Review of Thermodynamics. 4: Important Examples of Systems

Example: The Ideal Gas

• *Equations of state:* Gases are characterized by the state variables E, (T, S), (p, V), and (μ, N). In an ideal gas particles are taken to be non-interacting (except for the collisions needed to establish equilibrium), and in particular E does not depend on V. Their pressure and energy equations of state are

$$pV = Nk_{\mathrm{B}}T \; , \qquad E = \tfrac{1}{2}f\,Nk_{\mathrm{B}}T \; ,$$

where $k_{\mathrm{B}} = 1.381 \times 10^{-23}$ J/K is the Boltzmann constant. The value of f parametrizes the type of gas thermodynamically, and its value is phenomenologically often close to an integer. We will also need equations for the entropy $S = S(E, V)$ or $S(T, V)$ and chemical potential $\mu(T, V)$.

• *Compressibility and thermal expansion:* From the corresponding definitions we get, after short calculations,

$$\kappa_T = \frac{1}{p} \; , \quad \text{and} \quad \alpha = \frac{1}{T} \; ; \quad \text{from these we can then obtain} \quad \kappa_S = \frac{f}{2+f}\frac{1}{p} < \kappa_T.$$

• *Heat capacity and entropy:* Experimentally, for an ideal gas C_V and C_p are constant over a wide range of temperatures. Their values can be calculated from the equations of state; C_V is immediate, and we can get C_p either from the general relationship between heat capacities, $C_p = C_V + (TV/\kappa_T)\,\alpha^2$, or using the enthalpy, for which $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}N$ and, for transformations with constant p and N, $\mathrm{d}H = T\,\mathrm{d}S$,

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{V,N} = \frac{f}{2}\,Nk_{\mathrm{B}} \; , \quad C_p = \left.\frac{\partial H}{\partial T}\right|_{p,N} = \frac{\partial}{\partial T}(E + pV) = \left(1 + \frac{f}{2}\right)Nk_{\mathrm{B}} \; , \quad \text{so} \quad \gamma = \frac{C_p}{C_V} = 1 + \frac{2}{f} \; ,$$

in agreement with experimental results for integer f [⋆ find κ_S]. Notice that $C_V \nrightarrow 0$ as $T \to 0$. (We will see later using a microscopic model in statistical mechanics that this has a justification and expresses the principle of equipartition of energy.) For the T and V dependence of the entropy we can then write, starting from the fundamental identity in the $\mathrm{d}E$ form and keeping N constant,

$$\mathrm{d}S = \frac{\mathrm{d}E}{T} + \frac{p\,\mathrm{d}V}{T} - \frac{\mu\,\mathrm{d}N}{T} = \frac{f}{2}\,Nk_{\mathrm{B}}\frac{\mathrm{d}T}{T} + Nk_{\mathrm{B}}\frac{\mathrm{d}V}{V} \; , \quad \text{or} \quad S(T, V) = S(T_0, V_0) + Nk_{\mathrm{B}}\ln\left[\frac{V}{V_0}\left(\frac{T}{T_0}\right)^{f/2}\right].$$

• *Chemical potential:* Substituting E and S into $F = E - TS$, we get

$$\mu(T, V) = \left.\frac{\partial F}{\partial N}\right|_{T,V} = \tfrac{1}{2}f\,k_{\mathrm{B}}T - k_{\mathrm{B}}T\ln\left[\frac{V}{V_0}\left(\frac{T}{T_0}\right)^{f/2}\right].$$

Non-Ideal Gases

• *Idea:* Gases with different equations of state, in which the pressure and other quantities get contributions from finite particle sizes, finite-range interactions between particles, and quantum statistics effects.

• *Virial expansion:* A way to systematically treat deviations from the behavior of an ideal gas. Those deviations arise when particles spend enough time close to each other to feel the effect of the interparticle potentials v_{ij}, so we replace V in functions of (T, V, N) by the number density $\rho := N/V$, and express them in terms of power-series expansions in ρ. For example, the pressure equation of state is of the form

$$p = k_{\mathrm{B}}T\,\rho\left[1 + B_2(T)\,\rho + B_3(T)\,\rho^2 + ...\right] \; ,$$

where $B_i(T)$ is the i-th virial coefficient. At relatively low densities we only need to take the first correction term, $B_2(T) = B(T)$, into account, and we expect B_2 to be an increasing function of T (see, e.g., Reif §5.10). (In a gas, power series in the density converge reasonably quickly; if they do not converge, we call the fluid a liquid.) Other equations of state may be expressed in similar ways.

Example: The van der Waals Fluid

• *Idea:* A phenomenological model of a realistic gas, in which the equation of state incorporates the effects of a weak attractive force at large distances and a strong repulsive force at very small distances.

