac{\mathrm{d}z}{\mathrm{d}\mathbf{T}}$$

For $\mathbf{T} < \mathbf{T}_c$, $z = 1$ and $\mathrm{dLi}_{5/2}/\mathrm{d}z = 0$. Hence $\mathbf{C_V} = \frac{15}{4}\frac{k_B}{\lambda^3} \propto \mathbf{T}^{3/2}$. For $\mathbf{T} > \mathbf{T}_c$ the second term is non-zero; although $\mathbf{C_V}$ is continuous its derivative turns out not to be. $\mathbf{C_V}$ eventually saturates at $\frac{3}{2}\mathbf{N}k_B$.

3.3 Non-Relativistic Fermions

Two fermions cannot occupy the same state, so each fermionic state can have either 0 or 1 particles. The single-state grand partition function is then simply:

$$\mathcal{Z}_{|r\rangle} = e^{-\beta(0)(\mathbf{E}_r-\boldsymbol{\mu})} + e^{-\beta(1)(\mathbf{E}_r-\boldsymbol{\mu})} = 1 + e^{-\beta(\mathbf{E}_r-\boldsymbol{\mu})}$$

The total grand partition function is then $\prod_r \mathcal{Z}_{|r\rangle}$, and hence the number of particles is

$$\langle \mathbf{N} \rangle = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \boldsymbol{\mu}} = \frac{1}{\beta}\frac{\partial}{\partial \boldsymbol{\mu}} \sum_{|r\rangle} \ln\left(1 + e^{-\beta(\mathbf{E}_r-\boldsymbol{\mu})}\right) = \sum_{|r\rangle} \frac{e^{-\beta(\mathbf{E}_r-\boldsymbol{\mu})}}{1 + e^{-\beta(\mathbf{E}_r-\boldsymbol{\mu})}} = \sum_{|r\rangle} \frac{1}{e^{\beta(\mathbf{E}_r-\boldsymbol{\mu})} + 1}$$

$$\Rightarrow \qquad \boxed{\left\langle \mathbf{N}_{|r\rangle} \right\rangle = \frac{1}{e^{\beta(\mathbf{E}_r-\boldsymbol{\mu})} + 1}} \qquad (\mathfrak{FD})$$

which is very similar to $\mathfrak{BE}$ but with a $+$ in the denominator. Note that $\left\langle \mathbf{N}_{|r\rangle} \right\rangle \in [0, 1]$. The density of states can be written

$$g(\mathbf{E}) = \frac{g_s V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \mathbf{E}^{1/2}$$

where $g_s = 2s + 1$ is the spin degeneracy, analogous to the 2 polarisations of photons that can occupy a single pair of ω and $\mathbf{k}$. For fermions, the integrals become:

$$\mathbf{N} = \int_0^\infty \mathrm{d}\mathbf{E}\, \frac{g(\mathbf{E})}{z^{-1}e^{\beta\mathbf{E}} + 1} \qquad \mathbf{E} = \int_0^\infty \mathrm{d}\mathbf{E}'\, \frac{\mathbf{E}' g(\mathbf{E}')}{z^{-1}e^{\beta\mathbf{E}'} + 1} \qquad \mathbf{pV} = \frac{2}{3}\mathbf{E}$$

For small z (high $\mathbf{T}$), approximating, eliminating z and substituting $\mathbf{E}$ for $\mathbf{pV}$ gives:

$$\mathbf{pV} = \mathbf{N}k_B\mathbf{T}\left(1 + \frac{1}{4\sqrt{2}}\frac{\mathbf{N}\lambda^3}{g_s\mathbf{V}} + \dots\right)$$

with a higher-than-ideal pressure at second order.

3.3.1 $\mathbf{T} \to 0$ and Fermi Energy

$$\lim_{\mathbf{T}\to 0} \frac{1}{e^{\beta(\mathbf{E}-\boldsymbol{\mu})} + 1} = 1 - \Theta(\mathbf{E} - \boldsymbol{\mu}) = \begin{cases} 1 & \mathbf{E} < \boldsymbol{\mu} \\ 0 & \mathbf{E} > \boldsymbol{\mu} \end{cases}$$

Each fermion settles into the lowest energy state with room, as shown in Figure 1. At $\mathbf{T} = 0$, $\boldsymbol{\mu}$ defines the *Fermi Energy* $\mathbf{E}_F$ as the highest occupied energy level:

$$\mathbf{N} = \int_0^{\mathbf{E}_F} g(\mathbf{E})\, \mathrm{d}\mathbf{E} = \frac{g_s\mathbf{V}}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \mathbf{E}_F^{3/2} \qquad \Rightarrow \qquad \mathbf{E}_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{g_s}\frac{\mathbf{N}}{\mathbf{V}}\right)^{2/3}$$

We then define $\mathbf{T}_F \equiv \mathbf{E}_F/k_B$ and $\mathbf{k}_F \equiv \sqrt{2m\mathbf{E}_F}$. Still at $\mathbf{T} = 0$, we also have

$$\mathbf{E} = \int_0^{\mathbf{E}_F} \mathbf{E}' g(\mathbf{E}')\, \mathrm{d}\mathbf{E}' = \frac{g_s\mathbf{V}}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\mathbf{E}_F} \mathbf{E}'^{3/2}\, \mathrm{d}\mathbf{E}' = \frac{3}{5}\mathbf{N}\mathbf{E}_F \qquad \Rightarrow \qquad \mathbf{pV} = \frac{2}{5}\mathbf{N}\mathbf{E}_F$$

so even at $\mathbf{T} = 0$, there is some residual (*degeneracy*) pressure.

3.3.2 Low $\mathbf{T}$

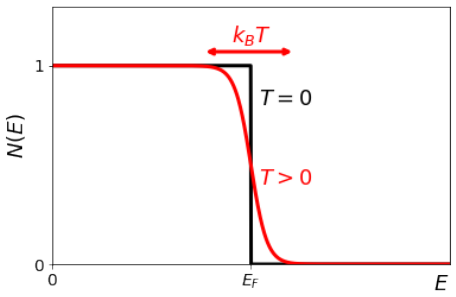

Figure 1 | Occupation of Fermionic Energy Levels. In the $\mathbf{T} \to 0$ limit, all states with $\mathbf{E} < \mathbf{E}_F$ are occupied and all others are unoccupied. For small $\mathbf{T}$ the distribution is smeared out around a region of size $\approx k_B\mathbf{T}$.

As shown in Figure 1, when $\mathbf{T}$ is slightly above 0, the distribution is smeared out over an energy range of order $k_B\mathbf{T}$. This section will necessarily be much less analytic.

For low $\mathbf{T}$, $\boldsymbol{\mu} \approx \mathbf{E}_F$ is approximately constant. The change in the number of particles with $\mathbf{T}$ is expected to be 0:

$$\begin{aligned}
\left.\frac{\mathrm{d}\mathbf{N}}{\mathrm{d}\mathbf{T}}\right|_{\mathbf{T}\approx 0} &= \left.\frac{\mathrm{d}}{\mathrm{d}\mathbf{T}}\right|_0 \int_0^\infty \mathrm{d}\mathbf{E}\, \frac{g(\mathbf{E})}{e^{\beta(\mathbf{E}-\boldsymbol{\mu})}+1} \\
&\approx g(\mathbf{E}_F) \int_{\mathbf{E}_F - k_B\mathbf{T}/2}^{\mathbf{E}_F + k_B\mathbf{T}/2} \mathrm{d}\mathbf{E} \frac{\partial}{\partial \mathbf{T}} \left(\frac{1}{e^{\beta(\mathbf{E}-\mathbf{E}_F)}+1}\right) \\
&= g(\mathbf{E}_F) \int_-^+ \mathrm{d}\mathbf{E}\, \frac{\mathbf{E}-\mathbf{E}_F}{k_B\mathbf{T}^2} \frac{e^{\beta(\mathbf{E}-\mathbf{E}_F)}}{\left(e^{\beta(\mathbf{E}-\mathbf{E}_F)}+1\right)^2} \\
&= \frac{g(\mathbf{E}_F)}{4k_B\mathbf{T}^2} \int_-^+ (\mathbf{E}-\mathbf{E}_F) \operatorname{sech}^2\left(\frac{\beta(\mathbf{E}-\mathbf{E}_F)}{2}\right)
\end{aligned}$$

where in the approximation we have used the fact that the only energies whose occupations will change much will be those within about $k_B\mathbf{T}$ of $\mathbf{E}_F$ The final integral is 0 because the first term in the integrand is odd about $\mathbf{E} = \mathbf{E}_F$ and the second is even.

