Thus,
$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}$$

$$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial E}{\partial V}\right)_S$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

There are many of these!

<u>Ex</u>: Difference between heat capacities.

Recall, before we found $C_p - C_v = Nk$

We would like to

① derive a relation in terms of easy to measure quantities

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{thermal expansion coefficient}$$

$$k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{isothermal compressibility}$$

We would now like to compute $C_p - C_V$ in terms of these quantities.

$\Rightarrow$ it is easier to calculate C_V, but easier to measure C_p

$\Rightarrow$ would like to relate them in terms of known quantities

$dE = TdS - PdV + \mu dN$

Recall: $C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_V$

$dH = TdS + VdP + \mu dN$

Similarly, $C_p = \left(\frac{\partial H}{\partial T}\right)_{P,N} = T\left(\frac{\partial S}{\partial T}\right)_P$

Now, consider $S = S(T, P, N)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_{P,N} dT + \left(\frac{\partial S}{\partial P}\right)_{T,N} dP + \cancel{\left(\frac{\partial S}{\partial N}\right)_{P,T}}^{0} dN$$

$\rightarrow$ take $\frac{\partial}{\partial T}$ both sides at constant V

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial T}\right)_P + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{C_V}{T} = \frac{C_P}{T} + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

$\Rightarrow$ we want $C_P - C_V$ in terms of measurable quantities like κ, α, etc

$\left(\frac{\partial V}{\partial P}\right)_T$ $\left(\frac{\partial V}{\partial T}\right)_P$

(1) Use maxwell relations!

we have $\left(\frac{\partial S}{\partial P}\right)_T$, want $\left(\frac{\partial V}{\partial P}\right)_T$ or $\left(\frac{\partial V}{\partial T}\right)_P$

$\Rightarrow$ want potential that is function of T, P

$\Rightarrow dG = -S\,dT + V\,dP$

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad \checkmark$$

Then, we have

this is like α, we want it...

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

these are cyclic...

<u>triple product rule</u>: $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T \qquad k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$= -T(V\alpha)^2 \frac{-1}{Vk} \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\boxed{C_p - C_v = \frac{VT\alpha^2}{k}}$$

Check: ideal gas $\qquad PV = NkT$

$$k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(-\frac{NkT}{P^2}\right) = -\frac{1}{V}\left(\frac{-PV}{P^2}\right) = \frac{1}{P}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{Nk}{P}\right) = \frac{1}{V}\left(\frac{PV}{T}\frac{1}{P}\right) = \frac{1}{T}$$

$$C_p - C_v = VT\left(\frac{1}{T}\right)^2(P) = \frac{PV}{T} = Nk \quad \checkmark$$

Furthermore, if we assume $k > 0$, which is quite plausiable, as it is reciprocal of bulk modulus, $C_p > C_v$ in general

Probability

recall: goal of stat mech is to relate

macroscopic $\Longleftrightarrow$ microscopic

→ we have seen this requires a statistical description, and we need some ideas from probability

The Rules

process → outcomes / events ← mutually exclusive

roll die roll 1, 2, etc

(1) $P(i) \geq 0$ ← probabilities are positive

(2) $\sum_i P(i) = 1$ ← something must happen

(3) $P(i \text{ OR } j) = P(i) + P(j)$

(4) $P(i \text{ and } j) = P(i)\,P(j)$ (i, j independent)

Ex: what is probabibility of throwing an even number when rolling one six-sided die?

can roll 1, 2, 3, 4, 5, 6 all with $p = \frac{1}{6}$

want $P(2 \text{ OR } 4 \text{ OR } 6) = \frac{1}{6} + \frac{1}{6} + \frac{1}{6} = \frac{1}{2}$

Ex: what is probability of throwing same number twice in a row on six-sided die?

$$P(1 \text{ AND } 1) = \frac{1}{6} \cdot \frac{1}{6} = \frac{1}{36}$$

$$P(2 \text{ AND } 2) = \frac{1}{6} \cdot \frac{1}{6} = \frac{1}{36}$$

$$\vdots$$

$$P(6 \text{ AND } 6) = \frac{1}{6} \cdot \frac{1}{6} = \frac{1}{36}$$

$$P(P(1 \text{ AND } 1) \text{ OR } P(2 \text{ AND } 2) \text{ OR} \dots \text{ OR } P(6 \text{ ANN } 6))$$

$$= \frac{1}{36} + \frac{1}{36} + \dots + \frac{1}{36} = \frac{1}{6}$$

Ex: What is probability of rolling at least one six in four throws of the die?

recall: $\sum_i P(i) = 1$

$$p(\text{one six}) + p(\text{no six}) = 1$$

$$P(\text{not six AND not six AND not six AND not six})$$

$$= \frac{5}{6} \cdot \frac{5}{6} \cdot \frac{5}{6} \cdot \frac{5}{6}$$

$$\Rightarrow P(\text{one six}) = 1 - \left(\frac{5}{6}\right)^4 = \frac{671}{1296} \approx 0.517$$

Probability distributions can be discrete or continuous

Discrete (coin flips, dice, etc)

$P(k) \equiv$ probability of outcome k

$$\sum_k P(k) = 1$$

Continuous (ex: gaussian distribution)

$P(x) \equiv$ probability density of outcome x

$P(x)\,dx$ = probability to observe x in the interval $[x, x+dx]$