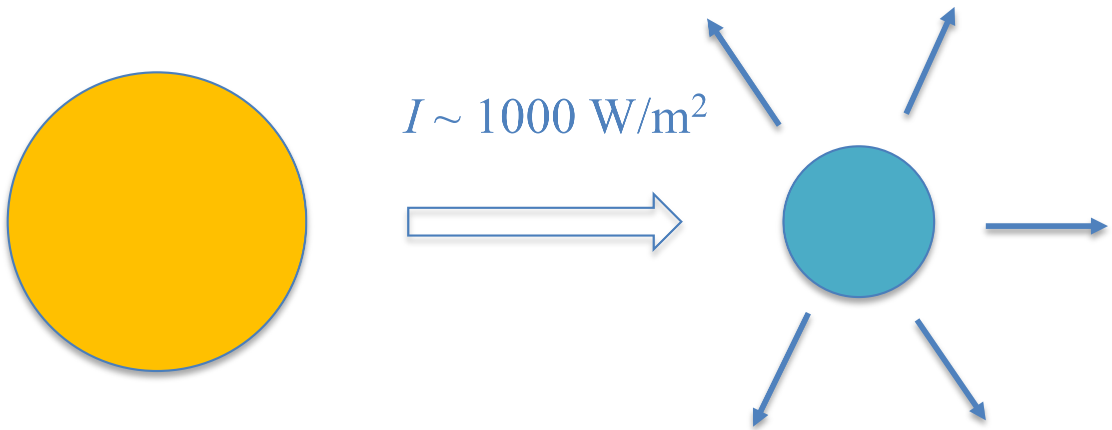
Notes for today

- Reading: continuing Ch. 3.

- Reminder about lecture recording, I can send a recording link if you have to miss.

Remark on Sun-Earth system:



Sun ~ 5000 K

Earth ~ 255 K

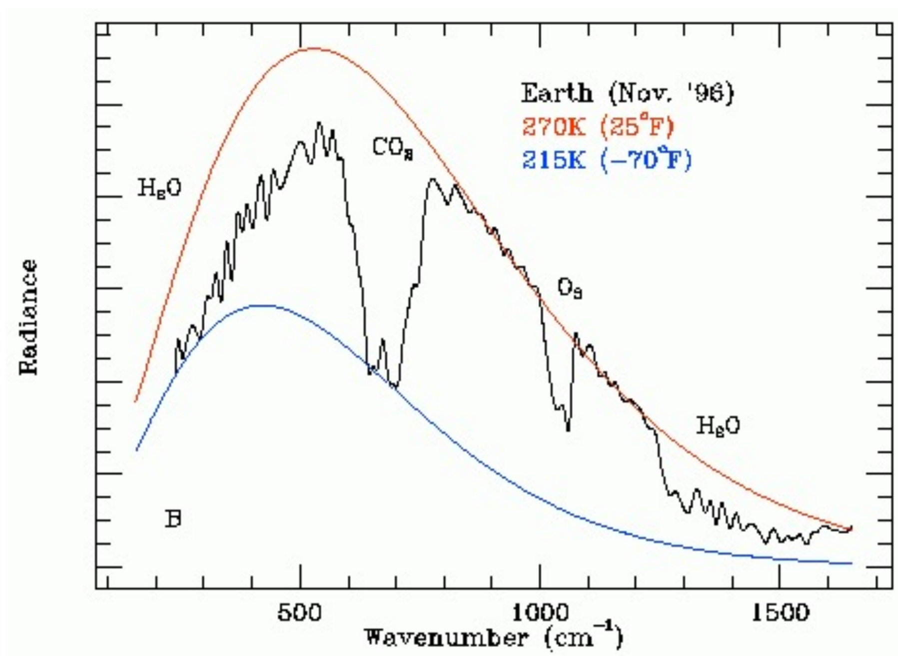
Steady state: **same absorbed & radiated power**

Can see, entropy *must* increase in this process.

$$S = \frac{4U}{3T} \cong 3.6 N k_B$$

Thermal EM radiation

Earth emissivity ~0.8. [depends strongly on frequency; greenhouse effect.]

