

Announcements

canvas.oregonstate.edu <- use this from now on.

The recurring zoom meeting id will change.

slack channel for this course will come (this weekend).

We start homework in week 2.

Plan for future lectures: start next week with traditional lectures using a complete set of lecture slides and notes. Add in interactivity and in class exercises as we'll learn the online process together.

Today we'll experiment some more with exercises.

Zero-th Law

Transitivity of equilibria. If two systems, A and B, are separately in equilibrium with a third system, C, then they are also in equilibrium with one another.

First Law

Conservation of energy. The total energy of an isolated system is constant.

Second Law

Entropy always increases. An isolated system may undergo irreversible processes, whose effects can be measured by a state function called entropy.

Third Law

Entropy goes to zero at absolute zero temperature. The entropy per particle of any two large equilibrium systems will approach the same value as the temperature approaches absolute zero. This value is set to zero.

State (State of a system)

Most familiar are *state functions* related to mechanical work:

- pressure and volume (gas, fluid, solid: 3D matter)
- surface tension and area (soap film: 2D matter)
- tension and length (wire, rubber band: 1D matter)

Other work:

- electrical work: electric field and polarization (dielectric)
- magnetic work: magnetic field and magnetization (magnet)

State functions not related to work:

- temperature and entropy
- internal energy

Generalized forces and displacements

State functions come in pairs (p,V) , (T,S) where one of them acts as **generalized force** and the other as the corresponding **generalized displacement**.

Generalized forces are **intensive** quantities, i.e they do not scale with the size of the system and are of order $O(1)$.

Generalized displacements are **extensive** quantities, i.e they do scale with the size of the system and are of order $O(N)$ where N is the number of particles.

Quasi-static processes

Any process slow enough that all relevant state functions are well defined throughout the process.

