

Sept. 09 2002: Lecture 3:

Thermodynamic Variables

Last Time

L'Art d'Ennuyer Consiste a Tout Dire

Thermodynamic variables versus microscopic variables

A primary goal of this course is the description, characterization, and hopefully the prediction of the properties and behaviors of a real material. Of course, any description or characterization requires a certain amount of forethought about the lexicon that will be used. Our lexicon involves the variables that will efficiently describe the properties of materials.

Question: What kinds of variables describe a material body and the changes that occur as it is manipulated

How does one describe a body or a system completely? There are at least two plausible approaches:

Method of description: 1

Describe for each particle in the body

- position (x, y, z)
- velocity (V_x, V_y, V_z)
- charge q
- spin
- \vdots
- etc.

Question: Why is Avogadro's number, N_{avag} , so big?

Keeping track of $N_{\text{avog.}}$ molecules is just not humanly (or even, in this decade at least, *computerly*) possible.

Method of description: 2

Determine a quantity that reflects the average or sum total properties of the body

Examples:

1. Volume V
2. Total number of atoms of type A, N_A
3. Total number of B-molecules N_B
4. Total charge
5. Size of system?

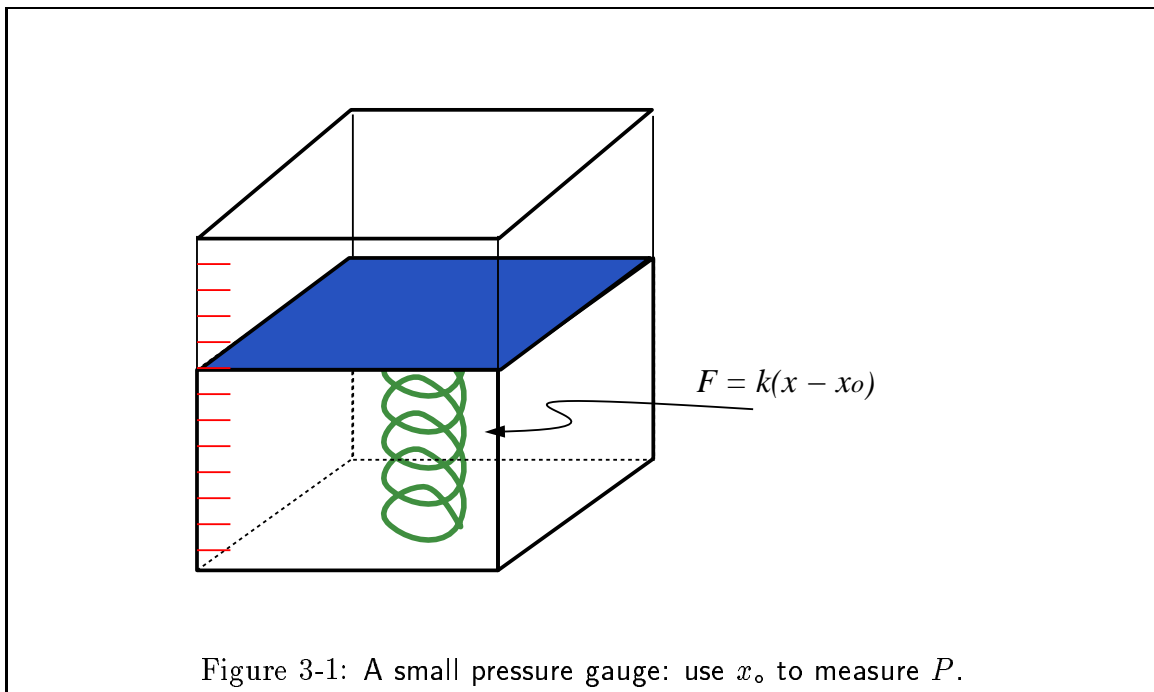
6. charge per volume.

Question: Can you identify others?

Question: If an applied force, F , tries to make a spring get shorter (larger opposing forces \rightarrow shorter spring)—what is it that makes the volume of a body get smaller?

