

L21: review

$W(E, V, \dots)$ increases with E

$\Rightarrow S = k_B \ln W$ increases with E

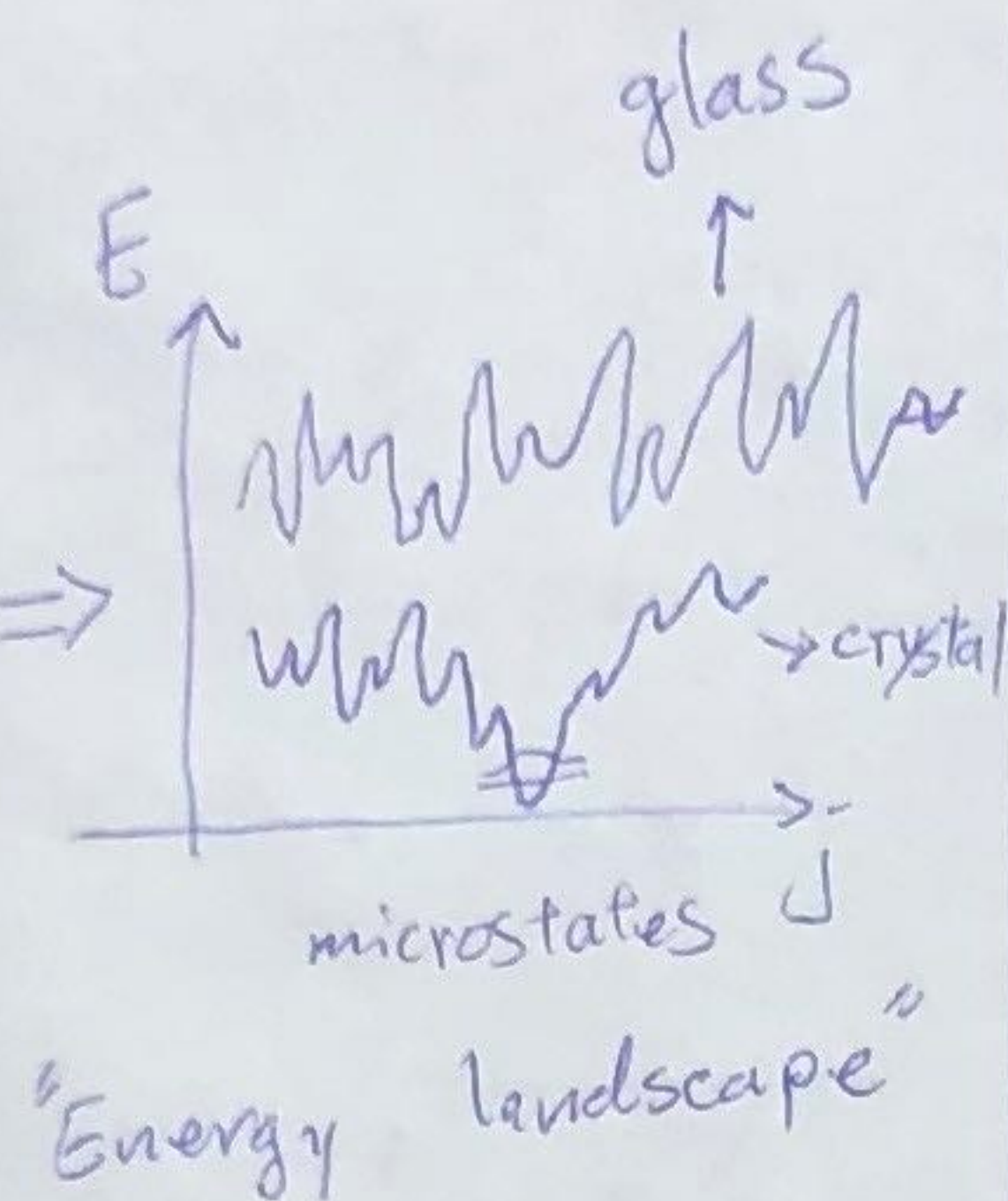
$$E_1 + E_2 = E_{tot}$$

$$S_1 + S_2 = S_{tot}$$

$$S(t > 0) \geq S(t = 0)$$

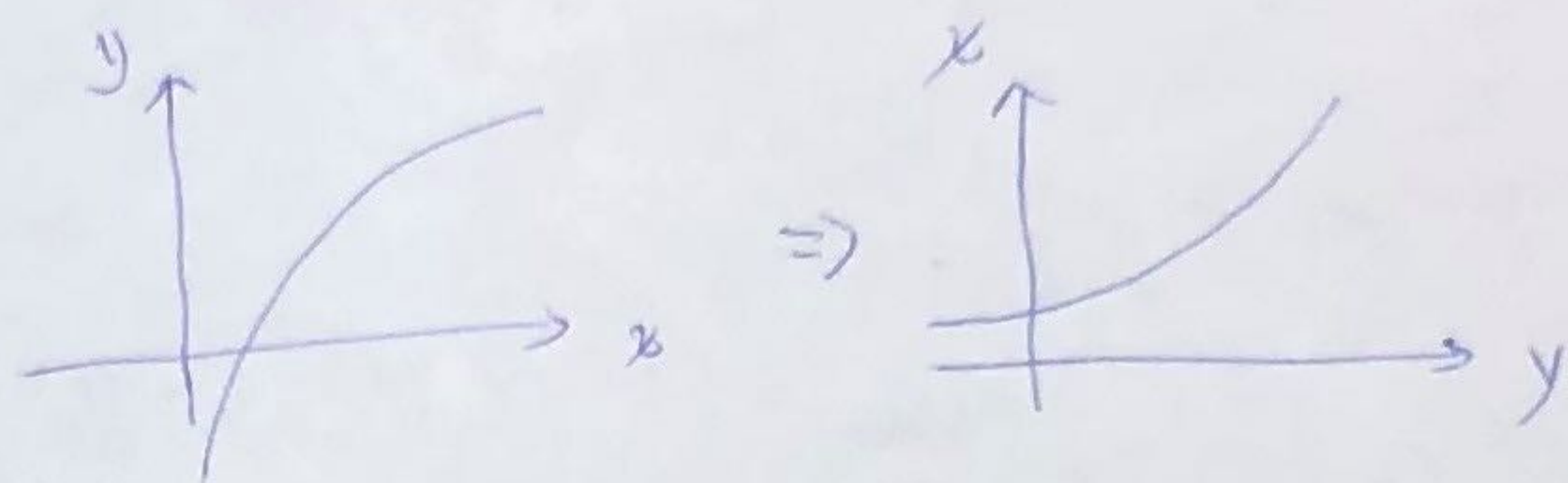
$$\lim_{E \rightarrow \min} S \rightarrow 0$$

$$W \rightarrow 1$$



* in crystals there is a well-defined energy minimum whereas glasses lack a unique energy minimum; therefore, even at $T \rightarrow 0$ glasses have $W > 1$.

Today: temperature and formula for the energy



$$y \equiv S, \quad x \equiv E$$

$$\left(\frac{\partial S}{\partial E} \right) \geq 0$$