The calculation of the heat capacity uses similar assumptions:

$$\begin{aligned}
\mathbf{C_V} \equiv \frac{\mathrm{d}\mathbf{E}}{\mathrm{d}\mathbf{T}} &= \frac{\mathrm{d}}{\mathrm{d}\mathbf{T}} \int_0^\infty \frac{\mathbf{E}g(\mathbf{E})\,\mathrm{d}\mathbf{E}}{e^{\beta(\mathbf{E}-\boldsymbol{\mu})}+1} \\
&\approx \int_-^+ \mathrm{d}\mathbf{E} \left[\mathbf{E}_F g(\mathbf{E}_F) + \frac{3}{2\mathbf{E}_F}\mathbf{E}_F g(\mathbf{E}_F)(\mathbf{E}-\mathbf{E}_F)\right] \frac{\partial}{\partial \mathbf{T}} \left(\frac{1}{e^{\beta(\mathbf{E}-\mathbf{E}_F)}+1}\right) \\
&= \frac{1}{4k_B\mathbf{T}^2} \int_-^+ \mathrm{d}\mathbf{E} \left[\mathbf{E}_F g(\mathbf{E}_F) + \frac{3}{2\mathbf{E}_F}\mathbf{E}_F g(\mathbf{E}_F)(\mathbf{E}-\mathbf{E}_F)\right] (\mathbf{E}-\mathbf{E}_F) \operatorname{sech}^2\left(\frac{\beta(\mathbf{E}-\mathbf{E}_F)}{2}\right) \\
&\approx \frac{1}{4k_B\mathbf{T}^2} \frac{3g(\mathbf{E}_F)}{2} \frac{1}{\beta^3} \int_{-\infty}^\infty x^2 \operatorname{sech}^2\left(\frac{x}{2}\right) \mathrm{d}x \sim \mathbf{T}g(\mathbf{E}_F)
\end{aligned}$$

where the first approximation comes from Taylor expanding $\mathbf{E}g(\mathbf{E}) \propto \mathbf{E}^{3/2}$ about $\mathbf{E}_F$, the first term of which roughly cancels by parity, and in the final approximation we have substituted $x = \beta(\mathbf{E}-\mathbf{E}_F)$ and extended the integral because it doesn't make much difference. This result makes sense because only fermions within around $k_B\mathbf{T}$ of $\mathbf{E}_F$ are going to move when the gas is heated, of which there are about $g(\mathbf{E}_F)k_B\mathbf{T}$. On heating to $\mathbf{T}$, each of these gains an energy $\sim k_B\mathbf{T}$, so the "active" thermal energy is proportional to $g(\mathbf{E}_F)\mathbf{T}^2$ and hence $\mathbf{C_V} \propto g(\mathbf{E}_F)\mathbf{T}$.

Finally, because $\mathbf{N} \propto \mathbf{E}_F^{3/2}$, $g(\mathbf{E}_F) \propto \mathbf{E}_F^{1/2}$, $\mathbf{T}_F \propto \mathbf{E}_F$, and $\mathbf{C_V} \propto \mathbf{T}g(\mathbf{E}_F)$, we can write

$$\mathbf{C_V} \sim \mathbf{N}k_B \frac{\mathbf{T}}{\mathbf{T}_F}$$

which is proportional to $\mathbf{T}\mathbf{E}_F^{1/2}$ as required, but also proportional to $\mathbf{N}$.

Metal electrons can be modelled as a Fermi gas. Hence a metal's heat capacity at low $\mathbf{T}$ can be modelled as a combination of electronic and phononic contributions $\mathbf{C_V} = \gamma\mathbf{T} + \alpha\mathbf{T}^3$.

3.3.3 Paramagnetism

When electrons are in a magnetic field they couple to it and gain an energy[1] $\mathbf{E}_s = \mu_B B s$ where $s = \pm 1$ and $\mu_B = e\hbar/2m$. We then have

$$\frac{\mathbf{N}_\uparrow}{\mathbf{V}} = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \mathrm{d}\mathbf{E}\,\frac{\mathbf{E}^{1/2}}{e^{\beta(\mathbf{E}+\mu_B B-\boldsymbol{\mu})}+1} \quad\Big|\quad \frac{\mathbf{N}_\downarrow}{\mathbf{V}} = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \mathrm{d}\mathbf{E}\,\frac{\mathbf{E}^{1/2}}{e^{\beta(\mathbf{E}-\mu_B B-\boldsymbol{\mu})}+1}$$

The *magnetisation* $\mathbf{M} \equiv -\partial\mathbf{E}/\partial B$. For high $\mathbf{T}$ (that is, $z \ll 1$), we have

$$\int_0^\infty \mathrm{d}\mathbf{E}\,\frac{\mathbf{E}^{1/2}}{z^{-1}e^{\beta(\mathbf{E}+\mu_B B)}+1} \approx \frac{ze^{-\beta\mu_B B}}{\beta^{3/2}}\int_0^\infty x^{1/2}e^{-x}\,\mathrm{d}x = \frac{\sqrt{\pi}}{2}\frac{z}{\beta^{3/2}}e^{-\beta\mu_B B}$$

$$\Rightarrow \mathbf{N}_\uparrow \approx \frac{\mathbf{V}}{\lambda^3}ze^{-\beta\mu_B B}, \qquad \mathbf{N}_\downarrow \approx \frac{\mathbf{V}}{\lambda^3}ze^{\beta\mu_B B}$$

$$\Rightarrow \mathbf{N} = \frac{2\mathbf{V}z}{\lambda^3}\cosh(\beta\mu_B B) \qquad \Rightarrow z = \frac{\mathbf{N}\lambda^3}{2\mathbf{V}\cosh(\beta\mu_B B)}$$

$$\Rightarrow \mathbf{E} = \mu_B B(\mathbf{N}_\uparrow - \mathbf{N}_\downarrow) \approx -\frac{2\mu_B B\mathbf{V}z}{\lambda^3}\sinh(\beta\mu_B B) = \mathbf{N}\mu_B B\tanh(\beta\mu_B B)$$

$$\Rightarrow \mathbf{M} \approx \mathbf{N}\mu_B\tanh(\beta\mu_B B)$$

to first order. The *susceptibility* $\chi \equiv \partial\mathbf{M}/\partial B = \mathbf{N}\beta\mu_B^2\,\mathrm{sech}^2(\beta\mu_B B) \sim \mathbf{T}^{-1}$: Curie's Law.

4 Classical Thermodynamics

4.1 Classical Temperature and Energy

4.1.1 The 0th Law

$\mathfrak{0}\mathfrak{L}\mathfrak{T}$: If A is in equilibrium with B, and B with C, then A is in equilibrium with C.

In Classical Physics there are only macrostates. A system is located by a point in $(\mathbf{p}, \mathbf{V})$-space. Whether or not two states are in equilibrium thus depends on the $\mathbf{p}_i$ and $\mathbf{V}_i$. Write this dependence for two systems A and B as $V_B = f_{AB}(\mathbf{p}_A, \mathbf{V}_A, \mathbf{p}_B)$. Suppose B and C are also in equilibrium, so $V_B = f_{CB}(\mathbf{p}_C, \mathbf{V}_C, \mathbf{p}_B)$. Thus

$$f_{AB}(\mathbf{p}_A, \mathbf{V}_A, \mathbf{p}_B) = f_{CB}(\mathbf{p}_C, \mathbf{V}_C, \mathbf{p}_B)$$

Now according to $\mathfrak{0}\mathfrak{L}\mathfrak{T}$, this is all equivalent to A and C being in equilibrium – but *that* relationship has nothing to do with $\mathbf{p}_B$. Thus $\mathbf{p}_B$ must somehow cancel from the above; that is to say that there exist functions θ_i such that $\theta_A(\mathbf{p}_A, \mathbf{V}_A) = \theta_C(\mathbf{p}_C, \mathbf{V}_C)$. These functions are the temperatures, e.g. $\theta_C(x, y) = xy/\mathbf{N}_C k_B$ if system C is an ideal gas of $\mathbf{N}_C$ particles.