How would you measure pressure?

Design a small gauge:



$$F_{\text{spring}} = \frac{-P}{A} \implies P = Ak(x - x_0) \quad (3-1)$$

Compression, caused by large positive pressures, **compresses** the spring. In other words, a negative force in a spring is compressive; thus pressure and force have different sign conventions. **Tensile** forces **extend** the spring and are associated with negative pressures.²

What kinds of things might be wrong with our little device to cause it to give bad measurements of pressure?

Imagine that we made our device very small. In the limit of an infinitely small device, we could use it to measure pressure from point to point: $P(\vec{x})$.

²There is yet another type of force distributed over an area that we will discuss—it is the stress tensor. Unfortunately for students, there is another minus sign that comes in when going from pressure to stresses. A positive stress is tensile.

Question: Practically, how small would be too small?

Question: Would two bodies be in equilibrium if they were in mechanical contact *and their pressures are different?*

Question: Are pressure and volume similar variables? How are they naturally coupled?

Intensive and Extensive Variables

Consider two bodies each with the same volume V_1 and the same pressure. Bring the bodies together, what is the result?

$$\begin{aligned} V^{\text{total}} &= V_1 + V_2 \\ P^{\text{total}} &= P_1 = P_2 \end{aligned} \quad (3-2)$$

Variables that are additive like V are called *extensive variables*, they depend on the size or the extent of the system.

Variables that do not add, but combine like P are called *intensive variables*, they are intrinsic to the system and can vary from point to point. Fields and potentials are intensive variables.

Another example: Temperature:³

Question: Is T an extensive or intensive variable?

³Note that we have not defined temperature yet, but let's proceed anyways

Can you design a small device that would measure the temperature at a point? (what does it resist changes in?)

This is a difficult question because we haven't defined temperature.

Leads to difficult argument found in thermodynamics books (e.g., Denbigh §1.4) which can be extended to an even more difficult argument that defines the *absolute zero* of temperature.

Zeroeth Law of Thermodynamics

Let's just state the zeroeth Law of Thermodynamics

If bodies A and B are in thermal but not mechanical contact *and* heat flows from A to B and if B is in thermal contact with C and heat flows from B to C then

Heat will flow from A to C if they are in thermal contact. In other words,

$$\text{if } \Theta_A > \Theta_B \quad \text{and} \quad \Theta_B > \Theta_C \quad \implies \quad \Theta_A > \Theta_C \quad (3-3)$$

$$\text{if } \Theta_A = \Theta_B \quad \text{and} \quad \Theta_B = \Theta_C \quad \implies \quad \Theta_A = \Theta_C \quad (3-4)$$

We can call the body B a thermometer and use the zeroeth law.⁴

The temperature can be related to Θ , we can just call $T = \Theta$. This can be done rigorously and it defines an absolute zero ($T = 0$) but let's not do this and move on.

Later we may use the entropy, S and internal energy, U , of a body to define the temperature.⁵

⁴Think about what a thermometer is for a moment. How do they work? How are materials properties important in the construction of a thermometer? What kinds of precautions do you need to take to make sure that you are measuring the temperature of the object about which you are making an inquiry and not the thermometer itself.

⁵The body must also be in equilibrium or uniform temperature.

$$T = \left(\frac{\partial U}{\partial S} \right)_{\text{no work}} \quad (3-5)$$

For a body that does no work, or has no work performed on it, the temperature is the rate at which internal energy changes with entropy.

$$T > 0 \implies \left(\frac{\partial U}{\partial S} \right)_{\text{no work}} > 0 \quad (3-6)$$

U tends to increase with S .

In this lecture, we have discussed state variable that gives us information about a body, an efficient way.

— Intensive Variables—	— Extensive Variables—
P Pressure	N Number of Molecules/Atoms
T Temperature	V Volume
	S Entropy
	U Internal Energy
	M Total Mass

All of these quantities rely on measurement but are assumed to be independent of the type of measurement.