$$\left(\frac{\partial E}{\partial S} \right) \geq 0$$

changes in S, E, \dots : dS, dE, \dots

ex: $y = x^2 \Rightarrow \frac{\partial y}{\partial x} = 2x \Rightarrow dy = (2x) dx$

Derivative (change) in E or S :

$$E(S, V, n, \dots) \Rightarrow dE = \left(\frac{\partial E}{\partial S} \right)_{V, n} dS + \left(\frac{\partial E}{\partial V} \right)_{n, S} dV + \left(\frac{\partial E}{\partial n} \right)_{V, S} dn + \dots$$

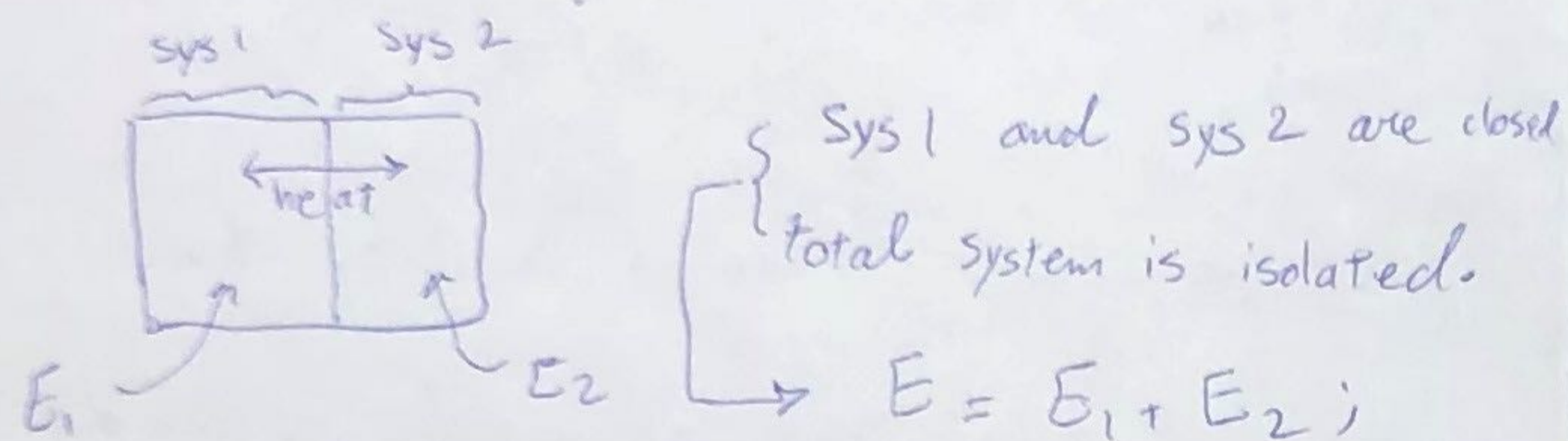
derivative of E to S with V, n and other variables held constant. $+ \dots = T dS + (-P) dV + \mu dn + \dots$

