

# Physics 415 - Lecture 9: Thermodynamics and Equilibrium

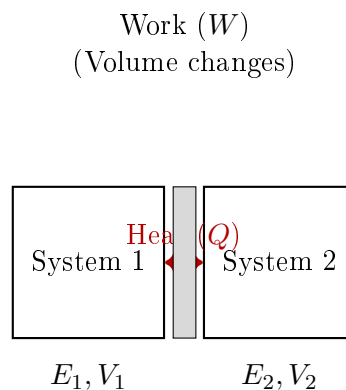
February 10, 2025

## Summary

- $\Omega(E) = \#$  accessible states with energy  $(E, E + \delta E)$ .
- Entropy:  $S = \ln \Omega$ . (Dimensionless). State function.
- Temperature:  $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_x$ . ( $T$  in energy units). State function. (Here  $x$  represents all fixed external parameters, e.g.,  $V$ ).
- Interacting systems 1 & 2 (isolated total): Total entropy  $S = S_1 + S_2$  (additive for  $N \gg 1$ ).
- Equilibrium corresponds to maximum probability  $\implies$  maximum total entropy  $S$ .
- For thermal interaction only ( $V_1, V_2$  fixed): Equilibrium condition is  $T_1 = T_2$ .
- For isolated system, spontaneous processes always increase total entropy:  $\Delta S \geq 0$ .
  - Irreversible process:  $\Delta S > 0$ .
  - Reversible process:  $\Delta S = 0$ . (Quasi-static through equilibrium states).

## General Interaction Between Macroscopic Bodies

In general, systems 1 & 2 interact by exchanging both heat and doing work on each other (e.g., by changing volume).



Constraints for isolated total system:

- $E = E_1 + E_2 = \text{constant}$ .
- $V = V_1 + V_2 = \text{constant}$ . (If total volume is fixed).

System 1 state depends on  $E_1, V_1$ :  $\Omega_1 = \Omega_1(E_1, V_1) \implies S_1 = \ln \Omega_1 = S_1(E_1, V_1)$ . System 2 state depends on  $E_2, V_2$ :  $\Omega_2 = \Omega_2(E_2, V_2) \implies S_2 = \ln \Omega_2 = S_2(E_2, V_2)$ . (More generally,  $V \rightarrow (x_1, x_2, \dots, x_n)$  external parameters). For simplicity, consider single parameter  $x = V$ . All results generalize easily.

We have seen that, in equilibrium, the distribution for  $E_1$  is sharply peaked about  $E_1 = \tilde{E}_1 = \bar{E}_1$ . Similarly, the distribution of  $V_1$  will be sharply peaked about  $V_1 = \tilde{V}_1 = \bar{V}_1$ . Fluctuations of macroscopic observables about their most probable (=mean) values are entirely negligible. Thus, when referring to macroscopic quantities in equilibrium, we will omit the averaging symbol (e.g.,  $\bar{E} \rightarrow E$ ,  $\bar{p} \rightarrow p$ , etc.).

## Equilibrium Conditions

Since  $S = S(E, V)$ , we should make our definition of temperature  $T$  more precise:

$$\frac{1}{T} \equiv \left( \frac{\partial S}{\partial E} \right)_V$$

The partial derivative is taken at fixed volume  $V$  (and other external parameters  $x_\alpha$ ). More generally:  $\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{x_1, x_2, \dots, x_n}$ .

