

Statistical Mechanics

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with L^AT_EX



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Mathematics

Thermodynamics

Key Concepts

Few Terminologies

1. **Heat and energy.** Heat is considered a form of energy. It can be converted to work, and in turn can be produced by consuming work. Work and heat together obey law of conservation of energy.
2. **Thermodynamic equilibrium.** The state of a thermodynamic system which does not change with time is called the state of thermodynamic equilibrium.
3. **State variable.** The state variables—such as pressure P , volume V , and temperature T —in the state of equilibrium are not independent. The relationship between them is known as the equation of state.
4. **Thermodynamic transformation.** The state of a system changes when the external conditions are changed. When its state changes, the system is said to undergo thermodynamic transformation.
5. **Quasi-static.** If the state variables change so slowly that the system can be assumed to be in thermodynamic equilibrium at any instant then the transformation of the system is said to be quasi-static.
6. **Reversible and irreversible.** If the transformation is carried such that it is possible to retrace the steps from its final to the initial state by reversing the external conditions then it is called reversible. Else the transformation is called irreversible.
7. **Adiabatic.** If the transformation is such that the system does not exchange heat with its surroundings then the transformation is said to be adiabatic.
8. **Isothermal.** A transformation in which temperature of the system remains unchanged is called isothermal.
9. **Isobaric.** A transformation in which pressure of the system remains unchanged is called isobaric.
10. **Heat reservoir.** A thermal or heat reservoir is a system so large that addition or removal of a finite amount of heat from it does not change its temperature.
11. **Cyclic transformation.** If a transformation is such that it restores the system to its initial state then it is called cyclic.

The Ideal Gas

The ideal gas model represents the gas particles as point particles (i.e. a material body having mass but no spatial extent), and assumes that there are no (attractive or repulsive) physical interactions between

them. For an ideal gas composed of N particles or n moles in equilibrium, the pressure P is related with the volume V occupied by the gas and its temperature T , through the ideal gas equation:

$$PV = nRT = Nk_B T$$

where $R = 8.315$ joule/mole K $k_B = 1.38 \times 10^{-16}$ erg/K. The ideal gas equation was stated in 1834 by Benoit Emile Clapeyron (1799-1864) and results from combining the old gas laws:

1. **Boyle's law.** If temperature is kept constant, the pressure is proportional to the density, $P \propto \rho$.
2. **Amonton's law.** If volume is kept constant, the pressure is proportional to the temperature, $V \propto T$.
3. **Gay-Lussacs' law.** If pressure is kept constant, the volume is proportional to the temperature, $V \propto T$

Van der Waals Equation of State. The equation of state for a real gas derived by van der Waals was also based on the kinetic theory and the virial theorem. Here we give standard phenomenological derivation of the equation, obtained by introducing following modifications in the ideal gas law:

1. **Specific volume.** It is assumed that the molecules are not point particles but are hard spheres. This results in each molecule excluding some volume, say b , from the total volume V . It was argued that the ideal gas law should therefore be modified to replace V by $V - Nb$.
2. **Force of attraction.** The molecules attract each other when separated by distances greater than the molecular radius r_0 . Assuming that the molecules are distributed uniformly, each molecule in the interior is acted upon by forces on all sides resulting in net zero force; however near the boundary surfaces therefore experience a net inward force resulting in reduction of pressure. This causes net reduction of pressure proportional to $(N/V)^2$ which must be subtracted from the pressure appearing in the ideal gas law.

Under the suggested modifications, the ideal gas law assumes the form

$$P = \frac{Nk_B T}{V - Nb} - \frac{a}{(V/N)^2} = \frac{k_B T}{v - b} - \frac{a}{v^2}$$

where $v = V/N$ is the specific volume. Since, in addition to the equation of state relating pressure, volume, and temperature, complete description of thermodynamic properties requires also the knowledge of its internal energy as a function of the state variables, we give (without the derivation)

$$u = ck_B T - \frac{a}{v}$$

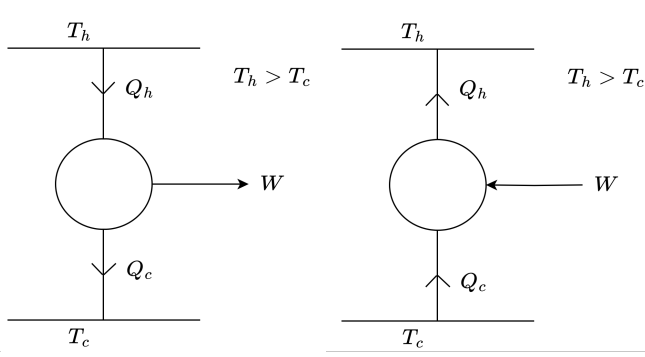


Figure: Carnot engine and reverse carnot engine.