4.1.2 The 1st Law

$\mathfrak{1}\mathfrak{L}\mathfrak{T}$: The work required to change an *isolated* system between two states does not depend on how the work was done.

This suggests another state function $\mathbf{E}(\mathbf{p}, \mathbf{V})$, where no matter how the work $\mathbf{W}$ is done, $\Delta\mathbf{E} = \mathbf{W}$. For *non-isolated* systems, another form of energy transfer (called heat, $\mathbf{Q}$) can

[1] $s = \pm 1$ rather than $\pm 1/2$ relates to the fact that the electron's intrinsic magnetic moment is the product of the spin ($\pm 1/2$) and the *g-factor* which happens to be about 2.

occur due to differences in $\mathbf{T}$. Thus $\Delta\mathbf{E} = \mathbf{Q} + \mathbf{W}$. In infinitesimal form, this is written $\mathrm{d}\mathbf{E} = \delta\mathbf{Q} + \delta\mathbf{W}$. Note that $\delta\mathbf{W} = -\mathbf{p}\,\mathrm{d}\mathbf{V}$ refers to a small *amount* of $\mathbf{W}$, not a small "change" in $\mathbf{W}$; $\delta\mathbf{W}$ is not an exact differential.

For two different paths for a non-isolated system in $(\mathbf{p}, \mathbf{V})$-space between two states $(\mathbf{p}_1, \mathbf{V}_1)$ and $(\mathbf{p}_2, \mathbf{V}_2)$, the energy change will be the same $\Delta\mathbf{E} = \mathbf{E}(\mathbf{p}_2, \mathbf{V}_2) - \mathbf{E}(\mathbf{p}_1, \mathbf{V}_1)$. However, the work done is $\mathbf{W} = \int \delta\mathbf{W} = -\int \mathbf{p}\,\mathrm{d}\mathbf{V}$, which will depend on the path $\mathbf{p}(\mathbf{V})$; $\mathbf{Q} = \int \delta\mathbf{Q}$ will depend on the path in the exact opposite way so that $\Delta\mathbf{E}$ is the same for both paths.

4.2 The 2nd Law

$2\mathfrak{LT}$ has two phrasings, which can be shown to be equivalent:

- **Kelvin:** No process can just extract heat from a reservoir and convert it all to work
- **Clausius:** No process can just transfer heat from cold to hot

4.2.1 The Carnot Cycle

Reversible processes are quasistatic processes that can be reversed; e.g. without friction.

The Carnot Cycle is a particular cyclic series of reversible processes, operating between two reservoirs at temperatures $\mathbf{T}_H$, $\mathbf{T}_C < \mathbf{T}_H$:

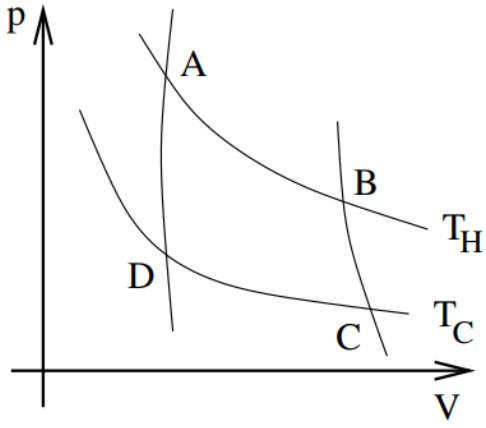

Figure 2 | The Carnot Cycle.

1. **Isothermal expansion at $\mathbf{T}_H$, from $\mathbf{V}_A$ to $\mathbf{V}_B$.** To do the necessary work for this expansion without taking any internal energy from the system ($\mathbf{E} = \mathbf{E}(\mathbf{T})$ and $\mathbf{T}$ is constant), a heat $\mathbf{Q}_H$ is absorbed from the $\mathbf{T}_H$ reservoir.
2. **Adiabatic expansion, from $\mathbf{T}_H$ to $\mathbf{T}_C$.** No heat is absorbed — adiabatic.
3. **Isothermal compression at $\mathbf{T}_C$, from $\mathbf{V}_C$ to $\mathbf{V}_D$.** The internal energy is constant (isothermal) so heat $\mathbf{Q}_C$ must be squeezed out into the $\mathbf{T}_C$ reservoir.
4. **Adiabatic compression from $\mathbf{T}_C$ to $\mathbf{T}_H$, back to the beginning.** Again, no heat.

As the system is back where it started after one full cycle, there is 0 net energy change in the system: $\oint \mathrm{d}\mathbf{E} = 0$. Thus the total work done **by** the system $\oint -\mathrm{d}\mathbf{W} = \oint \mathrm{d}\mathbf{Q} = \mathbf{Q}_H - \mathbf{Q}_C$, the net heat absorbed. The efficiency η is defined as the work done $(\mathbf{Q}_H - \mathbf{Q}_C)$ divided by the gross heat absorbed $(\mathbf{Q}_H)$. Hence

$$\eta = \frac{\mathbf{Q}_H - \mathbf{Q}_C}{\mathbf{Q}_H} = 1 - \frac{\mathbf{Q}_C}{\mathbf{Q}_H}$$

According to Kelvin's formulation of $2\mathfrak{LT}$, $\mathbf{Q}_C > 0$ so $\eta < 1$.

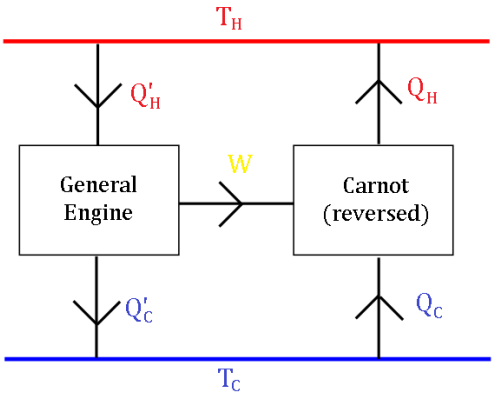

Figure 3 | Illustration for Proof of Carnot's Theorem.

Carnot's Theorem says that among heat engines operating between two reservoirs, reversible heat engines (such as Carnot's) are the most efficient. A corollary is that all reversible heat engines have the same efficiency, depending on $\mathbf{T}_H$ and $\mathbf{T}_C$ alone: $\eta = \eta(\mathbf{T}_H, \mathbf{T}_C)$. To prove, consider a general heat engine, extracting $\mathbf{Q}'_H$ from $\mathbf{T}_H$, depositing $\mathbf{Q}'_C$ to $\mathbf{T}_C$, and using all its work $\mathbf{W}$ to run a Carnot engine in reverse (extracting $\mathbf{Q}_C$ from $\mathbf{T}_C$ and depositing $\mathbf{Q}_H$ to $\mathbf{T}_H$). No net work is being done by the combination of engines, $\mathbf{Q}'_H - \mathbf{Q}_H$ is taken from $\mathbf{T}_H$ and $\mathbf{Q}'_C - \mathbf{Q}_C$ is deposited into $\mathbf{T}_C$; these must be equal by conservation of energy. Now according to Clausius' $2\mathfrak{LT}$, $\mathbf{Q}'_H - \mathbf{Q}_H (= \mathbf{Q}'_C - \mathbf{Q}_C) \geq 0$, i.e. the heat is not going from cold to hot, so $\mathbf{Q}'_H \geq \mathbf{Q}_H$. The efficiency of the general heat engine which we attached to the Carnot is then

$$\eta \equiv \frac{\mathbf{W}}{\mathbf{Q}'_H} \leq \frac{\mathbf{W}}{\mathbf{Q}_H} = \eta_{\text{Carnot}} \qquad \Rightarrow \qquad \eta \leq \eta_{\text{Carnot}}$$

If this general engine happens also to be reversible, the whole argument can be run in reverse and we would obtain $\eta_{\text{rev}} \geq \eta_{\text{Carnot}}$ as well, so in this case $\eta_{\text{rev}} = \eta_{\text{Carnot}}$, proving the corollary. This reversible efficiency is $\eta(\mathbf{T}_C, \mathbf{T}_H)$ simply because there's nothing else it could depend on.

