KINETIC THEORY AND THERMODYNAMICS - TUTORIAL 3

Non p-V systems

For a general thermodynamic system, first law can be written

$$dU = đQ + đW = T dS - X dx.$$

where X is some intensive (ind. of system size) generalised force and x is some extensive (scales linearly with system size) generalised displacement. We then have that

$$đQ \leq T dS, \quad đW \geq -X dx,$$

where the equality holds if and only if the change is reversible.

System	X	x	$đW$
Gas	$-p$	V	$-p\,dV$
Elastic rod	f	L	$f\,dL$
Liquid film	γ	A	$\gamma\,dA$
Dielectric	$\mathbf{E}$	$\mathbf{p}_E$	$-\mathbf{p}_E \cdot d\mathbf{E}$
Magnetic	$\mathbf{B}$	$\mathbf{m}$	$-\mathbf{m} \cdot d\mathbf{B}$

Maxwell relations for non p-V systems follow from the corresponding first law. Mnemonics for these are shown in fig. 1[1].

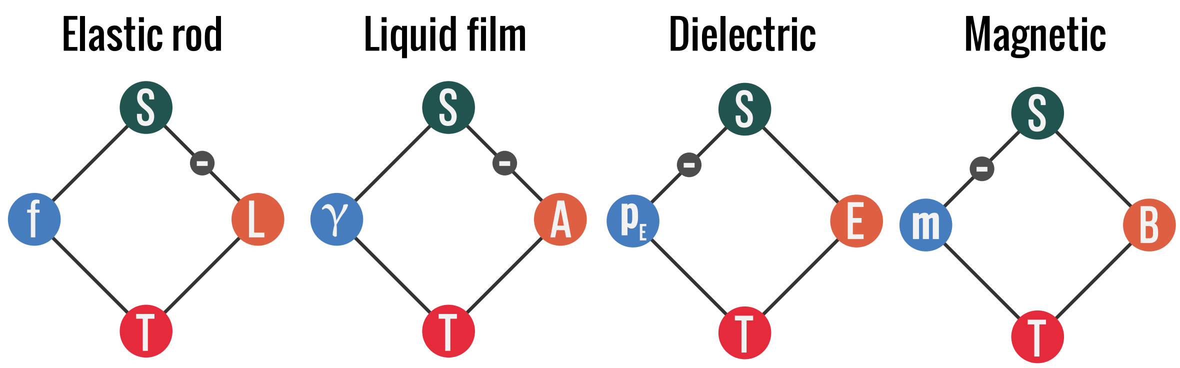

Figure 1: Maxwell relation mnemonics for non p-V systems.

[1]Careful with the position of the minus sign. Note the relationship with the relative sign of the heat and work terms: different sign = LHS, same sign = RHS

Probability distributions

The probability that an n-dimensional vector $\mathbf{q} = (q_1, q_2, ..., q_n)$ lies in the interval $[q_1,\, q_1 + \mathrm{d}q_1] \times [q_2,\, q_2 + \mathrm{d}q_2] \times ..... \times [q_n,\, q_n + \mathrm{d}q_n]$ is given by

$$P(\mathbf{q})\,\mathrm{d}\mathbf{q} = P(q_1, q_2, ..., q_n)\,\mathrm{d}q_1\,\mathrm{d}q_2 \ldots \mathrm{d}q_n.^2 \tag{1}$$

The the expectation value of some function of $\mathbf{q}$, $f(\mathbf{q})$ is then given by

$$\langle f(\mathbf{q})\rangle = \frac{\int_{\mathbf{q}} f(\mathbf{q})\,P(\mathbf{q})\,\mathrm{d}\mathbf{q}}{\int_{\mathbf{q}} P(\mathbf{q})\,\mathrm{d}\mathbf{q}}$$

where the denominator ensures a normalised probability distribution (and is unity if $P(\mathbf{q})$ is already normalised).

Velocity and speed distributions

In three dimensions, the probability a particle has a velocity in the interval $[\mathbf{v}, \mathbf{v} + \mathrm{d}\mathbf{v}]$ is given by $f(\mathbf{v})\,\mathrm{d}\mathbf{v}$ where $f(\mathbf{v}) = f(v_x, v_y, v_z)$ is the *velocity* distribution function. We can use this to calculate expecation values of functions of the velocity of a particle, for example:

$$\langle v_x^2\rangle = \int_{\mathbf{v}} v_x\, f(\mathbf{v})\,\mathrm{d}\mathbf{v} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} v_x\, f(v_x, v_y, v_z)\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z.$$

If the velocities are distributed isotropically, the velocity distribution function then only depends on the magnitude of the velocity v i.e. $f(\mathbf{v}) = f(v)$. This still describes a velocity distribution, *not* a speed distribution, it just takes the speed as its argument. In the isotropic case, the most natural coordinate system is spherical polar coordinates, in which case we can re-express the velocity distribution:

$$\widetilde{f}(v,\,\theta,\,\phi)\,\mathrm{d}v\,\mathrm{d}\theta\,\mathrm{d}\phi = f(v)\left|\frac{\partial(v_x, v_y, v_z)}{\partial(v, \theta, \phi)}\right|\,\mathrm{d}v\,\mathrm{d}\theta\,\mathrm{d}\phi = \overbrace{f(v)\,v^2\sin(\theta)}^{\widetilde{f}(v,\theta,\phi)}\,\mathrm{d}v\,\mathrm{d}\theta\,\mathrm{d}\phi.$$

Comparing this to Equation (1), we see that the particle distribution function $\widetilde{f}(v,\,\theta,\,\phi) = f(v)\,v^2\sin(\theta)$ still describes a velocity distribution but it is parameterised in terms of the speed v and the spherical polar angles θ and ϕ. To obtain the 'speed distribution' we need to just integrate out the angular dependence, obtaining:

$$\widetilde{f}(v) = \int_0^{\pi}\int_0^{2\pi} \widetilde{f}(v,\,\theta,\,\phi)\,\mathrm{d}\theta\,\mathrm{d}\phi = 4\pi\, v^2\, f(v),$$

where $f(v)$ is the isotropic *velocity* distribution function.

Noah Waterfield Price
Michaelmas 2016

[2]Note it is wholly possible for $P(\mathbf{q})$ to depend only a subset of the components of $\mathbf{q}$; it could even be constant and not have any $\mathbf{q}$ dependence at all.