Entropy of ideal gas. Consider a reversible process which takes N molecules of an ideal gas be in equilibrium in the state A to the equilibrium state B . The process being reversible is described by the form of the first law which, on reversible process takes the form of

$$dU = T dS - P dV \quad (1)$$

Solving for the entropy

$$dS = \frac{dT}{T} + \frac{P}{T} dV \quad (2)$$

Considering T can be written as

$$T = \frac{PV}{Nk_B} = \frac{U}{cNk_B}$$

then

$$dS = Nk_B \left(c \frac{dU}{U} + \frac{dV}{V} \right)$$

On integrating the equation above, we get

$$S = nK_B [c \ln U + \ln V] + K$$

where K is the integration constant. Determination of absolute value of entropy in a state would, of course, require knowledge of K . However, it plays no role in computing entropy change in going from state A to state B as in that case

$$S(B) - S(A) = Nk_B \left[c \ln \frac{U_B}{U_A} + \ln \frac{V_B}{V_A} \right]$$

Carnot Engine

The Carnot engine (or machine) is a theoretical heat engine envisioned by Sadi Carnot that operates a reversible cyclic process termed Carnot cycle.

If it is assumed that heat cannot be transported from a cold to a hot reservoir without doing any work then

1. No engine is more efficient than reversible Carnot engine.

2. All reversible Carnot engines operating between same reservoirs have same efficiency.

The work produced in one cycle of the process is the difference in the amount of heat absorbed and the heat $-W = Q_h - Q_c$. Hence efficiency μ defined as the ratio of work W produced by the engine to the amount of heat Q_h received by it,

$$\mu = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

where the last line is obtain from clever derivation. I wont go into the derivation itself, but one important part of the derivation also prove, for a reversible Carnot engine operating with any fluid and process,

$$\frac{Q_h}{T_h} = \frac{Q_c}{T_c}$$

Also note that the T in question is measure in kelvin, not celcius.

Cyclic Process. Consider the cyclic process comprises a sequence of four reversible processes of a thermodynamic system, namely, an isothermal expansion, an adiabatic expansion, an isothermal compression, and an adiabatic compression. Suppose also that the working fluid is an ideal gas. Those processes are as follows.

1. **Point A.** The gas is initially in equilibrium at temperature T_h and its pressure and volume P_A, V_A . The temperature is kept constant by keeping the gas in contact with a heat reservoir at the desired temperature. The gas is then let to expand isothermally to volume V_B with P_B as its pressure.
2. **Point B.** At B the gas is isolated from the heat reservoir. The amount of heat absorbed along $A \rightarrow B$ may be evaluated using the first law $dU = dQ - P dV$, along with the two equation of state $PV = Nk_B T$ and $U = cNk_B T$. Since the temperature has the constant value, $dU = 0$. Therefore,

$$dQ = Nk_B T_h \frac{dV}{V}$$

Integrating between initial and final volumes

$$Q_h = Nk_B T_h \ln \frac{V_B}{V_A}$$

The gas is then expands further but without exchanging heat with the environment, an adiabatic expansion. It continues till it volume and pressure become V_C and P_C .