At this point, one can *define* the Classical temperature through

$$\eta_{\text{Carnot}} \equiv 1 - \frac{\mathbf{Q}_C}{\mathbf{Q}_H} = 1 - \frac{\mathbf{T}_C}{\mathbf{T}_H}$$

That this is a good choice can be seen by using an ideal gas as the system. For the isothermal stages, $\mathbf{E} = \mathbf{E}(\mathbf{T})$ and so $\mathrm{d}\mathbf{E} = 0$ and $\delta\mathbf{Q} = -\delta\mathbf{W} = \mathbf{p}\mathrm{d}\mathbf{V} = \frac{\mathbf{N}k_B\mathbf{T}}{\mathbf{V}}\mathrm{d}\mathbf{V} = \mathbf{N}k_B\mathbf{T}\,\mathrm{d}(\ln\mathbf{V})$. Thus[2]

$$\mathbf{Q}_H = \int_{\mathbf{V}_A}^{\mathbf{V}_B} \mathbf{N}k_B\mathbf{T}_H\,\mathrm{d}(\ln\mathbf{V}) = \mathbf{N}k_B\mathbf{T}_H \ln\left(\frac{\mathbf{V}_B}{\mathbf{V}_A}\right)$$
$$\mathbf{Q}_C = -\int_{\mathbf{V}_C}^{\mathbf{V}_D} \mathbf{N}k_B\mathbf{T}_C\,\mathrm{d}(\ln\mathbf{V}) = \mathbf{N}k_B\mathbf{T}_C \ln\left(\frac{\mathbf{V}_C}{\mathbf{V}_D}\right)$$

Now for the adiabatic stages, $\mathbf{p}\mathbf{V}^{5/3} \propto \mathbf{T}\mathbf{V}^{2/3}$ is constant, so $\mathbf{T}_H\mathbf{V}_B^{2/3} = \mathbf{T}_C\mathbf{V}_C^{2/3}$, and $\mathbf{T}_C\mathbf{V}_D^{2/3} = \mathbf{T}_H\mathbf{V}_A^{2/3}$. As such

$$\frac{\mathbf{T}_H}{\mathbf{T}_C} = \left(\frac{\mathbf{V}_D}{\mathbf{V}_A}\right)^{2/3} = \left(\frac{\mathbf{V}_C}{\mathbf{V}_B}\right)^{2/3} \Rightarrow \frac{\mathbf{V}_B}{\mathbf{V}_A} = \frac{\mathbf{V}_C}{\mathbf{V}_D} \qquad \Rightarrow \qquad \frac{\mathbf{Q}_C}{\mathbf{Q}_H} = \frac{\mathbf{T}_C}{\mathbf{T}_H}\frac{\ln(\mathbf{V}_C/\mathbf{V}_D)}{\ln(\mathbf{V}_B/\mathbf{V}_A)} = \frac{\mathbf{T}_C}{\mathbf{T}_H}$$

justifying the definition of Classical temperature above.

Defining $\mathbf{Q}_1 = \mathbf{Q}_H$ and $\mathbf{Q}_2 = -\mathbf{Q}_C$, (so that $\mathbf{Q}_i$ is always heat done *on* the system),

$$\sum_{i=1}^{2} \frac{\mathbf{Q}_i}{\mathbf{T}_i} = 0$$

[2]The minus sign is because $\mathbf{Q}_C$ is *defined* as the heat *released*, i.e. as negative heat done to the system.

For any reversible cycle, we can break it down into a series of infinitesimal Carnot cycles, in which case the above generalises to $\oint \delta \mathbf{Q}_{\text{rev}}/\mathbf{T} = 0$. This has the consequence that between any two states, the integral for two different reversible paths between them $\int_I \delta \mathbf{Q}_{\text{rev}}/\mathbf{T} = \int_{II} \delta \mathbf{Q}_{\text{rev}}/\mathbf{T}$ is the same. This motivates the definition of the differential of a state function called, oh I don't know, $\mathbf{S}$, such that $\mathrm{d}\mathbf{S} = \delta \mathbf{Q}_{\text{rev}}/\mathbf{T}$. Using $\delta \mathbf{W}_{\text{rev}} = -\mathbf{p}\mathrm{d}\mathbf{V}$, we can then substitute into $\mathfrak{1}\mathfrak{L}\mathfrak{T}$:

$$\mathrm{d}\mathbf{E} = \mathbf{T}\mathrm{d}\mathbf{S} - \mathbf{p}\mathrm{d}\mathbf{V}$$

showing that this $\mathbf{S}$ is indeed the entropy, as this matches the expression for $\mathrm{d}\mathbf{E}$ at the start. As $\mathbf{S}$ is a state function, it actually doesn't matter how we get between two states, reversible or ir-, so the above is valid even for irreversible processes, even though $\delta \mathbf{Q} \neq \mathbf{T}\mathrm{d}\mathbf{S}$ unless the heat is transferred reversibly.

4.2.2 Irreversible Processes

Consider an irreversible engine that does the same amount of work $\mathbf{W}$ as a Carnot engine: $\mathbf{W} = \mathbf{Q}'_H - \mathbf{Q}'_C = \mathbf{Q}_H - \mathbf{Q}_C$. The entropy change over a cycle of the irreversible engine is

$$\Delta \mathbf{S}_{\text{irrev}} = \frac{\mathbf{Q}'_H}{\mathbf{T}_H} - \frac{\mathbf{Q}'_C}{\mathbf{T}_C} = \overbrace{\frac{\mathbf{Q}_H}{\mathbf{T}_H} - \frac{\mathbf{Q}_C}{\mathbf{T}_C}}^{0} + \frac{\mathbf{Q}'_H - \mathbf{Q}_H}{\mathbf{T}_H} - \frac{\mathbf{Q}'_C - \mathbf{Q}_C}{\mathbf{T}_C} = \overbrace{(\mathbf{Q}'_H - \mathbf{Q}_H)}^{\geq 0} \overbrace{\left(\frac{1}{\mathbf{T}_H} - \frac{1}{\mathbf{T}_C}\right)}^{\leq 0} \leq 0$$

where $\mathbf{Q}'_H \geq \mathbf{Q}_H$ because irreversible engines are less efficient than reversible ones and they are doing the same work. Thus $\oint \delta \mathbf{Q}/\mathbf{T} \leq 0$, for not-necessarily-reversible processes. Now consider going from some state A to B along an irreversible path I, and returning along a reversible path II. We then require:

$$\int_A^B \frac{\delta \mathbf{Q}}{\mathbf{T}} \leq \int_A^B \frac{\delta \mathbf{Q}_{\text{rev}}}{\mathbf{T}} = \mathbf{S}(B) - \mathbf{S}(A)$$

For an isolated system, $\delta \mathbf{Q} = 0$, so $\mathbf{S}(B) \geq \mathbf{S}(A)$: entropy always increases. Taking a small limit we see that $\mathrm{d}\mathbf{S} \geq \delta \mathbf{Q}/\mathbf{T} \Rightarrow \delta \mathbf{Q} \leq \mathbf{T}\mathrm{d}\mathbf{S}$. As $\mathrm{d}\mathbf{E} = \delta \mathbf{Q} + \delta \mathbf{W} = \mathbf{T}\mathrm{d}\mathbf{S} - \mathbf{p}\mathrm{d}\mathbf{V}$, we thus also have that $-\delta \mathbf{W} \leq \mathbf{p}\mathrm{d}\mathbf{V}$, giving a limit on the amount of work $-\mathbf{W}$ that a system can do.

4.3 The 3rd Law

$$3\mathfrak{L}\mathfrak{T}: \qquad \lim_{\substack{\mathbf{T}\to 0 \\ \mathbf{N}\to\infty}} \frac{\mathbf{S}}{\mathbf{N}} = 0$$

This just provides a constraint on heat capacities: as $\mathbf{S}(B) - \mathbf{S}(A) = \int_A^B \mathbf{C}_{\mathbf{V}} \mathrm{d}\mathbf{T}/\mathbf{T}$, we require that for small $\mathbf{T}$, $\mathbf{C}_{\mathbf{V}}$ tends to $\mathbf{T}^n$ for $n \geq 1$ for $\mathbf{S}$ to be finite.