Just as with purely thermal interaction, equilibrium is characterized by the maximum of the total entropy  $S = S_1 + S_2$ . ( $S$  is maximized in the most probable state). We require  $dS = dS_1 + dS_2 = 0$  for arbitrary variations  $dE_1, dV_1$  (subject to constraints).  $S_1 = S_1(E_1, V_1)$  and  $S_2 = S_2(E_2, V_2) = S_2(E - E_1, V - V_1)$ .

$$dS = \left( \frac{\partial S_1}{\partial E_1} \right)_{V_1} dE_1 + \left( \frac{\partial S_1}{\partial V_1} \right)_{E_1} dV_1 + \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2} dE_2 + \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2} dV_2$$

Using the constraints  $dE_2 = -dE_1$  and  $dV_2 = -dV_1$ :

$$dS = \left[ \left( \frac{\partial S_1}{\partial E_1} \right)_{V_1} - \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2} \right] dE_1 + \left[ \left( \frac{\partial S_1}{\partial V_1} \right)_{E_1} - \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2} \right] dV_1$$

Using  $1/T = (\partial S / \partial E)_V$ :

$$dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left[ \left( \frac{\partial S_1}{\partial V_1} \right)_{E_1} - \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2} \right] dV_1$$

For  $dS = 0$  for arbitrary independent variations  $dE_1$  and  $dV_1$ , the coefficients must be zero:

1.  $\frac{1}{T_1} - \frac{1}{T_2} = 0 \implies T_1 = T_2$ . (Thermal equilibrium condition, as before).
2.  $\left( \frac{\partial S_1}{\partial V_1} \right)_{E_1} = \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2}$ . (New condition related to volume change).

## Interpretation of $(\partial S / \partial V)_E$

What is the physical meaning of  $(\partial S / \partial V)_E$ ? Consider doing quasi-static, reversible work on a thermally isolated system A.

- Reversible  $\implies dS = 0$ .
- Quasi-static work done \*by\* the system is  $dW = pdV$ .
- Work done \*on\* the system is  $dW_{on} = -pdV$ .
- Thermally isolated  $\implies dQ = 0$ .

- First Law:  $dE = dQ - dW = 0 - (pdV) = -pdV$ .

Now consider the change in entropy  $S(E, V)$  during this process. The energy changes by  $dE = -pdV$  and volume changes by  $dV$ . Since  $dS = 0$ :

$$dS = \left( \frac{\partial S}{\partial E} \right)_V dE + \left( \frac{\partial S}{\partial V} \right)_E dV = 0$$

Substitute  $dE = -pdV$  and  $(\partial S / \partial E)_V = 1/T$ :

$$\begin{aligned} \left( \frac{1}{T} \right) (-pdV) + \left( \frac{\partial S}{\partial V} \right)_E dV &= 0 \\ \implies \left[ -\frac{p}{T} + \left( \frac{\partial S}{\partial V} \right)_E \right] dV &= 0 \end{aligned}$$

Since  $dV$  can be non-zero, we must have:

$$\left( \frac{\partial S}{\partial V} \right)_E = \frac{p}{T}$$

This gives the physical interpretation of the derivative.

## The Thermodynamic Identity

We can now write the total differential for entropy  $S = S(E, V)$ :

$$dS = \left( \frac{\partial S}{\partial E} \right)_V dE + \left( \frac{\partial S}{\partial V} \right)_E dV$$

Substituting the definitions we found:

$$dS = \frac{1}{T} dE + \frac{p}{T} dV$$

Multiplying by  $T$ :  $TdS = dE + pdV$ . Rearranging gives the fundamental thermodynamic identity:

$$dE = TdS - pdV \quad (*)$$

This provides a relation between the differentials of macroscopic state functions  $(E, S, V)$  and state variables  $(T, p)$  for a system in equilibrium, when undergoing an infinitesimal change from one equilibrium state to another.

**Example:** Ideal Gas To illustrate the utility of (\*), consider the classical monatomic ideal gas. Recall from Lecture 4 (using large  $N$  approximation):  $\Omega(E) \propto V^N E^{3N/2}$ .

$$S = \ln \Omega = N \ln V + \frac{3N}{2} \ln E + \text{constant}$$

(Here  $N$  is the number of particles).

