

## Statistical Physics and Thermodynamics

Our experience involves systems of many degrees of freedom: many atoms in a solid; many electrons in a wire; many photons in the cosmic microwave background; many spins in a magnet.

Thermodynamics provides a phenomenological description of such systems in equilibrium over relevant time scales, based on empirical observations of these systems.

Statistical Physics attempts to explain emergent properties of systems of many degrees of freedom from microscopic rules governing these degrees of freedom.

As in the development of classical mechanics, as much as possible we consider idealizations of systems of interest. For example, we may consider isolated closed systems insulated from the environment by adiabatic walls that don't allow heat exchange.

To describe the state of a thermodynamic system in equilibrium we need to identify the relevant thermodynamic coordinates, or state functions.

Some state functions:

Pressure, Volume — fluids

Surface tension, Area — film

Tension, Length — wire

Electric field, polarization — dielectric

order 1.2

### The Zeroth Law

\* If two systems are ~~in~~ separately in equilibrium with a third system, then they are also in equilibrium with each other.

Consider systems A, B, and C in equilibrium, with thermodynamic coordinates  $\{A_1, A_2, \dots\}$ ,  $\{B_1, \dots\}$ ,  $\{C_1, \dots\}$  respectively.

Equilibrium of A and C  $\rightarrow$  constant

$$f_{AC}(A_1, A_2, \dots; C_1, C_2, \dots) = 0$$

Equilibrium of B and C  $\rightarrow$

$$f_{BC}(B_1, B_2, \dots; C_1, C_2, \dots) = 0$$

Also assume that each system is separately in mechanical equilibrium, so that the systems do not do work on one another.

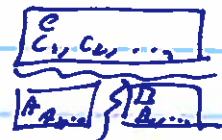


diathermal wall - allows heat transfer

adiabatic wall

- does not allow heat transfer

0<sup>th</sup> law: Can remove adiabatic wall and allow heat transfer between A & B, and nothing changes.



Suppose we solve the A & C and B & C equilibrium constraint conditions for one of the C coordinates, say  $C_1$ :

$$C_1 = F_{AC}(A_1, \dots; C_2, \dots)$$

$$C_1 = F_{BC}(B_1, \dots; C_2, \dots)$$

$$\rightarrow F_{AC}(A_1, \dots; C_2, \dots) = F_{BC}(B_1, \dots; C_2, \dots)$$

0<sup>th</sup> law  $\rightarrow$  equilibrium constraint between A & B:

$$F_{AB}(A_1, A_2, \dots; B_1, B_2, \dots) = 0$$

Choose a set  $\{A_1, \dots; B_1, \dots\}$  that solves this constraint.

With that choice,  $F_{AC}(A_1, \dots; C_2, \dots) = F_{BC}(B_1, \dots; C_2, \dots)$  independent of C state variables  $\{C_2, \dots\}$ .

$\rightarrow$  Must be possible to simplify  $F_{AC} = F_{BC}$  equation so that the coordinates  $C_2, \dots$  are cancelled.

Then in mutual equilibrium, we have that some function of just the A coordinates  $\{A_1, \dots\}$  is equal to some function of just the B coordinates  $\{B_1, \dots\}$

$$\rightarrow \boxed{\Theta_A(A_1, \dots) = \Theta_B(B_1, \dots)}$$

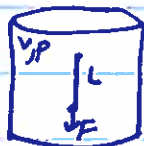
Equilibrium is characterized by the equation of state with isotherms (for system A)

$$\boxed{\Theta_A(A_1, \dots) = \Theta}$$

← some fixed value.

Different definitions for  $\Theta$  are possible, but what we have learned is that the zeroth law (transitivity of thermal equilibrium) implies the existence of an empirical temperature  $\Theta$  that is equal for systems in thermal equilibrium.

Example: System A — wire of length  $L$ , tension  $F$   
 B — paramagnet of magnetization  $M$ , magnetic field  $B$   
 C — gas, volume  $V$ , pressure  $P$



A & C



B & C

systems in equilibrium.