4.4 Thermodynamic Potentials

Any system can be described by any pair of $\mathbf{p}, \mathbf{V}, \mathbf{E}, \mathbf{S}, \mathbf{T}, \ldots$, except where a pair is degenerate e.g. $\mathbf{E}$ and $\mathbf{T}$ in an ideal gas.

As $\mathrm{d}\mathbf{E} = \mathbf{T}\mathrm{d}\mathbf{S} - \mathbf{p}\mathrm{d}\mathbf{V}$, it is most natural to consider $\mathbf{E}$ as a function of $\mathbf{S}$ and $\mathbf{V}$, though it can be considered a function of any pair by rewriting the differential.

We may define also $\mathbf{F} = \mathbf{E} - \mathbf{T}\mathbf{S}$; $\mathbf{G} = \mathbf{F} + \mathbf{p}\mathbf{V}$; $\mathbf{H} = \mathbf{E} + \mathbf{p}\mathbf{V}$, so that:

$$\mathrm{d}\mathbf{E} = \mathbf{T}\mathrm{d}\mathbf{S} - \mathbf{p}\mathrm{d}\mathbf{V}; \quad \mathrm{d}\mathbf{F} = -\mathbf{S}\mathrm{d}\mathbf{T} - \mathbf{p}\mathrm{d}\mathbf{V}; \quad \mathrm{d}\mathbf{G} = -\mathbf{S}\mathrm{d}\mathbf{T} + \mathbf{V}\mathrm{d}\mathbf{p}; \quad \mathrm{d}\mathbf{H} = \mathbf{T}\mathrm{d}\mathbf{S} + \mathbf{V}\mathrm{d}\mathbf{p}$$

By taking mixed partial derivatives of any potential, a Maxwell relation pops out; they can be deduced more quickly using the Born square, in Figure 4.

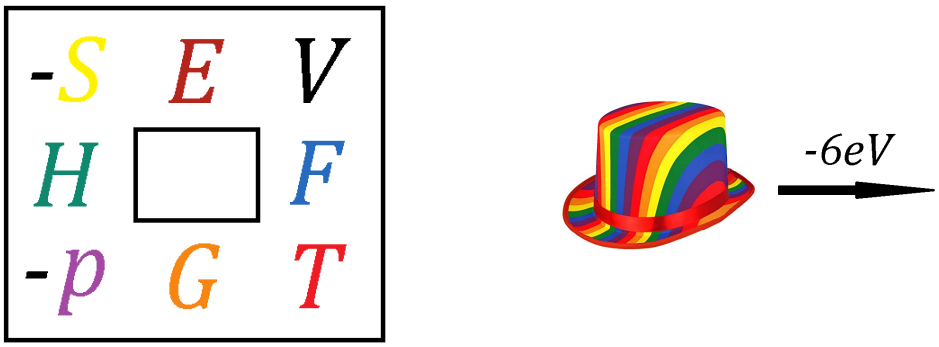

Figure 4 | The Born Square. Clockwise from top left, $-$6eV From The Gay-pride Hat

If N is not fixed (as it is above), then G depends on it: $\mathrm{d}\mathbf{G} = -\mathbf{S}\mathrm{d}\mathbf{T} + \mathbf{V}\mathrm{d}\mathbf{p} + \boldsymbol{\mu}\mathrm{d}\mathbf{N}$. Now $\mathbf{G}(\mathbf{T}, \mathbf{p}, \mathbf{N})$ is extensive, but its only extensive dependent is N, so by scaling, $\mathbf{G} = \boldsymbol{\mu}\mathbf{N}$.

F and G are also useful because they are minimised under different conditions. For instance, F is minimised at constant V and T:

$$\mathrm{d}\mathbf{F}\Big|_{\mathbf{V},\mathbf{T}} = \mathrm{d}\mathbf{E}\Big|_{\mathbf{V},\mathbf{T}} - \mathbf{T}\mathrm{d}\mathbf{S} = \delta\mathbf{Q} - \mathbf{T}\mathrm{d}\mathbf{S} \leq 0$$

So F decreases until it no longer can. The same thing happens with G at constant p.

5 Phase Transitions

5.1 Van der Waals Fluids

Van der Waals modelled fluids as interacting gases with the following potential:

$$U(r) = \begin{cases} \infty & r > r_0 \\ -U_0(r_0/r)^6 & r \geq r_0 \end{cases}$$

Using the techniques of §2.2, this gives the van der Waals equation of state:

$$\mathbf{p} = \frac{k_B\mathbf{T}}{\mathbf{v} - b} - \frac{a}{\mathbf{v}^2}$$

$$\Leftrightarrow \mathbf{v}^3 - \left(b + \frac{k_B\mathbf{T}}{\mathbf{p}}\right)\mathbf{v}^2 + \frac{a}{\mathbf{p}}\mathbf{v} - \frac{ab}{\mathbf{p}} = 0 \quad (\mathfrak{vdW})$$

where $\mathbf{v} = \mathbf{V}/\mathbf{N}$. Isotherms of this are plotted in Figure 5. We see that for high p and low T, the system reaches almost fixed v, becoming almost incompressible – this describes a liquid. For low p and high T, the behaviour tends to the ideal gas law. Although only really valid for dilute gases, $\mathfrak{vdW}$ gives insights into liquids.

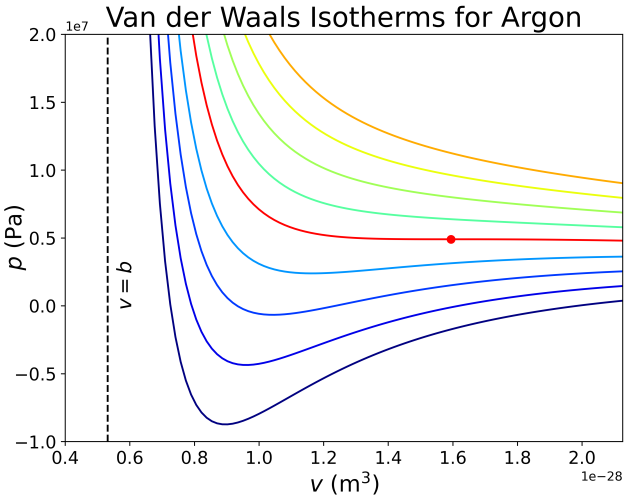

Figure 5 | Van der Waals Isotherms of Argon. The isotherms shown are between 100K and 200K. Argon has $a = 3.7 \times 10^{-49}\mathrm{Pam}^6$ and $b = 5.3 \times 10^{-29}\mathrm{m}^3$, and hence $\mathbf{T}_c$ is about 150K. This critical isotherm is in red; the dot is the critical point.

5.1.1 Critical Point

There is one isotherm ($\mathbf{T}_c$) with a point of inflection: the *critical point* $(\mathbf{v}_c, \mathbf{p}_c)$. Consider plotting the cubic form of $\mathfrak{vdW}$ against v, with p and T as parameters of the cubic. For

$\mathbf{T} > \mathbf{T}_c$, there would be three $\mathbf{v}$s that satisfy the cubic; for $\mathbf{T} < \mathbf{T}_c$ there would only be one. *At* $\mathbf{T}_c$, the three roots of the cubic merge into one repeated root, at $\mathbf{v}_c$. Therefore with $\mathbf{T} = \mathbf{T}_c$ and $\mathbf{p} = \mathbf{p}_c$, $\mathfrak{vdW}$ must be equivalent to $(\mathbf{v} - \mathbf{v}_c)^3 = 0$. Expanding, comparing and solving:

$$\mathbf{v}_c = 3b \qquad \mathbf{p}_c = \frac{a}{27b^2} \qquad k_B\mathbf{T}_c = \frac{8a}{27b}$$

5.1.2 Maxwell Construction

The $\mathfrak{vdW}$ isotherms for $\mathbf{T} < \mathbf{T}_c$ are unstable, as there are regions where $\mathbf{p}$ increases with $\mathbf{v}$, so squeezing decreases the pressure. This cannot represent a substance in stable equilibrium – $\mathfrak{vdW}$ is erroneous here. Also some isotherms dip below $\mathbf{p} = 0$ which seems bad.

In this region, a phase equilibrium exists between two *different systems*: one liquid, one gas. To be in equilibrium, these systems must have the same $\mathbf{T}$ (and hence lie on the same isotherm) and $\mathbf{p}$ (and hence be on one of the "dipping" isotherms with $\mathbf{T} < \mathbf{T}_c$). We can correct the $\mathfrak{vdW}$ isotherms by truncating the dip with a horizontal line at some constant pressure $\mathbf{p}_{\text{vap}}$, on which the substance is an equilibrium mix of liquid and gas: this is the Maxwell construction.