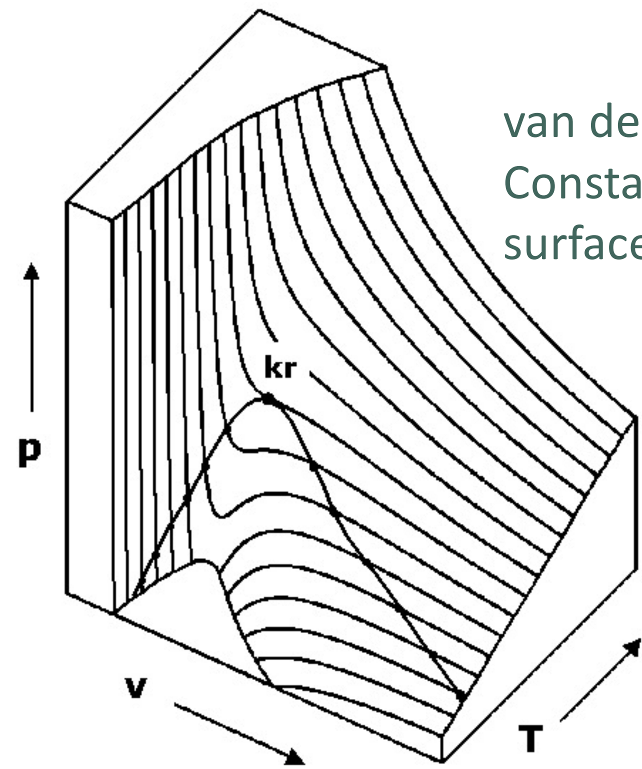


Ideal gas vs. van der Waals gas:

Recall, ideal gas has no inter-particle interactions; point-like particles take no volume.
Van der Waals approximation, 2 parameters better characterize atomic/molecular gases. (A different approach: *virial expansion*, is an infinite series is in principle exact in dilute limit. Ch. 13 has more on this.)

van der Waals

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$$



van der Waals
Constant - *N*
surface

van der Waals gas:

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$$

per-particle

$$P + \frac{a}{v^2} = \frac{kT}{v - b}$$

(1) $b \approx$ intrinsic volume of gas particle.

e.g. for $a = 0$, $P(V - Nb) = NkT$

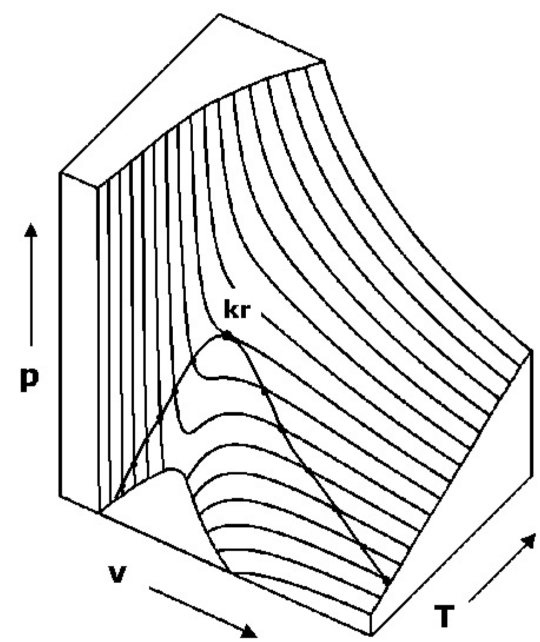
(2) $\frac{aN}{V} \approx$ potential energy of attraction between particles.

e.g. isothermal expansion with $b = 0$, additional work required:

$$\int PdV = NkT ln(V/Vi) + \left.\frac{aN^2}{V}\right]_{Vi}^{V}$$

Ideal gas *TdS*

additional: *attractive interaction*



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$$P + \frac{a}{v^2} = \frac{kT}{v - b}$$

Can we find entropy?

van der Waals gas:

$$\left(P+\frac{aN^2}{V^2}\right)(V-Nb)=NkT$$

per-particle

$$P+\frac{a}{v^2}=\frac{kT}{v-b}$$

Can we find entropy?

$$ds=\left[\frac{1}{T}(u,v)\right]du+\left[\frac{P}{T}(u,v)\right]dv$$

<No direct help.

$$\frac{\partial^2 s}{\partial u\partial v}=\frac{\partial^2 s}{\partial v\partial u}\Longrightarrow\frac{\partial(\frac{1}{T})}{\partial v}=\frac{\partial(\frac{P}{T})}{\partial u}$$

Differentials:

$$dU = TdS - PdV \equiv \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV$$ example of exact differential

Useful general mathematical properties:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$ order of differentiation

Sometimes can't measure *S* directly, could measure adiabatic temperature change.

a Maxwell relation

e.g. $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = -1/\left(\frac{\partial S}{\partial P}\right)_V$$

$$\left(\frac{\partial x}{\partial y}\right)_z = 1/\left(\frac{\partial y}{\partial x}\right)_z$$ reciprocal

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial t}\right)_z = \left(\frac{\partial x}{\partial t}\right)_z$$ chain rule; same as: $$\left(\frac{\partial x}{\partial y}\right)_z = \frac{\left(\frac{\partial x}{\partial t}\right)_z}{\left(\frac{\partial y}{\partial t}\right)_z}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$ cyclical

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial t}\right)_y \left(\frac{\partial t}{\partial y}\right)_z + \left(\frac{\partial x}{\partial y}\right)_t$$ converting partials

Reminder from last week:

$$SdT - VdP + \sum N_i \, d\mu_i = 0$$ Gibbs-Duhem relation

- Can integrate to find e.g. μ in terms of other parameters.