For quasi-static process we arrive at thermodynamic identity

$$dU = TdS - pdV + \mu dN$$

Not every system is a gas or liquid and in general we write

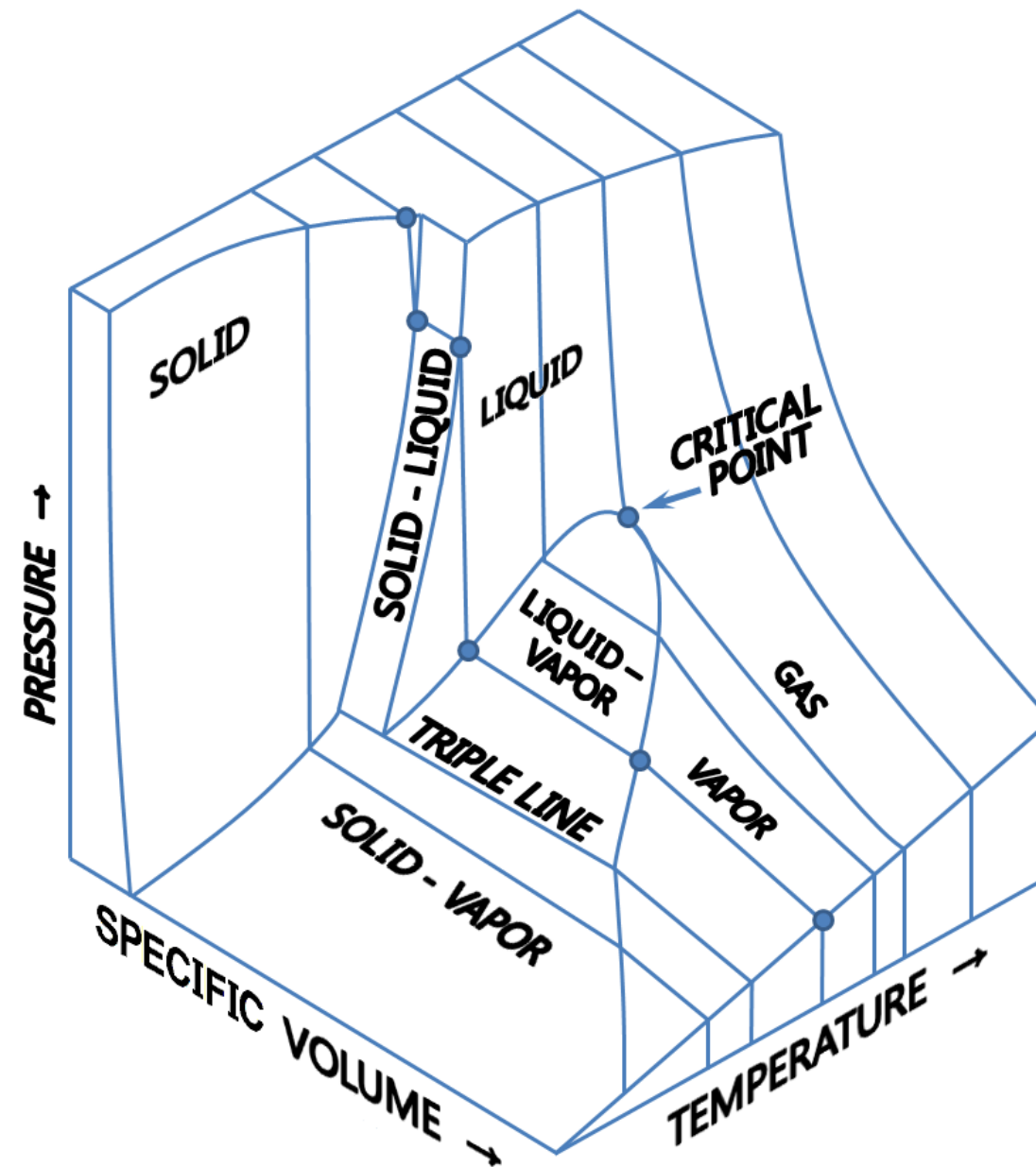
$$dU = TdS + \sum y_i dX_i$$

where y_i is a generalized force and X_i is generalized displacement.

April 3, 2020. Exercise 1: Given the equation of state below, what is the amount of work done when a system isothermally expands from initial volume V_0 to final volume $2V_0$?

$$p = \frac{Nk_B T}{V - Nb}$$

Equations of state are well behaved mathematically. i.e they are continuous and differentiable, except when something dramatic happens such as at a phase transition.



April 3, 2020. Exercise 2: Given the definitions below, evaluate the requested partial derivative.

$$U = x^2 + y^2 + z^2$$

$$z = \ln(y - x) + x^2$$

Find $\left(\frac{\partial U}{\partial z}\right)_y$

Equations of state

In thermodynamics these are empirically determined, i.e. by experiment. One goal of Statistical Mechanics is to derive these from first principles, i.e. from the fundamental laws of physics.

Ideal gas:

$$pV = Nk_B T$$

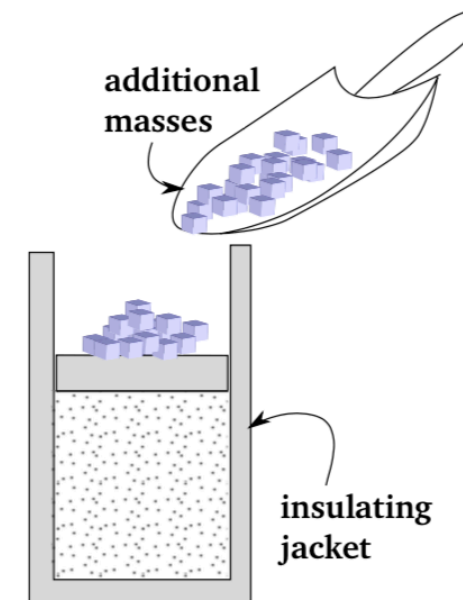
$$U = \frac{3}{2} NkT$$

April 3, 2020. Exercise 3: An ideal gas is contained in a cylinder with a tightly fitting piston. Several small masses are on the piston. (Neglect friction between the piston and cylinder walls.) The cylinder is placed in an insulating jacket, and a large number of masses are then added to the piston.