To be in equilibrium, the liquid and gas must *also* have the same $\boldsymbol{\mu}$. This turns out to require that $\mathbf{p}_{\text{vap}}$ should be such that the area between the isotherm and the line $\mathbf{p} = \mathbf{p}_{\text{vap}}$ is 0. The van der Waals isotherms are modified as shown in Figure 6. In the shaded region (bounded by the "coexistence curve"), liquid and gas coexist as two separate systems. Here, $\mathbf{v}$ is the average $\mathbf{V}$ per particle of the two; we see that we can move along the construction at constant $\mathbf{p}$, changing the $\mathbf{v}$ – that is, the relative amounts of liquid and gas. Sliding to the left end, the $\mathbf{v}$ is that of the liquid; at the right it is a gas (called a *vapour* when $\mathbf{T} < \mathbf{T}_c$).

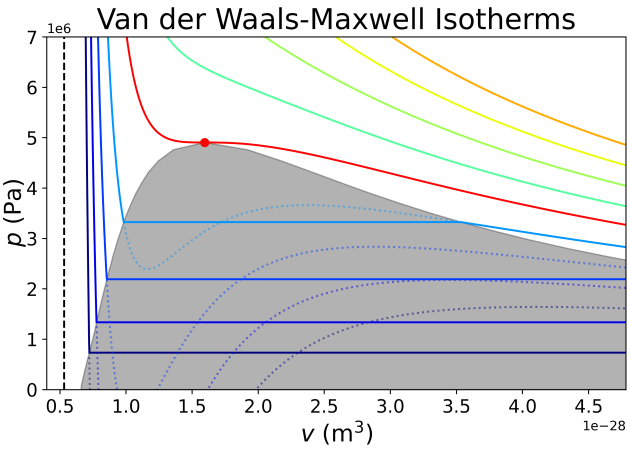

Figure 6 | Isotherms with Maxwell constructions. The $\mathbf{T} < \mathbf{T}_c$ isotherms of Figure 5 are shown in dotted lines, truncated by the Maxwell constructions. The shaded area is where liquid and gas exist in equilibrium, at the vapour pressure for that temperature.

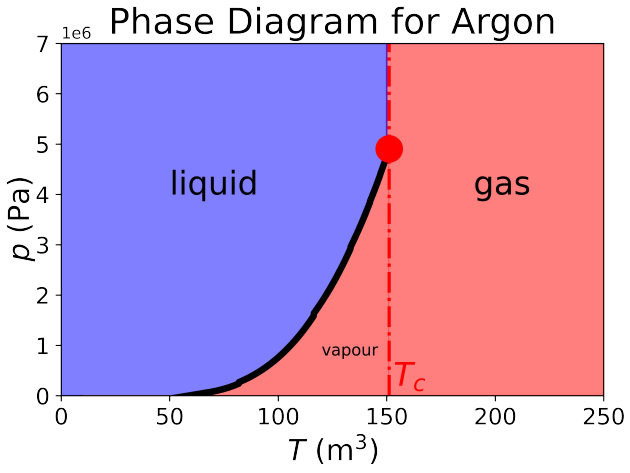

Figure 7 | Phase Diagram for Argon.

Above the critical temperature, there is no pressure at which the system forms a liquid-gas system; a substance cannot be in liquid form above its $\mathbf{T}_c$. Water has $\mathbf{T}_c = 650\text{K}$.

It is possible to decompress a pure liquid across the coexistence curve without any gas forming, so long as it doesn't reach the unstable region with $\partial\mathbf{p}/\partial\mathbf{v}\,\big|_{\mathbf{T}} > 0$ (bounded by the "spinodal curve", within the coexistence curve). Similarly, a pure gas can be compressed across the coexistence curve from the right. These *superheated liquids* and *supercooled vapours* are metastable states; within the spinodal curve things are completely unstable.

5.1.3 Clausius-Clapeyron Equation

Phase diagrams are in the $\mathbf{p}$-$\mathbf{T}$ plane, such as that in Figure 7. Crossing the liquid-gas (black) line amounts to following the entire Maxwell construction: the coexistence curve is folded up. On either side, the substance is thus either all liquid or all gas – at constant pressure, it depends which has the lower $\mathbf{G}$, or equivalently $\boldsymbol{\mu}$. At every point *on* the line, the two are equal, so if we move along it $\boldsymbol{\mu}_l$ and $\boldsymbol{\mu}_g$ will change by the same amount: $\mathrm{d}\boldsymbol{\mu}_l = \mathrm{d}\boldsymbol{\mu}_g$.

$$\mathrm{d}\boldsymbol{\mu} = \frac{\mathrm{d}\mathbf{G}}{\mathbf{N}} = \frac{-\mathbf{S}\mathrm{d}\mathbf{T} + \mathbf{V}\mathrm{d}\mathbf{p}}{\mathbf{N}} \qquad \Rightarrow \qquad \frac{-\mathbf{S}_g\mathrm{d}\mathbf{T} + \mathbf{V}_g\mathrm{d}\mathbf{p}}{\mathbf{N}_g} = \frac{-\mathbf{S}_l\mathrm{d}\mathbf{T} + \mathbf{V}_l\mathrm{d}\mathbf{p}}{\mathbf{N}_l}$$

$$\Rightarrow \qquad \frac{\mathrm{d}\mathbf{p}}{\mathrm{d}\mathbf{T}} = \frac{\frac{\mathbf{S}_g}{\mathbf{N}_g} - \frac{\mathbf{S}_l}{\mathbf{N}_l}}{\frac{\mathbf{V}_g}{\mathbf{N}_g} - \frac{\mathbf{V}_l}{\mathbf{N}_l}} = \frac{L/\mathbf{T}}{\mathbf{v}_g - \mathbf{v}_l} = \frac{L}{\mathbf{T}\Delta\mathbf{v}}$$

where the latent heat $L = \mathbf{T}(s_g - s_l)$ is the heat required per particle to convert liquid to gas. $L > 0$, and usually $\Delta\mathbf{v} > 0$, though an exception is the solid-liquid transition for H_2O.

A phase transition is said to be nth order if the nth derivative of $\mathbf{F}$ or $\mathbf{G}$ is discontinuous. For the liquid-gas transition, $\mathbf{S} = -\left.\partial\mathbf{F}/\partial\mathbf{T}\right|_{\mathbf{V}}$ (latent heat) and $\mathbf{V} = \left.\partial\mathbf{G}/\partial\mathbf{p}\right|_{\mathbf{T}}$ are both discontinuous, so this is a 1st-order phase transition.

5.1.4 Critical Exponents

The critical constants (β, γ, δ) are defined such that near the critical point,

$$\mathbf{v}_g - \mathbf{v}_l \sim (\mathbf{T}_c - \mathbf{T})^{\beta} \qquad \kappa \equiv -\frac{1}{\mathbf{v}}\left.\frac{\partial\mathbf{v}}{\partial\mathbf{p}}\right|_{\mathbf{T}} \sim (\mathbf{T}_c - \mathbf{T})^{-\gamma} \qquad \mathbf{p} - \mathbf{p}_c \sim (\mathbf{v} - \mathbf{v}_c)^{\delta}$$

We now deduce these constants for a $\mathfrak{vdW}$ gas.