$$S(E, V, n) \Rightarrow dS = \left(\frac{\partial S}{\partial E} \right)_{V, n} dE + \dots$$

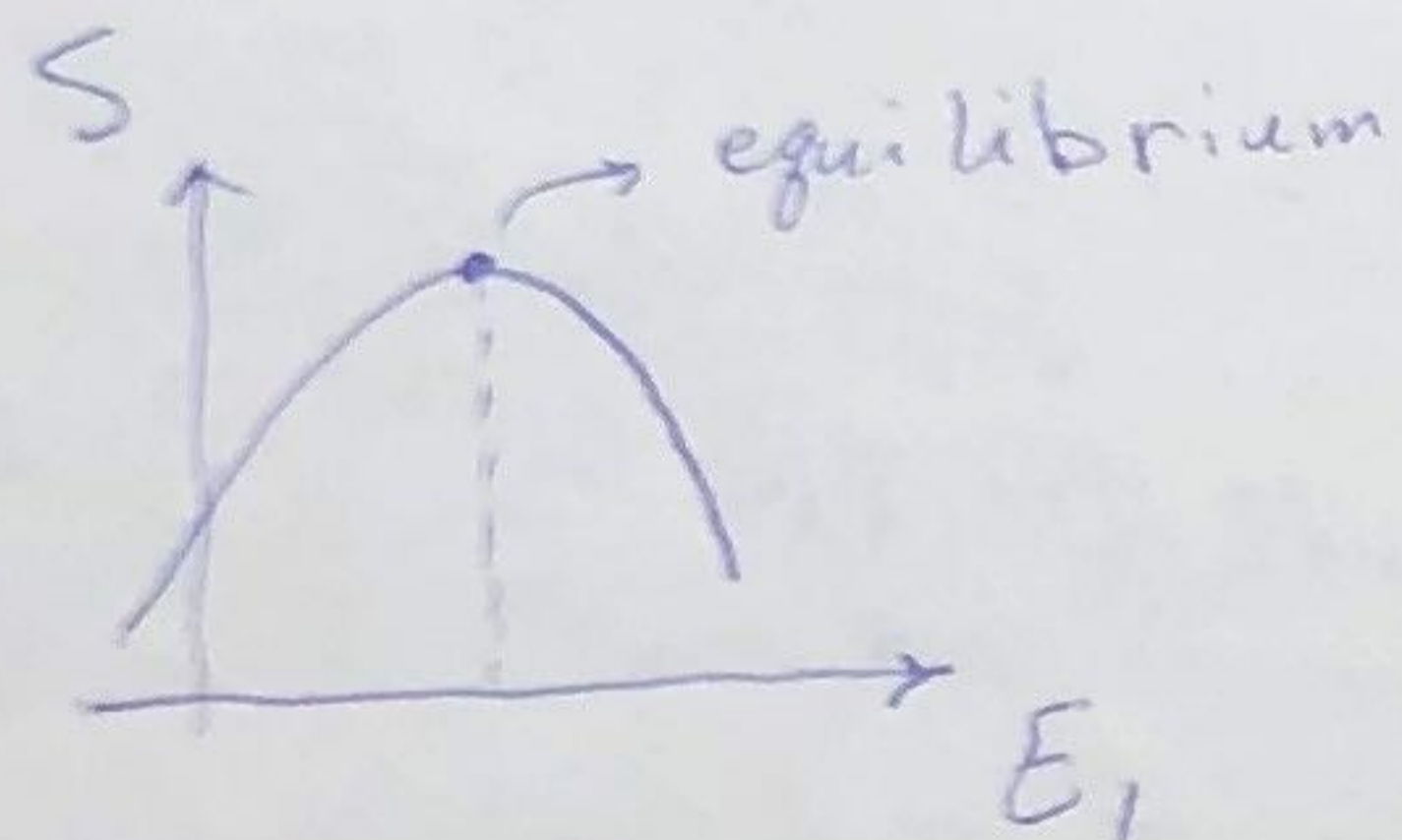
$$= \frac{1}{T} dE + \dots$$

$\Rightarrow T \equiv \left(\frac{\partial E}{\partial S} \right) \geq 0$; this is the definition of T . We don't know what it means yet.