• *Equation of state:* If b is the excluded volume arising from the short-range repulsion between particles, and a measures the long-range attraction between them, the equation of state is

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_{\mathrm{B}}T \,, \qquad \text{or} \qquad p = \frac{Nk_{\mathrm{B}}T}{V - Nb} - \frac{aN^2}{V^2} \,.$$

• *Virial coefficients:* Expanding the equation of state in powers of ρ for fixed N, one gets

$$p = k_{\mathrm{B}}T\rho\left[1 + \left(b - \frac{a}{k_{\mathrm{B}}T}\right)\rho + ...\right] \,, \qquad \text{from which we read off} \qquad B_2 = b - \frac{a}{k_{\mathrm{B}}T} \,.$$

• *Isothermal lines:* Based on this equation of state, for every T and p there are either 1 or 3 possible values of V, the real solutions of a cubic equation. For very high T, the second term on the right is negligible, and there is only one solution, of the modified ideal gas form $V = N(k_{\mathrm{B}}T/p + b)$. Two more real solutions appear below some critical isothermal line T_{c}, at pressure p_{c} and volume V_{c}, where $\partial p/\partial V|_T = 0$ and $\partial^2 p/\partial V^2|_T = 0$.

• *Critical point:* To find it, solve the set of equations given by the equation of state and the vanishing of the first two derivatives. One gets that $p_{\mathrm{c}} = a/27b^2$, $V_{\mathrm{c}} = 3Nb$, and $k_{\mathrm{B}}T_{\mathrm{c}} = 8a/27b$. If we use these to define the dimensionless variables $\tilde{p} = p/p_{\mathrm{c}}$, $\tilde{V} = V/V_{\mathrm{c}}$ and $\tilde{T} = T/T_{\mathrm{c}}$, we get the universal relation (in the sense that it holds for all values of a and b) that van der Waals called Law of Corresponding States,

$$\tilde{p} = \frac{8\tilde{T}}{3\tilde{V} - 1} - \frac{3}{\tilde{V}^2} \,. \hspace{4cm} [* \text{ plot}]$$

• *Other properties:* The energy equation of state is $E = \frac{f}{2}Nk_{\mathrm{B}}T - a/V$, as can be derived using statistical mechanics methods. ⋆ Find C_V, C_p, κ_T, κ_S, γ.

• *Phases:* Considered as an equation for V given values of p and T, the equation of state is cubic and has three solutions V_1, V_2, V_3 for $T < T_{\mathrm{c}}$, indicating the existence of more than one fluid phase. To determine what phase each solution corresponds to physically, plot the isothermal lines in the p-V plane. From the plot, or from the equation of state directly, we conclude that V_1 is a liquid phase, V_2 an unstable one with negative compressibility and therefore unphysical, and V_3 a gas phase. Also, at some temperatures the pressure can become negative, which is impossible as well, in this case. *Questions:* How does a system avoid these unphysical situations? How does it determine when to make a phase transition?

Some Non-Fluid Systems

• *Wire or rubber band:* The relevant variables are $(E; T, S; F, L)$, where L is the length and F is the tension ($F > 0$ when it pulls outwards), in terms of which the fundamental identity for E is

$$dE = T\,dS + F\,dL \,.$$

The tension equation of state is a generalized Hooke's law that includes a temperature dependence, and is parametrized by a spring constant K, a thermal coefficient D, and the unstretched length L_0,

$$F = (K + DT)(L - L_0) \,.$$

• *Magnetic system:* The variables are $(E; T, S; \mathbf{B}, \mathbf{M})$, where $\mathbf{B}$ is the magnetic field and $\mathbf{M}$ the magnetization, possibly in addition to (p, V). The magnetization equation of state is the relationship $\mathbf{M} = \mathbf{M}(T, \mathbf{B})$, and the response of the system is characterized by the magnetic susceptibility $\chi(T, B) := \partial M/\partial B|_T$, which is often of the form $\mathbf{M}/V = \chi\mathbf{B}$, with $\chi = c_0/T$ (Curie's law). The fundamental identity for E is

$$dE = T\,dS - \mathbf{M}\cdot d\mathbf{B} \,.$$

Reading

• *Kennett:* There is no specific chapter, but see §§4.5 and 4.6 for the statistical mechanics of gases.
• *Gases:* Pathria & Beale §§1.4-1.5, §10.2 and §12.2; Reif Ch 5 [detailed]; Schwabl §2.5 [and other examples].
• *Magnetic systems:* Pathria & Beale §§3.9-3.10; Plischke & Bergersen §1.7.
• *Virial expansion and van der Waals gas:* Huang §§4.4-4.7; Mattis & Swendsen §3.6; Reichl §4.4.4.