Using reduced variables $\bar{\mathbf{T}} = \mathbf{T}/\mathbf{T}_c$, $\bar{\mathbf{p}} = \mathbf{p}/\mathbf{p}_c$, $\bar{\mathbf{v}} = \mathbf{v}/\mathbf{v}_c$, $\mathfrak{vdW}$ can be rewritten as:

$$\bar{\mathbf{p}} = \frac{8\bar{\mathbf{T}}}{3\bar{\mathbf{v}} - 1} - \frac{3}{\bar{\mathbf{v}}^2}$$

For an equilibrium (and thus equal $\mathbf{p}$) mix of liquid and gas,

$$\bar{\mathbf{p}} = \frac{8\bar{\mathbf{T}}}{3\bar{\mathbf{v}}_g - 1} - \frac{3}{\bar{\mathbf{v}}_g^2} = \frac{8\bar{\mathbf{T}}}{3\bar{\mathbf{v}}_l - 1} - \frac{3}{\bar{\mathbf{v}}_l^2} \qquad \Rightarrow \qquad \bar{\mathbf{T}} = \frac{(3\mathbf{v}_g - 1)(3\mathbf{v}_l - 1)(\mathbf{v}_g + \mathbf{v}_l)}{8\mathbf{v}_g^2\mathbf{v}_l^2}$$

Let $\epsilon = \mathbf{v}_g - \mathbf{v}_l$, and near the critical point $\mathbf{v}_g = 1 + \epsilon/2$ and $\mathbf{v}_l = 1 - \epsilon/2$. Substituting and expanding to second order gives $\bar{\mathbf{T}} \approx 1 - \epsilon^2/16$, so $\mathbf{v}_g - \mathbf{v}_l \sim (\mathbf{T} - \mathbf{T}_c)^{1/2}$ and $\beta = 1/2$.

At the critical point, $\left.\partial\mathbf{p}/\partial\mathbf{v}\right|_{\mathbf{T}} = 0$. If we move vertically from the critical point (increasing the temperature), this gradient seems from Figure 5 to be decreasing, so for small $(\mathbf{T}_c - \mathbf{T})$,

$$\left.\frac{\partial\mathbf{p}}{\partial\mathbf{v}}\right|_{\mathbf{T}} \approx \left.\frac{\partial^2\mathbf{p}}{\partial\mathbf{v}\partial\mathbf{T}}\right|_{\text{crit}}(\mathbf{T} - \mathbf{T}_c) = -\frac{k_B}{4b^2}(\mathbf{T} - \mathbf{T}_c) \qquad \Rightarrow \qquad \kappa \sim \frac{4b}{3k_B}(\mathbf{T} - \mathbf{T}_c)^{-1} \Rightarrow \gamma = 1$$

Along the critical isotherm, $\left.\partial\mathbf{p}/\partial\mathbf{v}\right|_{\mathbf{T}} = \left.\partial^2\mathbf{p}/\partial\mathbf{v}^2\right|_{\mathbf{T}} = 0$, so about the critical point,

$$\mathbf{p} - \mathbf{p}_c \approx \frac{1}{6}\left.\partial^3\mathbf{p}/\partial\mathbf{v}^3\right|_{\mathbf{T},\text{crit}}(\mathbf{v} - \mathbf{v}_c)^3 = \frac{23a}{36b^4}(\mathbf{v} - \mathbf{v}_c)^3 \qquad \Rightarrow \qquad \delta = 3$$

Rather than $(\beta, \gamma, \delta) = (1/2, 1, 3)$, experiments give $(0.32, 1.2, 4.8)$. $\mathfrak{vdW}$ fails here as it does not account for density fluctuations. Recall:

$$-\Phi = \mathrm{p}\mathbf{V} = k_B \mathbf{T} \ln \mathcal{Z} \qquad \langle \mathbf{N} \rangle = k_B \mathbf{T} \left. \frac{\partial \ln \mathcal{Z}}{\partial \boldsymbol{\mu}} \right|_{\mathbf{T},\mathbf{V}} \qquad \Delta \mathbf{N}^2 = k_B \mathbf{T} \left. \frac{\partial \langle \mathbf{N} \rangle}{\partial \boldsymbol{\mu}} \right|_{\mathbf{T},\mathbf{V}}$$

$$\Rightarrow \Delta \mathbf{N}^2 = \langle \mathbf{N} \rangle \left. \frac{\partial \langle \mathbf{N} \rangle}{\partial \ln \mathcal{Z}} \right|_{\mathbf{T},\mathbf{V}} = \langle \mathbf{N} \rangle \frac{k_B \mathbf{T}}{\mathbf{V}} \left. \frac{\partial \langle \mathbf{N} \rangle}{\partial \mathrm{p}} \right|_{\mathbf{T},\mathbf{V}} = \langle \mathbf{N} \rangle k_B \mathbf{T} \kappa \left. \frac{\partial \langle \mathbf{N} \rangle}{\partial \mathbf{V}} \right|_{\mathbf{T},\mathrm{p}} \propto \kappa$$

But $\kappa \sim (\mathbf{T} - \mathbf{T}_c)^{-1}$ near the critical point, so $\Delta \mathbf{N}$ diverges and $\mathfrak{vdW}$ becomes very invalid.

5.2 Ising Model

Consider $\mathbf{N}$ sites in a d-dimensional lattice, at each of which lives a spin $s_i = \pm 1$. The Ising (EE-zing) model has an energy involving a magnetic field B and only nearest-neighbour interactions J:

$$\mathbf{E}[\{s_i\}] = -B \sum_i s_i - J \sum_{\langle ij \rangle} s_i s_j$$

where the second sum is over pairs of nearest neighbours. Let each site have q nearest neighbours (e.g. for a right lattice, $q = 2d$); the sum then has about $\frac{1}{2}\mathbf{N}q$ terms. $J > 0$ encourages neighbour alignment (a ferromagnet). In the canonical ensemble, the partition function is then

$$\mathbf{Z} = \sum_{\{s_i\}} \exp\left(-\beta \mathbf{E}[\{s_i\}]\right)$$

where the sum is over all $2^{\mathbf{N}}$ possible sets of s_i. With this Hamiltonian, each lattice site will have some average value $\langle s_i \rangle \in [-1, 1]$ depending on the likelihood of all the different sets of $\{s_i\}$. The *magnetisation* is

$$\mathbf{m} \equiv \frac{1}{\mathbf{N}} \sum_i \langle s_i \rangle = \frac{1}{\mathbf{N}\beta} \frac{\partial \ln \mathbf{Z}}{\partial B} = -\frac{1}{\mathbf{N}} \frac{\partial \mathbf{F}}{\partial B}$$

Suppose each s_i doesn't vary much about m. The product $s_i s_j$ is then:

$$s_i s_j = [\mathbf{m} + (s_i - \mathbf{m})][\mathbf{m} + (s_j - \mathbf{m})] \approx \mathbf{m}^2 + \mathbf{m}(s_i - \mathbf{m} + s_j - \mathbf{m}) = \mathbf{m}(s_i + s_j) - \mathbf{m}^2$$

With this approximation, the energy of a given set $\{s_i\}$ becomes

$$\mathbf{E} \approx -B \sum_i s_i - J \sum_{\langle ij \rangle} \left[\mathbf{m}(s_i + s_j) - \mathbf{m}^2\right] = -B \sum_i s_i - J\mathbf{m} \frac{q}{2} \sum_i 2 s_i + J\mathbf{m}^2 \frac{\mathbf{N}q}{2}$$

$$= \frac{1}{2} J \mathbf{N} q \mathbf{m}^2 - (B + Jq\mathbf{m}) \sum_i s_i$$

This "mean-field" approximation thus provides an offset and effectively modifies the magnetic field to $B_{\text{eff}} = B + Jq\mathbf{m}$. Now, each site simply contributes $\frac{1}{2}Jq\mathbf{m}^2 \pm B_{\text{eff}}$ to the energy, independently of all the other sites. The partition function for 1 site is then:

$$\mathbf{Z}_i = \exp\left(-\beta\left(\frac{1}{2}Jq\mathbf{m}^2 + B_{\text{eff}}\right)\right) + \exp\left(-\beta\left(\frac{1}{2}Jq\mathbf{m}^2 - B_{\text{eff}}\right)\right) = 2e^{-\beta J q \mathbf{m}^2/2} \cosh\left(\beta B_{\text{eff}}\right)$$

$$\Rightarrow \mathbf{Z} = \mathbf{Z}_i^{\mathbf{N}} = 2^{\mathbf{N}} e^{-\beta J \mathbf{N} q \mathbf{m}^2/2} \cosh^{\mathbf{N}}\left(\beta B_{\text{eff}}\right)$$

We can then calculate $\mathbf{m}$ from this and find self-consistent solutions:

$$\mathbf{m} = \frac{1}{\mathbf{N}\beta} \frac{\partial \ln \mathbf{Z}}{\partial B} = \frac{1}{\beta} \frac{\partial \ln \cosh\left(\beta B_{\text{eff}}\right)}{\partial B} = \tanh(\beta B_{\text{eff}}) = \tanh(\beta B + \beta J q \mathbf{m})$$