3. **Point C.** At C it is brought in contact with the reservoir at temperature T_C . First we consider the transformation of $B \rightarrow C$. Since it is adiabatic, it does not involve exchange of heat. The first law reads as

$$dU + P dV = 0$$

Now we use the equations of state

$$\begin{aligned} C_V dT + P dV &\Rightarrow dT + \frac{P dV}{C_V} \Rightarrow \frac{dT}{T} + \frac{P dT}{cNk_B T} \\ &\Rightarrow \frac{dT}{T} + \frac{dV}{cV} \Rightarrow \frac{dT}{T} + (\gamma - 1) \frac{dV}{V} \end{aligned}$$

And we obtain

$$\frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0$$

On integrating the equation above between the state, we get

$$\ln \frac{T_C}{T_B} + (\gamma - 1) \ln \frac{V_C}{V_B} = 0$$

We can write

$$\ln \frac{T_C}{T_B} + (\gamma - 1) \ln \frac{V_C}{V_B} = \ln \frac{T_C}{T_B} \frac{V_C^{\gamma-1}}{V_B^{\gamma-1}}$$

which implies

$$\frac{V_C^{\gamma-1}}{V_B^{\gamma-1}} = 1$$

In another words

$$TV^{\gamma-1} = \text{constant.}$$

expressing T in terms of P and V

$$PV^{\gamma-1} = \text{constant.}$$

and expressing V in terms of P and T

$$TP^{-v} = \text{constant.}$$

where $v = (\gamma - 1)/\gamma$. These equation are called **adiabatic equations of state**.

Due to the reservoir T_c , the gas compresses isothermally till its volume and pressure become V_D , P_D .

4. **Point D.** At D it is again isolated. As before, we consider the transformation of $C \rightarrow D$ first. Along CD , the temperature has the constant value T_c and volume varies from V_C to V_D leads to the following expression for the heat **received** by the gas:

$$Q'_C = Nk_B T_c \ln \frac{V_D}{V_C}$$

Since $V_D < V_C$, the heat absorbed by the gas is negative, which means that a positive amount of heat is delivered to the reservoir. Hence the amount of heat delivered to the reservoir is

$$Q_C = -Q'_C = Nk_B T_c \ln \frac{V_C}{V_D}$$

The gas is then compressed adiabatically till its pressure, volume, and temperature attain their initial values P_A , V_A , and T_h . Also, since the process from D to A is adiabatic, no heat is exchanged with the surroundings.

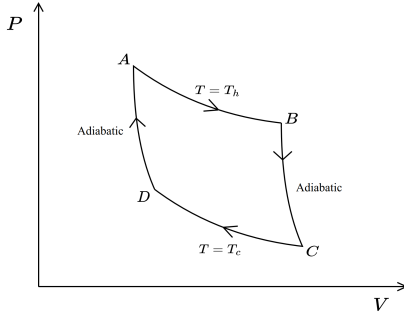


Figure: PV diagram of a cyclic Carnot process.

Carnot's equation in cyclic processes. The Carnot's equation still holds true even in cyclic process. To prove this, first we applying adiabatic equation to path BC

$$T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1} \Rightarrow \left(\frac{V_B}{V_C} \right)^{\gamma-1} = \frac{T_C}{T_B} \Rightarrow \left(\frac{V_B}{V_C} \right)^{\gamma-1} = \frac{T_c}{T_h}$$

In similar manner, the adiabatic transformation along DA gives

$$\left(\frac{V_D}{V_A} \right)^{\gamma-1} = \frac{T_A}{T_D} \Rightarrow \left(\frac{V_D}{V_A} \right)^{\gamma-1} = \frac{T_h}{T_c}$$

On comparing these, it is seen that

$$\frac{V_B}{V_C} = \frac{V_A}{V_D} \Rightarrow \frac{V_C}{V_D} = \frac{V_B}{V_A}$$

This leads to

$$\frac{Q_h}{Q_c} = \frac{Nk_B T_h \ln V_B/V_A}{Nk_B T_c \ln V_C/V_D} \Rightarrow \frac{Q_h}{Q_c} = \frac{T_h}{T_c}$$

which is the Carnot's equation.

