

SM 7 -- Entropy

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7. Statistical Mechanics and Thermodynamics (Fall 2005)

In a temperature range near some absolute temperature T , the tension force F of a stretched plastic rod is related to its length L by the expression

$$F = aT^2(L - L_0)$$

where a and L_0 are positive constants, L_0 being the unstretched length of the rod. When $L = L_0$, the heat capacity C_L of the rod (measured at constant length) is given by the relation $C_L = bT$, where b is a constant.

- (a) Write down the fundamental thermodynamic relation for this system, expressing dS in terms of dL and dE .
- (b) The entropy $S(T, L)$ of the rod is a function of T and L . Compute $\left(\frac{\partial S}{\partial L}\right)_T$.
- (c) Knowing $S(T_0, L_0)$, find $S(T, L)$ at any other temperature T and length L . (It is most convenient to calculate first the change of entropy with temperature at the length L_0 where the heat capacity is known.)
- (d) If you start at $T = T_i$ and $L = L_i$ and stretch the thermally insulated rod quasi-statically until it attains the length L_f , what is the final temperature T_f ?
- (e) Calculate the heat capacity $C_L(L, T)$ of the rod when its length is L instead of L_0 .
- (f) Calculate $S(T, L)$ by writing $S(T, L) - S(T_0, L_0) = [S(T, L) - S(T_0, L)] + [S(T_0, L) - S(T_0, L_0)]$ and using the result of part (e) to compute the first term in square brackets. Show that the final answer agrees with the one found in part (c).

Known

- entropy $S(T, L) \Leftrightarrow E(T, L)$

- $C_L = \left(\frac{\partial E}{\partial T}\right)_L$

- $C_L(L=L_0) = bT$

(a) $dE = TdS - PdV$
 $= TdS + FdL$

$$P = -\left(\frac{\partial E}{\partial V}\right)_S$$

$$ds = \frac{1}{T}(dE - FdL)$$

$dE = -dW = -(-FdL)$ alternatively, we're interested in the force on the rod, $dE = +FdL$, not the force of the rod on environment

$$PdV = -FdL$$

(b) Compute $\left(\frac{\partial S}{\partial L}\right)_T$:

$$\text{Expand } dE(T, L) \Rightarrow dE(T, L) = \left(\frac{\partial E}{\partial T}\right)_L dT + \left(\frac{\partial E}{\partial L}\right)_T dL$$

$$ds = \frac{1}{T} \left[\left(\frac{\partial E}{\partial T}\right)_L dT + \left(\frac{\partial E}{\partial L}\right)_T dL - FdL \right]$$

$$ds|_T = \frac{1}{T} \left[\left(\frac{\partial E}{\partial L}\right)_T - F \right] dL$$

We can now use that $dE = -FdL$ to rewrite as

$$\left(\frac{\partial S}{\partial L}\right)_T = -\frac{2F}{T} = -2aT(L - L_0)$$

(c) Find $S(T, L)$ given $S(T_0, L_0)$

First we find $\left(\frac{\partial S}{\partial T}\right)_{L_0} \Rightarrow ds|_L = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_{L_0} dT$
 $= \frac{1}{T} C_L dT$

Expand ds in terms of T & L ,

1251 from (b)

Expand dS in terms of T & L ,

$$\Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_L dT + \left(\frac{\partial S}{\partial L}\right)_T dL \quad \text{from (b)}$$

$$= \frac{1}{T} C_L dT - aT(L-L_0) dL$$

$$\int_{S(T_0, L_0)}^{S(T, L)} dS = \int_{T_0}^T \left(\frac{1}{T} \right) (bT) dT - aT \int_{L_0}^L (L-L_0) dL$$

$$= b(T-T_0) - aT \left(\frac{1}{2} (L-L_0)^2 \right)$$

$$S(T, L) - S(T_0, L_0) = b(T-T_0) - aT(L-L_0)^2$$

$$S(T, L) = S(T_0, L_0) + b(T-T_0) - aT(L-L_0)^2$$

(d) • Quasi-statically stretch thermally insulated rod

- This implies adiabatically — no heat; no Δ in entropy: $\Delta S(T_f, L_f; T_i, L_i | T_0, L_0) = 0$

