# Lanford on StatMech, Jan 13 2010

January-13-10
10:06 AM

Equilibrium states:

- Something like a manifold
- Equipped with "state functions": $E, p, V, T, \ldots$
- Empirical temperature scale

Digression: The ideal gas temp. scale:

$$pV = \underbrace{n}_{\text{\# of moles}} \underbrace{R}_{\text{ideal gas constant}} T$$

Experiments show that $\frac{pV}{n}$ approaches a limit (indep. of the type of gas) as the density goes to 0. That limit, divided by some constant $R$, is the empirical temp. scale.

---

Transitions between equilibrium states.

Example Gas in a cylinder with a movable piston.

- Can constrain the volume $V$.
- Can put a fixed weight on the piston to fix the pressure $p$.
- Can put in a bath ("temperature bath") to fix $T$.

Consider a trasition $A \to B$ between equilibrium states. The system does some amount $W$ of work on the environment. The system also absorbs a certain amount $Q$ of heat from the environment.

The first law of thermodynamics:

## The first law of thermodynamics:

$$E(B) - E(A) = Q - W$$

Remark E is a state function but Q & W are not.

Transition 1: Pull the piston so fast that the gas can't keep up. Then $W=0$. If everything is isolated, $E(B)=E(A)$.

Gay-Lussac did this on dilute gases, & found $T(B)=T(A)$.

$\Longrightarrow$ The energy of an ideal gas depends only on the temperature.

Transition 2: Expand very slowly, so that at all times the system is at equilibrium.

$$\text{Force on piston} = F = \underset{\substack{\uparrow \\ \text{area of piston}}}{\Sigma} \cdot p(V) \;\nwarrow \text{pressure at volume } V$$

So $$\text{infinitesimal change in } W = \Sigma \cdot p(V) \cdot dy = p\,dV$$

so $$W = \int_{y_0}^{y_1} \underbrace{p(V)\,dV}_{\delta W}$$

This process is reversible.

So "work done" is the integral of a 1-form along a path.

In the same spirit there is a 1-form $\delta Q$ s.t. for reversible transitions, $Q = \int_\gamma \delta Q$.

So the first law, infinitesimally,

$$dE = \delta Q - \delta W \qquad (\text{or } \delta Q = dE + p\,dV)$$

becomes $TdS = dE + pdV$

---

Imagine now pulling out the piston at an intermediate,

"Finite" speed: - Complicated. Has to do w/ gas dynamics, sound waves, ...
- The system will not have a well-defined overall temperature.

So while the process is going on, the system is not in equilibrium.

- typically not reversible.

So the thermodynamic setup is:

- * A "manifold" of equilibrium states.
- * State functions: $E, T, p, V, \ldots$
- * Two 1-forms: $\delta W, \delta Q$
- * A notion of "reversibility"

"Extensive": proportional to the amount of matter present. (E.g. $V$, $E$)

"Intensive": Independent of the amount of matter present. (e.g.: $p, T$)

"Specific" quantities: $v := V/N$ , $\epsilon = E/N$ - these are intensive

<u>The Second Law of Thermodynamics</u>. A cyclic process is

$$A_1 \rightarrow A_2 \rightarrow \ldots \quad A_m = A_1 \qquad \text{(seq. of processes)}$$

The individual steps need not be reversible.

<u>Kelvin's form</u>: No thermodynamic system admits a cyclic process whose only effect is to extract a positive amount of heat from a bath and to convert it to work. [The other direction is]

possible!! ]

<u>Suggestion</u> Read about Carnot cycles in Fermi or in class notes.

<u>Consequence 1:</u> Second law, reversible part:
There exists an empirical temperature scale $T$ so that $\frac{\delta Q}{T}$ is exact; $\frac{\delta Q}{T} = ds$ where $s$ is the "entropy".

This $T$ is called "the absolute temp.".

... at the end one shows that the absolute temp is equal to the ideal gas temp., up to a multiplicative scale.

In practice, $\delta Q$ is always replaced with $T\,ds$

<u>Consequence 2</u> Second law, irreversible part: If a thermally isolated system can make a transition from a state $A$ to a state $B$, then $S(B) \geq S(A)$. If an amount $Q$ of heat is absorbed at temp $T$, then

$$S(B) - S(A) \geq Q/T$$

regardless of work done.

---

<u>Question</u> 1. Is there a notion of a "thermodynamic manifold"?

2. Is there a notion of a "thermodynamic reality", a system of combining / breaking up thermodynamic manifolds.

---

$\delta Q$ annihilates the tangent vector to $\gamma$, if $\gamma$ is

Thermally isolated $\Rightarrow \delta S(\gamma) \equiv 0 \Rightarrow S(B) = S(A)$