Empirically:  $(P + \frac{a}{V^2})(V-b)(L-l_0) - c[F - K(L-l_0)] = \mathcal{D} \equiv f_{AC}$

and  $(P + \frac{a}{V^2})(V-b)M - dB = \mathcal{D} \equiv f_{BC}$

w/ phenomenological parameters  $a, b, c, d$ , etc.

We can rewrite the  $f_{AC} = 0$  and  $f_{BC} = 0$  conditions as

$$\left(P + \frac{a}{V^2}\right)(V-b) = c \left(\frac{F}{L-l_0} - k\right) = \frac{d B}{M} \equiv \Theta$$

$$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ \Theta_C(V, P) & \Theta_A(L, F) & \Theta_B(M, B) \end{array}$$

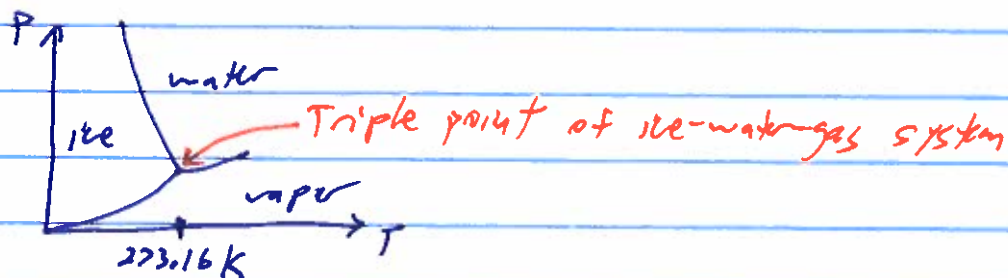
In terms of the Kelvin temperature  $T$ , these are the equations of state

$$\left(P + \frac{a}{V^2}\right)(V-b) = N k_B T \quad \text{van der Waals gas}$$

$$M = \frac{N \mu_B^2 B}{3 k_B T} \quad \text{Curie paramagnet}$$

$$F = (k + DT)(L - l_0) \quad \text{Hooke's law for rubber}$$

### Ideal Gas Temperature Scale



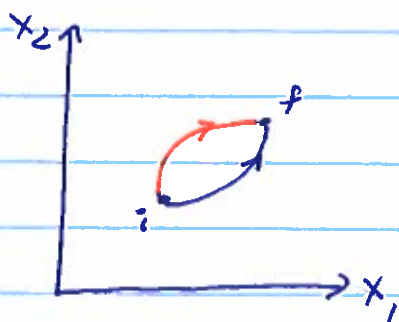
Empirically for dilute gases as  $P \rightarrow 0$  (i.e. ideal gases)

$$T(K) = 273.16 \times \frac{\lim_{P \rightarrow 0} (PV)_{\text{system}}}{\lim_{P \rightarrow 0} (PV)_{\text{ice-water-gas}}}$$

Kardar 1.3

## The First Law

The amount of work required to change the state of an otherwise adiabatically isolated system depends only on the initial and final states, and not on the means by which the work is performed, or on the intermediate states through which the system passes.



State Variables  $x_1, x_2, \dots$

→ Can define an internal energy variable  $E(x_1, x_2, \dots)$ , such that the work  $\Delta W$  needed for an adiabatic transformation from  $\vec{x}_i$  to  $\vec{x}_f$  is

$$\Delta W = E(\vec{x}_f) - E(\vec{x}_i)$$

work done on system

adiabatic transformation

(c.f. work-energy theorem in classical mechanics.)

For non-adiabatic transformations, i.e. allowing heat transfer into or out of system,  $\Delta W \neq \Delta E$  generally.

Define heat intake

$$\Delta Q = \Delta E - \Delta W$$

For differential transformations, we write

$$\boxed{dQ = dE - dW}$$

$$dE = \sum_j \frac{\partial E}{\partial x_j} dx_j \quad \text{so that} \quad \int_{x_i}^{x_f} dE = E(x_f) - E(x_i)$$

↑  
exact differential

independent of path in state space.

$dQ$  and  $dW$  cannot generally be written this way.  
Example: Heat generated by friction — depends on path of object

Thermodynamic coordinates are defined in equilibrium, but we can consider quasi-static transformations in which the system is always in equilibrium.

For quasi-static transformations the work done on the system can be related to changes in the coordinates.

