Lecture 32 (2-15), Mar 31, 2023

Thermodynamic Equilibrium and Maxwell's Relations

- To actually maximize the entropy $S(U, V, N)$ we need both $\frac{\partial S}{\partial U} = \frac{\partial S}{\partial V} = \frac{\partial S}{\partial N} = 0$ and for the Hessian matrix of second derivatives to have negative eigenvalues
- Suppose we have some system with $S = S(U, V, N)$ which is some function; we know $\mathrm{d}S = \frac{\partial S}{\partial U}\,\mathrm{d}U + \frac{\partial S}{\partial V}\,\mathrm{d}V + \frac{\partial S}{\partial N}\,\mathrm{d}N$
  - This means $\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U + \frac{p}{T}\,\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}N$
  - In this form, the equation is known as the *thermodynamic identity for the entropy*
  - This equation gives the change in entropy for some change in energy, volume, or number of particles
- We can invert $S(U, V, N)$ to get $U(S, V, N)$, the energy in terms of entropy, volume, and number of particles
- Solving for $\mathrm{d}U$, we have $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\mathrm{d}N$; this is the *thermodynamic identify for the energy*
  - We can match this to what we get from $U(S, V, N)$
  - This gives us 2 new definitions: $p = \frac{\partial U}{\partial V}, \mu = \frac{\partial U}{\partial N}$
- These definitions are collectively known as *Maxwell's relations*: $\frac{1}{T} = \frac{\partial S}{\partial U}, \frac{p}{T} = \frac{\partial S}{\partial V}, \frac{\mu}{T} = -\frac{\partial S}{\partial N}, T = \frac{1}{\frac{\partial S}{\partial U}} p = \frac{\partial U}{\partial V}, \mu = \frac{\partial U}{\partial N}$
- To be a maximum, the Hessian must have all negative eigenvalues
- We define thermodynamic equilibrium to be stable when all these conditions hold:
  - $c_V > 0$
  - $\frac{\partial P}{\partial V} < 0$
    - Suppose $\frac{\partial P}{\partial V} > 0$ in some system, then P increases with pressure or v
    - In this case pushing on the substance causes is pressure to be even lower, so this is unstable since the system will just keep on increasing or decreasing in volume
    - This arises when we model particles that interact with each other
  - $\frac{\partial \mu}{\partial N} > 0$