Efficiency of cyclic Carnot engine. To find efficiency of the process under consideration from first principles note that total work done by the gas in the cycle, due to first law, is

$$W = \oint (dQ - dU) = \oint dQ$$

Since no heat is exchanged on adiabatic paths BC and DA , the closed integral becomes

$$\oint dQ = \int_A^B dQ + \int_C^D dQ = Q_h - Q_c$$

In another words

$$W = Q_h - Q_c$$

The relation derived above is independent of the equation of state obeyed by the working fluid. Using this equation, the efficiency reads

$$\mu = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

Specific Heat

Invoking the first law we have

$$dU = dQ - P dV \quad \left\{ \begin{array}{l} \left. \frac{\partial U}{\partial T} \right|_V = \left. \frac{\partial Q}{\partial T} \right|_V \\ \left. \frac{\partial U}{\partial T} \right|_P = \left. \frac{\partial Q}{\partial T} \right|_P - P \left. \frac{\partial V}{\partial T} \right|_P \end{array} \right.$$

The first quantity is defined as heat capacity at constant volume

$$C_V \equiv \left. \frac{\partial Q}{\partial T} \right|_V = \left. \frac{\partial U}{\partial T} \right|_V$$

While, from the second cases, heat capacity at constant pressure can be defined as

$$C_P \equiv \left. \frac{\partial Q}{\partial T} \right|_P$$

Both equation can be combined into

$$\begin{aligned} C_P - C_V &= \left. \frac{\partial U}{\partial T} \right|_P + P \left. \frac{\partial V}{\partial T} \right|_P - \left. \frac{\partial U}{\partial T} \right|_V \\ &= \left. \frac{\partial}{\partial T} C_V T \right|_P + P \left. \frac{\partial}{\partial T} \frac{Nk_B T}{P} \right|_P - \left. \frac{\partial}{\partial T} C_V T \right|_V \\ C_P - C_V &= Nk_B \end{aligned}$$

In terms of the parameter gamma γ , called adiabatic constant, defined by

$$\gamma = \frac{C_P}{C_V}$$

the equation yields

$$\begin{aligned} C_V \left(\frac{C_P}{C_V} - 1 \right) &= Nk_B \\ C_V &= \frac{Nk_B}{\gamma - 1} = cNk_B \end{aligned}$$

Internal Energy

The independence of internal energy to volume was proved by Thomson and Joule (in 1845) which involved direct measurement of temperature of the gas. It is also known experimentally that the heat capacity of ideal gas is independent of temperature. Consequently C_V is a constant so that

$$U(V, T) = C_V T = cNk_B T$$

For an ideal monoatomic gas, $c = 3/2$ thus $\gamma = 5/3$

Entropy

The relation for the reversible cyclic process may then be rewritten as $Q_h/T_h + (-Q_c/T_c) = 0$. The quantity

$$S \equiv \frac{Q}{T}$$

is called entropy of the system. The name entropy was coined by Clausius to describes some transformation taking place inside the system.

Total change in entropy of the system in a reversible Carnot cycle is zero, $\Delta S_{\text{sys}} \equiv 0$, while change in entropy of the environment during the process in question is also zero, $\Delta S_{\text{env}} \equiv 0$. Increase in entropy of the environment may be considered as the measure of the lost work, $W' = W - T\Delta S_{\text{env}}$.

For any reversible path with O as any reference point

$$S(A) = \int_O^A \frac{dQ}{T}$$

Thus, the change in entropy in going from A to B is given by

$$S(B) - S(A) = \int_A^B \frac{dQ}{T}$$

Thermodynamics' Law

Zeroth Law

The zeroth law states that if a system A is in thermal equilibrium with B and also separately with C then B and C are in thermal equilibrium with each other.

The consequences of this law is the equation

$$g(P_B, V_B) = g(P_C, V_C)$$

This shows that there exists a function $g(P, V)$ which has the same value for systems B and C in thermal equilibrium. However neither this law nor the other laws of thermodynamics determine the form of the function $g(P, V)$.

First Law

The first law is the statement of conservation of energy. It states that the internal energy dU of a thermodynamic system is a state function such that if dQ is the amount of heat absorbed and dW the amount of work done by the system in an arbitrary transformation then change dU in its internal energy is given by

$$dU = dQ - dW$$

The work may consist of several components each caused by change in some macroscopic control parameter, so that

$$dW = - \sum_{i=1}^m F_i d\xi_i$$

The F_i is the “force” associated with the change in ξ_i . The negative sign is due to dW as work performed by the system. If the volume V is the only macroscopic control parameter then the internal energy reads

$$dU = dQ - P dV$$

or gas gains energy when its volume decreases and loses energy when its volume increases. By applying the second law, we can also say

$$dU = T dS - P dV$$

Second Law

There are two equivalent ways of stating the second law:

1. **Kelvin statement:** There does not exist any thermodynamic transformation whose sole effect is to extract heat from a heat reservoir and convert it entirely into work.
2. **Clausius statement:** There does not exist any thermodynamic transformation whose sole effect is to extract heat from a body at lower temperature and deliver it to the one at higher temperature.