Divide state functions (thermodynamic coordinates) into generalized displacements  $\{\vec{\alpha}\}$  and their conjugate generalized forces  $\{\vec{J}\}$ .

$$dW = \sum_i J_i d\alpha_i \quad \text{quasi-static transformations.}$$

Examples:

<u>System</u>	<u>Force</u>	<u>Displacement</u>
Wire	tension $F$	length $L$
Film	surface tension $S$	area $A$
Fluid	pressure $-P$	volume $V$
Magnet	magnetic field $H$	magnetic flux $M$
Dielectric	electric field $E$	polarization $P$
Chemical reaction	chemical potential $\mu$	particle number $N$

Note:  $-P$  because convention is  $P$  is pressure exerted by system on walls.

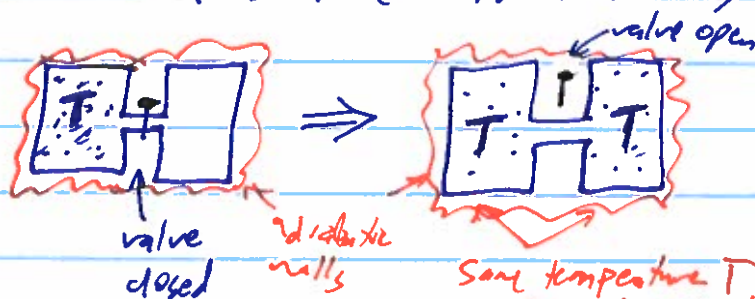
Displacements — usually extensive, i.e. proportional to system size.

Forces — usually intensive, i.e. independent of size.

Forces are usually equal between two systems in equilibrium, e.g. pressure is equal for two equilibrated gases in contact.

Ideal Gas: Equation of state  $PV \propto T$ .

Joule's Free Expansion Experiment:



No work done:

Internal energy  $E(P, V)$

$\rightarrow E(V, T) = E(T)$

independent of  $V$ .

Same temperature  $T$   
unchanged by free expansion



Response functions describe changes in thermodynamic coordinates in response to external probes.

Examples:

\* Heat capacities - change in temperature due to added heat

$$\text{For a gas, } C_V = \left. \frac{dQ}{dT} \right|_V \quad \text{Heat capacity at const. } V \\ = \left. \frac{dE - dW}{dT} \right|_V = \left. \frac{dE + PdV}{dT} \right|_V = \left. \frac{\partial E}{\partial T} \right|_V$$

$$C_P = \left. \frac{dQ}{dT} \right|_P \quad \text{Heat capacity at const. } P$$

$$= \left. \frac{dE - dW}{dT} \right|_P = \left. \frac{dE + PdV}{dT} \right|_P = \left. \frac{\partial E}{\partial T} \right|_P + P \left. \frac{\partial V}{\partial T} \right|_P$$

\* Force constants - displacement due to force

$$\text{Isothermal compressibility of gas } \kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T$$

$$\text{Susceptibility of Magnet } \chi_T = \frac{1}{V} \left. \frac{\partial M}{\partial B} \right|_T$$

$$\text{Ideal gas: } PV \propto T, \quad V \propto T/P, \quad \frac{\partial V}{\partial P} \propto -T/P^2$$

$$\kappa_T = \frac{+(\text{const})T}{(VP)P} = \frac{+(\text{const})T}{(\text{const})T} \cdot \frac{1}{P} = \frac{1}{P}$$

\* Thermal responses - displacement due to change in temperature

$$\text{Expansivity of gas } \alpha_P = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_P = \frac{1}{T} \text{ for ideal gas.}$$

For an ideal gas, internal energy  $E$  depends only on  $T$

$$\Rightarrow \frac{\partial E}{\partial T}|_V = \frac{\partial E}{\partial T}|_P = \frac{dE}{dT}$$

$$\Rightarrow C_p - C_v = P \frac{\partial V}{\partial T}|_P = PV\alpha_p = \frac{PV}{T} \equiv Nk_B$$

↑  
Extensive

$k_B$  = Boltzmann's constant  
 $\approx 1.4 \times 10^{-23} \text{ J K}^{-1}$