For $B = 0$, the self-consistency equation is $\mathbf{m} = \tanh(\beta J q \mathbf{m})$. $\mathbf{m} = 0$ is always a solution, but there may be others as well. As $\mathbf{m} \to \infty$, $\tanh(\beta J q \mathbf{m}) \to 1$, so if the tanh gradient is initially greater than 1, it will intersect the line $\mathbf{m} = \mathbf{m}$ again at some $\mathbf{m} = \mathbf{m}_0 > 0$, and also at $\mathbf{m} = -\mathbf{m}_0$. Now for small $\mathbf{m}$, $\tanh(\beta J q \mathbf{m}) \approx \beta J q \mathbf{m}$, so there is a critical temperature $\mathbf{T}_c = Jq/k_B$ above which the tanh gradient is too low and the only solution is at $\mathbf{m} = 0$. Below $\mathbf{T}_c$ there are two other solutions at $\mathbf{m} = \pm\mathbf{m}_0(\mathbf{T})$; the positive solution (if it exists) is shown in the lowest line of Figure 8. $\mathbf{m}$ is continuous at $\mathbf{T} = \mathbf{T}_c$, but $\partial\mathbf{m}/\partial\mathbf{T} \propto \partial^2\mathbf{F}/\partial\mathbf{T}\partial B$ changes abruptly. Thus a (second-order) phase transition occurs.

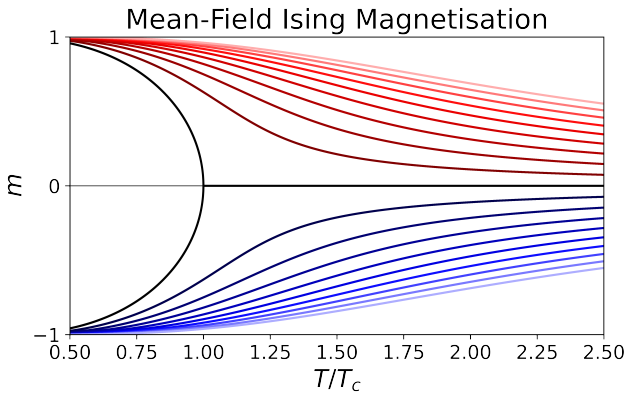

Figure 8 | Self-Consistent Magnetisations in the Ising Model. Magnetisation plots for several different B are shown; $B = 0$ falls to $\mathbf{m} = 0$ at $\mathbf{T} = \mathbf{T}_c$ and stays there.

For $B \neq 0$, we see that no phase transition occurs. Taking the limit of small βB, $\mathbf{m}$ (high $\mathbf{T}$), the self-consistency equation becomes $\mathbf{m} \approx \beta B + \beta J q \mathbf{m} \Rightarrow \mathbf{m}_0 \propto B$. Unlike with $B = 0$, one sign of $\mathbf{m}_0$ is now favoured over the other. Although there is no phase transition on changing $\mathbf{T}$, if $\mathbf{T}$ is fixed below $\mathbf{T}_c$ there *is* a (first-order) phase transition on changing B, as $\mathbf{m} \propto \partial\mathbf{F}/\partial B$ discontinuously flips from +ve to −ve.

5.2.1 Critical Exponents

In $B - \mathbf{T}$ space, the phase transition is simply a line along the $B = 0$ axis, ending at $\mathbf{T} = \mathbf{T}_c$.

Moving along this transition line, the self-consistent magnetisation becomes small near $\mathbf{T} = \mathbf{T}_c$, so $\mathbf{m} = \tanh(\beta J q \mathbf{m}) \approx \beta J q \mathbf{m} - \frac{1}{3}(\beta J q \mathbf{m})^3$. Thus $\mathbf{m} \sim (\mathbf{T}_c - \mathbf{T})^{1/2}$.

Now starting from $\mathbf{T} > \mathbf{T}_c$ and approaching along the $\mathbf{T}$-axis from the right, consider the behaviour of $\chi \equiv \mathbf{N}\,\partial\mathbf{m}/\partial B\,\big|_{\mathbf{T}}$. Differentiating the self-consistency equation and setting $B = \mathbf{m} = 0$,

$$\chi = \mathbf{N}\beta\left(1 + Jq\frac{\chi}{\mathbf{N}}\right)\operatorname{sech}^2(\beta J q \mathbf{m}) = \mathbf{N}\beta\left(1 + \frac{Jq}{\mathbf{N}}\chi\right) \qquad \Rightarrow \qquad \chi \approx \frac{\mathbf{N}\beta}{1 - \mathbf{T}_c/\mathbf{T}} \sim (\mathbf{T} - \mathbf{T}_c)^{-1}$$

Beginning at the critical point and fixing $\beta = 1/Jq$ while varying B up and down, we have

$$\mathbf{m} = \tanh\left(\frac{B}{Jq} + \mathbf{m}\right) \approx \mathbf{m} + \frac{B}{Jq} + \frac{1}{3}\mathbf{m}^3 \qquad \Rightarrow \qquad B \propto \mathbf{m}^3$$

These three impersonate the critical constants of $\mathfrak{vdW}$.

5.2.2 Landau Theory

Equilibrium configurations are those that minimise $\mathbf{F}$, which in the mean-field Ising model is

$$\mathbf{F} = -\frac{1}{\beta}\ln\mathbf{Z} = \frac{J\mathbf{N}q\mathbf{m}^2}{2} - \frac{\mathbf{N}}{\beta}\ln\left(2\cosh\left(\beta B_{\text{eff}}\right)\right)$$

Landau treats $\mathbf{F}$ as a valid function of $\mathbf{m}$, even at non-equilibrium values. Setting $\partial\mathbf{F}/\partial\mathbf{m} = 0$ gives the same equation for $\mathbf{m}$ as the self-consistency equation.

Consider a general 2nd-order phase transition, of a system symmetric in $\mathbf{m}$:

$$\mathbf{F}(\mathbf{m};\mathbf{T}) - \mathbf{F}_0 = C(\mathbf{T})\mathbf{m}^2 + D(\mathbf{T})\mathbf{m}^4 + \dots$$

where we expect $D(\mathbf{T}) > 0$ so that the system doesn't collapse for large $|\mathbf{m}|$. The shape of $\mathbf{F}(\mathbf{m})$ depends on the sign of $C(\mathbf{T})$; this sign may depend on $\mathbf{T}$, e.g. for Ising with $B = 0$:

$$\mathbf{F}(\mathbf{m};\mathbf{T}) + \mathbf{N}k_B\mathbf{T}\ln 2 = \overbrace{\frac{\mathbf{N}Jq}{2}\left(1 - \frac{\mathbf{T}_c}{\mathbf{T}}\right)}^{C(\mathbf{T})}\mathbf{m}^2 + \frac{\mathbf{N}\beta^3 J^4 q^4}{12}\mathbf{m}^4 + \dots$$

So depending on whether $\mathbf{T} \lessgtr \mathbf{T}_c$, $\mathbf{F}(\mathbf{m})$ will have a different shape. For $\mathbf{T} \geq \mathbf{T}_c$, $C(\mathbf{T}) > 0$ and $\mathbf{F}(\mathbf{m})$ curves upwards $\forall \mathbf{m}$ – the only equilibrium solution is $\mathbf{m} = 0$ and it is stable. However, for $\mathbf{T} < \mathbf{T}_c$, $C(\mathbf{T}) < 0$, and $\mathbf{F}(\mathbf{m})$ has valleys on either side of the $\mathbf{m} = 0$. There are three equilibrium solutions, but that of $\mathbf{m} = 0$ is unstable. The other two at $\pm\mathbf{m}_0$ are stable, and by setting $\partial\mathbf{F}/\partial\mathbf{m}\,\big|_{\mathbf{T}} = 0$ near $\mathbf{T}_c$, we find $\mathbf{m}_0 \sim (\mathbf{T} - \mathbf{T}_c)$ as above.

First-order phase transitions can be asymmetric in $\mathbf{m}$, such as Ising with $B \neq 0$. Depending on the temperature dependence of their coefficients, they can have more detailed behaviour, such as two different stable equilibrium solutions, one having higher $\mathbf{F}$ than the other (hence being metastable).