By yet another derivation that I do not show, the statement can be written as

$$\oint \frac{dQ}{T} = 0$$

Note that the equation only holds true for reversible Carnot process. It is straightforward to prove that the equation above implies that the integral is independent of path between A and B if the process is reversible. For irreversible process

$$\int_{\text{irr}} \frac{dQ}{T} < \int_{\text{rev}} \frac{dQ}{T}$$

In another words, the change in entropy over an irreversible path between two states is less than that on any reversible path between same states.

Here we also state some consequences of the second law.

Entropy of the universe. Consider a system interacting with a reservoir, drawing the amount dQ of heat from it at temperature T by reversible or irreversible process. The quantity dQ/T for the system therefore may or may not stand for change in its entropy. However, $-dQ/T$ stands for the reservoir's, since all processes inside a reservoir are reversible. As the system changes from A to B ,

$$\begin{aligned}\Delta S_{\text{sys}} &= \Delta S_{\text{sys}} + \Delta S_{\text{env}} \\ &= [S(B) - S(A)] - \int_A^B \frac{dQ}{T} \\ \Delta S_{\text{sys}} &\geq 0\end{aligned}$$

The equation above shows that entropy of the universe never decreases.

Entropy of thermally isolated system. Assume that the system is thermally isolated, then $dQ = 0$. Hence $\Delta S_{\text{env}} = 0$. As a consequence of, as the system transforms from state A to state B , its entropy cannot decrease:

$$S(B) - S(A) \geq 0$$

Maximum entropy principle. In approaching thermodynamic equilibrium, the entropy of an isolated system must tend to a maximum, and the final equilibrium state is the one for which the entropy is greatest.

Work lost. Consider a reversible process which takes a system from state A to state B . By the first law,

$$U_B - U_A = \int_{\text{rev}} T dS_{\text{sys}} - dW_{\text{rev}}$$

since for reversible process, $dQ = T dS_{\text{sys}}$. Now, consider another process which connects the same two states as in the said reversible process but now by an irreversible path, then

$$U_B - U_A = \int_{\text{irr}} dQ - dW_{\text{irr}}$$

due to $dQ \neq T dS_{\text{sys}}$ for irreversible process. Since internal energy is a state variable, the value of $U_B - U_A$ is same whether the process is reversible or not. Hence, on equating them

$$W_{\text{rev}} - W_{\text{irr}} = W_{\text{lost}} = \int_{\text{rev}} T dS_{\text{sys}} - \int_{\text{irr}} dQ$$

For an isothermal irreversible process

$$\begin{aligned} W_{\text{lost}} &= T \left[\int_{\text{rev}} dS_{\text{sys}} - \int_{\text{irr}} \frac{dQ}{T} \right] \\ &= T(\Delta S_{\text{sys}} + \Delta S_{\text{env}}) \\ W_{\text{lost}} &= T\Delta S_{\text{uni}} \end{aligned}$$

where the second line is obtained from the definition of change of entropy in environment.

Isentropic process. Adiabatic process is defined as the one which does not involve exchange of heat with the environment. We also know that $dQ = T dS$ if the process is irreversible. Hence entropy is unchanged in a reversible adiabatic process. Such a process is called isentropic.

Third Law

The second law determines change in entropy but not its absolute value. Third law achieves that end. An interesting consequence of it, not elaborated here, is the question of unattainability of $T = 0$.

Planck's formulation. The entropy of any system at $T = 0$ is zero

$$S_{T=0} = 0$$

Nernst's heat theorem. The change in entropy is zero as $T \rightarrow 0$:

$$\lim_{T \rightarrow 0} \Delta S = 0$$

Thermodynamics' Potentials

Statistical Mechanics