Thus 2 (or *r*+1) equations of state are sufficient.

- Nice trick when *r* = 1 : per-atom (or molar) relations.

$$u \equiv \frac{U}{N} = U(s, v) \longrightarrow \boxed{du = Tds - Pdv}$$

similar result for *dS*

$PV = Nk_BT, U = \frac{3}{2}Nk_BT;$ find s?

$$u \equiv \frac{U}{N} = U(s,v) \longrightarrow \boxed{du = Tds - Pdv}$$

first-order scaling makes it a 2-variable problem:

$$U(S,V,N) = N\frac{U}{N}(S,V,N) = N\boxed{U(s,v,N=1)}$$

$$u(s,v)$$

$$PV = Nk_BT,\ U = \frac{3}{2}Nk_BT;\ \text{find } s?$$

$$ds = \boxed{\frac{3}{2}\frac{k}{u}}du + \boxed{\frac{k}{v}}dv$$

Identify $\frac{\partial f}{\partial u}, \ \frac{\partial f}{\partial v} \Rightarrow s = f + so$

Result $s = k\ln\left[v\,u^{\frac{3}{2}}\right] + s_o$

$$S = Nk\ln\left[\frac{V}{N}\left(\frac{U}{N}\right)^{\frac{3}{2}}\right] + N\boxed{s_o}$$

$$s_o = \frac{5}{2}k + k\ln\left[\left(\frac{4\pi m}{3h^2}\right)^{\frac{3}{2}}\right]$$

$$dS = \frac{3}{2}\frac{Nk}{U}dU + \frac{Nk}{V}dV$$

$$f = Nk\ln\left(V\,U^{\frac{3}{2}}\right)$$

$$\boxed{S \neq f + N\times const.!}$$

van der Waals gas:

$$\left(P+\frac{aN^2}{V^2}\right)(V-Nb)=NkT$$

per-particle

$$P+\frac{a}{v^2}=\frac{kT}{v-b}$$

Can we find entropy?

$$ds=\left[\frac{1}{T}(u,v)\right]du+\left[\frac{P}{T}(u,v)\right]dv$$

$$\frac{\partial^2 s}{\partial u\partial v}=\frac{\partial^2 s}{\partial v\partial u}\Longrightarrow\frac{\partial(\frac{1}{T})}{\partial v}=\frac{\partial(\frac{P}{T})}{\partial u}\qquad=\frac{\partial}{\partial u}\left\{\frac{a}{v^2T}\right\}$$

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per-particle

$$P + \frac{a}{v^2} = \frac{kT}{v - b}$$

Can we find entropy?

$$ds = \left[\frac{1}{T}(u,v)\right]du + \left[\frac{P}{T}(u,v)\right]dv$$

$$\frac{\partial^2 s}{\partial u \partial v} = \frac{\partial^2 s}{\partial v \partial u} \Longrightarrow \frac{\partial(\frac{1}{T})}{\partial v} = \frac{\partial(\frac{P}{T})}{\partial u} \quad = \frac{\partial}{\partial u}\left\{\frac{a}{v^2 T}\right\}$$

See text, <u>one</u> solution is:

$$\Longrightarrow \frac{1}{T} = \frac{ck}{u + a/v}; \quad S = Nk \ln[(v - b)(u + a/v)^c] + Ns_o$$

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per-particle

$$P + \frac{a}{v^2} = \frac{kT}{v - b}$$

Can we find entropy?

$$ds = \left[\frac{1}{T}(u, v)\right] du + \left[\frac{P}{T}(u, v)\right] dv$$

Alternative, assume:

$$u = \frac{3}{2}kT - {}^{a}/_{v}$$

Recall work done in expanding at const. T

$$\frac{1}{T} = \frac{\frac{3}{2}k}{u + a/v} \qquad \frac{P}{T} = \frac{k}{v - b} - \frac{\frac{3}{2}k\frac{a}{v^2}}{u + a/v}$$

van der Waals gas:

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$$

per-particle

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Can we find entropy?

$$ds = \left[\frac{1}{T}(u, v)\right] du + \left[\frac{P}{T}(u, v)\right] dv$$

Alternative, <u>assume</u>: $u = \frac{3}{2}kT - {}^{a}/_{v}$ Recall work done in expanding at const. T

$$\frac{1}{T} = \frac{\frac{3}{2}k}{u + a/v} \qquad \frac{P}{T} = \frac{k}{v - b} - \frac{\frac{3}{2}k\frac{a}{v^2}}{u + a/v}$$

Solution $S = Nk \ln\left[(v - b)(u + a/v)^{\frac{3}{2}}\right] + Nso$

Note this is *<u>one possible</u>* solution of vdW eqn, but assuming a constant C_V specifies this result.