WHAT IS T ?



$$dE = dE_1 + dE_2 = 0$$



At equilibrium: $dS = 0 \xrightarrow{n_i, V = \text{constant}} \frac{1}{T} dE = 0$

$$\Rightarrow \left(\frac{\partial S_1}{\partial E_1} \right) dE_1 + \left(\frac{\partial S_2}{\partial E_2} \right) dE_2 = \frac{1}{T_1} dE_1 + \frac{1}{T_2} dE_2 = 0$$

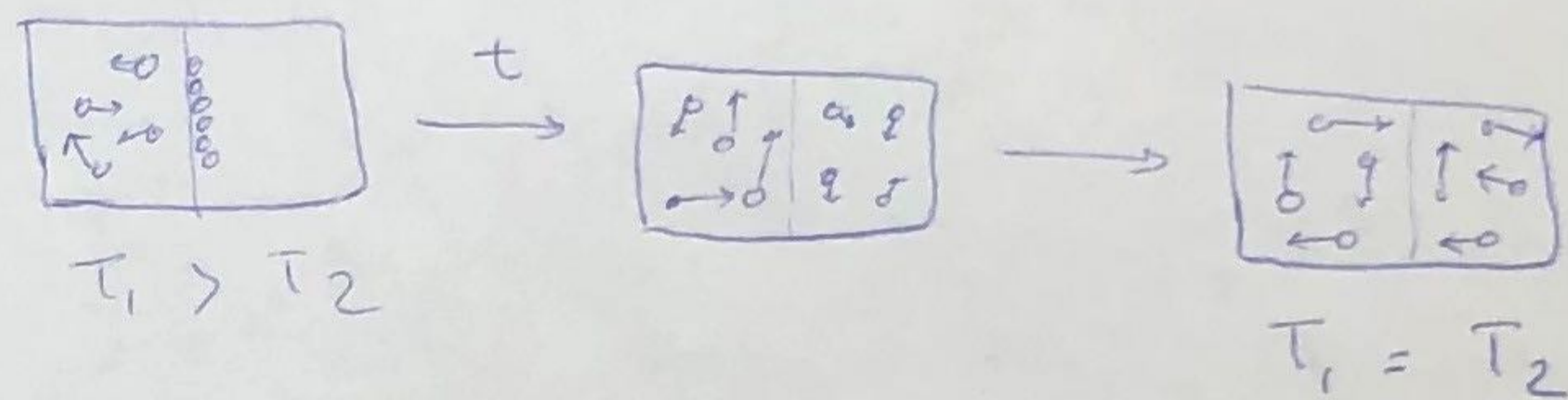
From the system being isolated we know:

$$dE_1 + dE_2 = 0 \Rightarrow dE_1 = -dE_2$$

$$\Rightarrow dS = \frac{1}{T_1} dE_1 - \frac{1}{T_2} dE_1 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 = 0$$

$$\Rightarrow T_1 = T_2$$

* T is the quantity that is equalized between two systems if heat (E) is allowed to flow between them. ($T > 0$)



(Prof. Gruebele showed a demo of molecular dynamics simulation to illustrate heat flow between a "hot" and "cold" droplet of particles until equilibrium is reached)

* A similar though experiment can be used to gain intuition into $\left(\frac{\partial E}{\partial V}\right)$ and $\left(\frac{\partial E}{\partial n}\right)$. See hw S3.1 and S3.2 for details

Simple formula for E :

E is extensive: $E(\lambda S, \lambda V, \lambda n, \dots) =$

$$\frac{d}{d\lambda} \Rightarrow \frac{\partial E}{\partial \lambda S} \cdot \frac{\partial \lambda S}{\partial \lambda} + \frac{\partial E}{\partial \lambda V} \cdot \frac{\partial \lambda V}{\partial \lambda} \dots = \frac{\partial \lambda}{\partial \lambda} E(S, V, n, \dots) = E(S, V, n, \dots)$$

The above equation has to be true for any size scaling.

$$\frac{\partial E}{\partial \lambda S} \cdot S + \dots = E(S, V, n, \dots)$$

for $\lambda=1$
and only S, V, n parameters

$$\frac{\partial E}{\partial S} \cdot S + \frac{\partial E}{\partial V} \cdot V + \frac{\partial E}{\partial n} \cdot n = E$$

$$\Rightarrow T \cdot S - P \cdot V + \mu \cdot n = E$$