You may use the following properties of an ideal gas:

- The internal energy is a function of N and T only.
- $pV = Nk_B T$

Tell whether the pressure, temperature, and volume of the gas will increase, decrease, or remain the same. Explain.



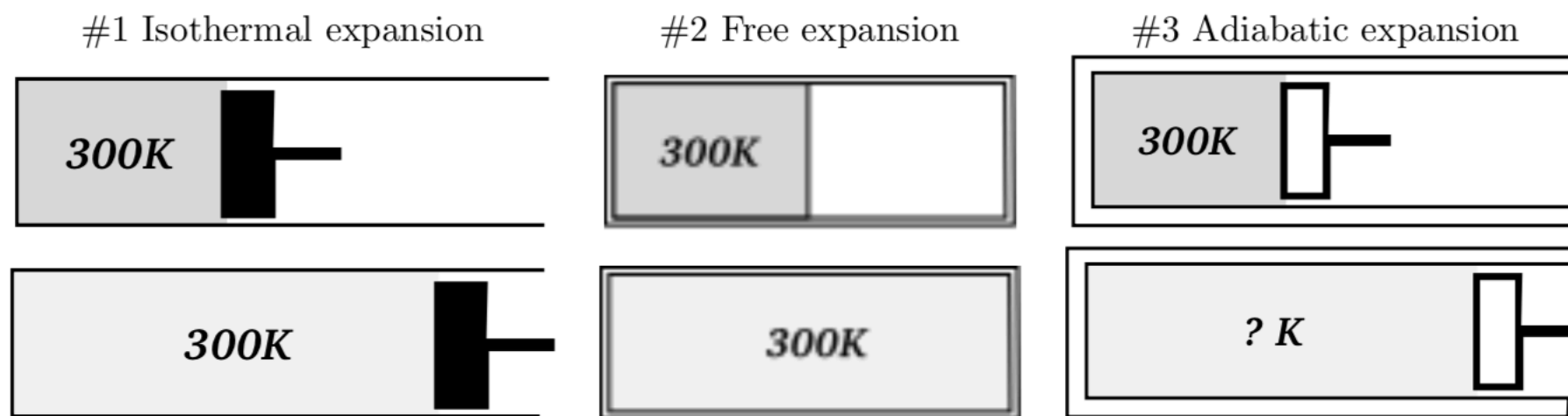
Activity: How many ways can you expand a gas in a piston?

Consider the three processes described below.

Process #1 Five moles of an ideal gas are initially confined in a one-liter cylinder with a movable piston, at a temperature of 300 K. Slowly the gas expands against the movable piston, while the cylinder is in contact with a thermal reservoir at 300 K. The temperature of the gas remains constant at 300 K while the volume increases to two liters.

Process #2 A thin plastic sheet divides an insulated two-liter container in half. Five moles of the same ideal gas are confined to one half of the container, at a temperature of 300 K. The other half of the container is a vacuum. The plastic divider is suddenly removed and the gas expands to fill the container. Because it is a free expansion of an ideal gas (no work is done on or by the gas), the final temperature of the gas is also 300 K.

Process #3 The same cylinder as in process #1 is thermally insulated and then allowed to slowly expand, starting at 300 K, to twice its original size (two liters).



1. Are $\Delta S_{\text{isothermal}}$, ΔS_{free} and $\Delta S_{\text{adiabatic}}$, the change in entropy of the gas for each process, positive, negative, or zero? Please explain your reasoning.
2. Is $\Delta S_{\text{isothermal}}$ greater than, less than, or equal to ΔS_{free} ? How do each of these compare with $\Delta S_{\text{adiabatic}}$? Please explain.
3. Are $\Delta S_{\text{surr-isothermal}}$, $\Delta S_{\text{surr-free}}$ and $\Delta S_{\text{surr-adiab}}$, the change in entropy of the surroundings for each process, positive, negative, or zero? Please explain.