- Calculate pressure:

$$\begin{aligned} p &= T \left( \frac{\partial S}{\partial V} \right)_E = T \left( \frac{\partial}{\partial V} [N \ln V + \dots] \right)_E = T \left( \frac{N}{V} \right) \\ &\implies pV = NT \end{aligned}$$

This is the ideal gas law! (Note:  $T$  is in energy units here. If using Kelvin,  $pV = Nk_B T$ ).

- Calculate energy relation:

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_V = \left( \frac{\partial}{\partial E} \left[ \frac{3N}{2} \ln E + \dots \right] \right)_V = \frac{3N}{2E}$$

$$\implies E = \frac{3}{2}NT$$

This is the (mean) energy of a classical monatomic ideal gas.

The relation  $pV = NT$  (or similar relations for other systems) is an example of an "equation of state", which is a relation connecting quantities characterizing a macroscopic equilibrium state.

## Connection to Heat

There is another important application of the result  $dE = TdS - pdV$  (\*). Recall the First Law: The change in (mean) energy  $dE$  is due to infinitesimal heat absorbed  $dQ$  and work done \*by\* the system  $dW$ :

$$dE = dQ - dW$$

Consider the special case of a quasi-static process. We have shown that for such processes, the work done by the system involving volume change is  $dW = pdV$ .

$$\implies dE = dQ - pdV \quad (\text{for quasi-static process})$$

Comparing this to the thermodynamic identity (\*):

$$TdS - pdV = dQ - pdV$$

$$\implies TdS = dQ$$

or

$$dS = \frac{dQ}{T} \quad (**)$$

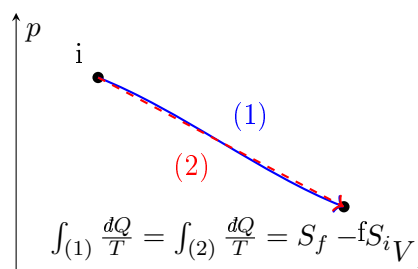
This provides a crucial relation between the change in entropy  $dS$  (an exact differential) and the heat absorbed  $dQ$  (an inexact differential) in a quasi-static process.

**Special Case:** Quasi-static process in a thermally isolated system ( $dQ = 0$ ). From (\*\*), we have  $dS = 0$ , so  $S = \text{constant}$ . If quasi-static work is done on (or by) a thermally isolated system, the entropy does not change. Such a process is reversible ( $dS_{\text{tot}} = 0$ ).

Equation (\*\*) is also notable because it relates the inexact differential  $dQ$  to the exact differential  $dS$  via the integrating factor  $1/T$ . Since  $S$  is a function only of the macrostate (e.g.,  $S = S(E, V)$ ), the change in entropy between any initial equilibrium state  $i$  and final equilibrium state  $f$  is:

$$\Delta S = S_f - S_i = \int_i^f dS = \int_i^f \frac{dQ}{T}$$

The integral  $\int dQ/T$  must be calculated along any quasi-static (reversible) path connecting states  $i$  and  $f$ . Because  $S$  is a state function, the value of this integral is independent of the reversible path chosen.



## Equilibrium Conditions Revisited

Finally, return to the initial problem of equilibrium between systems 1 & 2 allowing both energy and volume exchange. The equilibrium conditions derived from maximizing  $S = S_1 + S_2$  ( $dS = 0$ ) were:

1.  $T_1 = T_2$  (Thermal equilibrium).
2.  $\left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} = \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2}$ .

Using the relation  $(\partial S / \partial V)_E = p/T$ , the second condition becomes:

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Since we already have  $T_1 = T_2$  from the first condition, this implies:

$$p_1 = p_2$$

This is the condition for "mechanical equilibrium".

Thus, in full equilibrium, systems 1 & 2 have equal temperatures ( $T_1 = T_2$ ) and the pressure is balanced ( $p_1 = p_2$ ).

(Note: Mechanical equilibrium (equality of pressures) is often reached much more rapidly than thermal equilibrium (equality of temperatures)).