$$\Delta S = S(T_f, L_f | T_0, L_0) - S(T_i, L_i | T_0, L_0) = 0$$

$$= b(T_f - T_0) - aT_f(L_f - L_0)^2 - b(T_i - T_0) + aT_i(L_i - L_0)^2$$

Find T_f :

$$0 = T_f(b - a(L_f - L_0)^2) - T_i(b - a(L_i - L_0)^2)$$

$$T_f = T_i \left(\frac{b - a(L_i - L_0)^2}{b - a(L_f - L_0)^2} \right)$$

(e) Calculate heat capacity $C_L = \left(\frac{\partial E}{\partial T}\right)_L$ for any L

Method 1:

From part (b) we found that expanding $dE(T, L)$, the Thermodynamic Identity can be expressed as:

$$dS = \underbrace{\frac{1}{T} \left[\left(\frac{\partial E}{\partial T}\right)_L dT + \left(\frac{\partial E}{\partial L}\right)_T dL \right]}_{C_L} - F dL$$

$$\therefore \left(\frac{\partial S}{\partial T}\right)_L = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_L \Rightarrow C_L = T \left(\frac{\partial S}{\partial T}\right)_L$$

$$\left(\frac{\partial S}{\partial T}\right)_L = b - a(L-L_0)^2 \quad (\text{from part (c)})$$

$$C_L = bT - aT(L-L_0)^2$$

Method 2:

Take exact differential for S in part (c)

$$dS(T, L) = [b - a(L - L_0)^2]dT + [-2aT(L - L_0)]dL$$

We also have that $dS = \frac{1}{T} C_L dT - 2aT(L - L_0)dL$
from part (c)

Dividing dT and equating:

$$\frac{ds}{dT} = \frac{1}{T} C_L - 2aT(L - L_0) \left(\frac{dL}{dT} \right) = [b - a(L - L_0)^2] - 2aT(L - L_0) \left(\frac{dL}{dT} \right)$$

$$C_L = bT - aT(L - L_0)^2$$

$$(f) S(T, L) - S(T_0, L_0) = [S(T, L) - S(T_0, L)] + [S(T_0, L) - S(T_0, L_0)]$$

first compute first term in square bracket

$$S(T, L) - S(T_0, L) = \int_{S(T_0, L)}^{S(T, L)} ds \xrightarrow{\text{from (e)}} ds|_L = \frac{1}{T} \left[\left(\frac{\partial E}{\partial T} \right)_L dT \right]$$

$$= \int_{T_0}^T \left(\frac{1}{T} \right) [bT - aT(L - L_0)^2] dT$$

$$= (b - a(L - L_0)^2)(T - T_0) \quad \text{from (b)}$$

Second term:

$$S(T_0, L) - S(T_0, L_0) = \int_{S(T_0, L_0)}^{S(T_0, L)} ds \xrightarrow{\text{from (b)}} ds|_{T_0} = \frac{1}{T_0} \left[\left(\frac{\partial E}{\partial L} \right)_{T_0} - F \right] dL$$

$$= \int_{L_0}^L \frac{1}{T_0} (-2F) dL$$

$$= \int_{L_0}^L \frac{1}{T_0} (-2aT_0^2(L - L_0)) dL$$

$$= -aT_0(L - L_0)^2$$

$$S(T, L) - S(T_0, L_0) = b(T - T_0) - aT(L - L_0)^2 + aT_0(L - L_0)^2 - aT_0(L - L_0)^2$$

$$S(T, L) = S(T_0, L_0) + b(T - T_0) - aT(L - L_0)^2$$

$$S(T, L) = S(T_0, L_0) + b(T - T_0) - \alpha T (L - L_0)^2$$