MSAE3111, Thermodynamics and Statistical Mechanics

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Sep 20, 2011 (#5)

Squeeze gently

- Imagine a very gentle compression process
  $V \to V - \Delta V$
- Electron (e.g.) starts in state s, *ends* in state s
- Energy is a function of energy
  $\epsilon_s = \epsilon_s(V)$
- So

$$\epsilon = \epsilon_S^0 - \frac{\partial \epsilon_s}{\partial V} \Delta V \tag{1}$$

- A given state has fixed multiplicity g_S.
- Contours of g for E, V

Another definition of pressure

- Change of energy on (gentle) compression

$$U(V - \Delta V) - U(V) = \Delta U = -\frac{\partial \epsilon_s}{\partial V}\Delta V \tag{2}$$

- In compression, sides of box change by $\Delta x, \Delta y, \Delta z$
- Side area: A

$$\Delta V = A\left(\Delta x + \Delta y + \Delta z\right) \tag{3}$$

- Work done on box:

$$\Delta U = F\left(\Delta x + \Delta y + \Delta z\right) \tag{4}$$

$$\Delta U = F\frac{\Delta V}{A} \tag{5}$$

$$\Delta U = P\Delta V \qquad P \text{ is pressure} \tag{6}$$

Another definition of pressure

$$\Delta U = -\frac{\partial \epsilon_s}{\partial V}\Delta V \qquad \text{and} \qquad \Delta U = P\Delta V \tag{7}$$

$$P = -\frac{\partial U}{\partial V}_\sigma \qquad \text{const}\sigma\text{: gentle squeeze} \tag{8}$$

Natural variables for entropy

- Consider a "particle in a 3D box:"

$$\epsilon_{nx,ny,nz} = \frac{\hbar^2}{2m_e}\left(\frac{\pi}{L}\right)^2\left(nx^2 + ny^2 + nz^2\right) \tag{9}$$

- $n_{x,y,z} = 1, 2 \ldots$
- Index just by total n

$$n^2 = nx^2 + ny^2 + nz^2 \tag{10}$$

- Note: $g = g(n^2)$

$$\epsilon_{n^2} = \frac{\hbar^2}{2m_e}\left(\frac{\pi}{L}\right)^2 n^2 \tag{11}$$

- $n^2 = 3$, $g = 1$
- $n^2 = 6$, $g = 3$
- $n^2 = 9$, $g = 3$

Natural variables for entropy

- A given n^2 has fixed multiplicity g
- A given n^2 has fixed entropy σ
- A given σ is a trace in U and V.

$$d\sigma(U,V) = \left(\frac{\partial\sigma}{\partial U}\right)_V dU + \left(\frac{\partial\sigma}{\partial V}\right)_U dV \tag{12}$$

- Possible (if we're gentle) to stay on the constant σ trace

$$0 = \left(\frac{\partial\sigma}{\partial U}\right)_V dU + \left(\frac{\partial\sigma}{\partial V}\right)_U dV \tag{13}$$

$$0 = \left(\frac{\partial\sigma}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_\sigma + \left(\frac{\partial\sigma}{\partial V}\right)_U \tag{14}$$

Natural variables for entropy

- but:

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_V \qquad P = -\frac{\partial U}{\partial V}_\sigma \tag{15}$$

- So

$$0 = -\frac{P}{\tau} + \left(\frac{\partial \sigma}{\partial V}\right)_U \tag{16}$$

$$P = \tau \left(\frac{\partial \sigma}{\partial V}\right)_U \tag{17}$$

Natural variables for entropy

- Rewriting for the entropy differential,

$$d\sigma(U,V) = \left(\frac{\partial \sigma}{\partial U}\right)_V dU + \left(\frac{\partial \sigma}{\partial V}\right)_U dV \tag{18}$$

$$d\sigma(U,V) = \frac{1}{\tau}\, dU + \frac{P}{\tau}\, dV \tag{19}$$

$$dU = \tau\, d\sigma - P\, dV \tag{20}$$

- Recognize the First Law: *heat is a form of energy*
  $\delta Q = \tau\, d\sigma$

The Helmholtz free energy

- Define a new energy quantity, F

$$F \equiv U - \tau\sigma \tag{21}$$

- (somewhat) useful property: for const τ, V

$$dF = dU - \tau d\sigma \tag{22}$$

$$dU = \tau d\sigma - PdV = \tau d\sigma \tag{23}$$

$$dF = 0 \qquad \text{extremum} \tag{24}$$

The Helmholtz free energy

- Also a maximum

$$\sigma = \sigma_R + \sigma_S \tag{25}$$

$$U_R = U - \epsilon \tag{26}$$

$$\sigma = \sigma_R - \frac{\partial \sigma}{\partial U}\epsilon + \sigma_S \tag{27}$$

$$\sigma = \sigma_R - \frac{\epsilon}{\tau} + \sigma_S \tag{28}$$

The Helmholtz free energy

$$\frac{F}{\tau} = \frac{U}{\tau} - \sigma_R - \sigma_S \tag{29}$$

$$\sigma = -\frac{F}{\tau} \tag{30}$$

- Since σ maximized, $\tau > 0$, F minimized

Differential relations for F

$$dF = dU - \tau d\sigma - \sigma d\tau \tag{31}$$

$$dF = \tau d\sigma - P\, dV - \tau d\sigma - \sigma d\tau \tag{32}$$

$$dF = -P\, dV - \sigma d\tau \tag{33}$$

- Recognize

$$\left(\frac{\partial F}{\partial V}\right)_{\tau} = -P \qquad \left(\frac{\partial F}{\partial \tau}\right)_{V} = -\sigma \tag{34}$$

Strange pressure behavior

- Interesting:

$$P = -\left(\frac{\partial F}{\partial V}\right)_\tau \tag{35}$$

$$P = -\left(\frac{\partial}{\partial V}\right)_\tau (U - \tau\sigma) \tag{36}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_\tau + \tau\left(\frac{\partial \sigma}{\partial V}\right)_\tau \tag{37}$$

- Energy change is not the whole story
- System pushes back if you try to define it!