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Thermodynamics and Statistical Mechanics

Thermodynamics I
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- Limits of the continuum
- Temperature
- Zeroth law of thermodynamics
- Equation of state
- Work, internal energy, and heat
- First law of thermodynamics

ABOUT THE COURSE

This course consists of two branches of physics
which deal with systems of large number of particles at equilibrium

Thermodynamics studies relations among different macroscopic quantities
taking many inputs from the experiment

Statistical physics (to the contrary) uses the microscopic approach
to calculate macroscopic quantities
that thermodynamics has to take from the experiment

All thermodynamic relations can be obtained from statistical mechanics

However
we can't consider statistical mechanics as superior to thermodynamics

The point is that thermodynamic relations are universal
because they are model-independent

To contrast ☛ results of statistical physics for macroscopic quantities
are always based on a particular model and thus are less general

FROM MICROSCALE TO MACROSCALE

individual particles
classical mechanics
variables: $\{\boldsymbol{x}_i\,,\,\boldsymbol{p}_i\}$

$\xrightarrow{\text{statistical mechanics}}$

gases, liquids, solids
thermodynamics
variables: $T, p, V, \dots$

individual people
psychology
variables: ???

$\xrightarrow{\text{????}}$

human populations
sociology/politics
variables: ???

PHYSICAL VERSUS SOCIAL SCIENCES

TEXTBOOKS

E. Fermi, **Thermodynamics**
(Dover, 1956)

This outstanding and inexpensive little book is a model of clarity

A. H. Carter, **Classical and Statistical Thermodynamics**
(Prentice-Hall, 2001)

A very relaxed treatment appropriate for undergraduate physics majors

H. B. Callen, **Themodynamics and Introduction to Thermostatics**
(John Wiley & Sons, 1985)

A comprehensive text appropriate for an extended course on thermodynamics

R. K. Pathria, **Statistical Mechanics**
(Pergamon Press, 1972)

Excellent graduate level text

SYSTEM AND ENVIRONMENT

Thermodynamics studies a macroscopic system that can be in contact with other macroscopic systems and/or the environment

Environment (or bath, or heat reservoir) is a special type of system that has a very large size

The macroscopic system under consideration can change its state as a result of its contact to the bath ☛ but the state of the bath does not change due to interaction with a much smaller system

For example ☛ thermometer measuring temperature of body can be considered as system, whereas body itself plays role of bath

DEFINITIONS

State of system ☛ condition uniquely specified by set of quantities such as pressure P, temperature T, volume V, density ρ

Equilibrium state ☛ properties of system are uniform throughout and don't change in time unless system is acted upon by external influences

Non-Equilibrium state ☛ characterizes a system in which gradients exist and whose properties vary with time

State variables ☛ properties that describes equilibrum states

Equation of state ☛ is a functional relationship among state variables for a system in equilibrium

Path ☛ is a series of states through which a system passes

MORE DEFINITIONS

Process ☛ change of state expressed in terms of a path along the equation of state surface

Cyclical process ☛ initial and final state are the same

Quasi-static process ☛ at each instant the system departs only infinitesimally from an equilibrium state

Reversible process ☛ direction can be reversed by an infinitesimal change in some property

It is a quasi-static process in which no dissipative forces such as friction are present

All reversible processes are quasi-static but a quasi-static process is not necessarily reversible

e.g. a slow leak in a tire is quasi-static but not reversible

A reversible process is an idealization ➢ friction is always present

Irreversible process ☛ involves a finite change in a property in a given step and includes dissipation (energy loss)

All natural processes are irreversible

OPEN, CLOSE, ADIABATIC, AND ISOLATED SYSTEMS

Systems can be: **open, closed, adiabatic, isolated**

Open system can exchange mass and energy with the environment

Closed system cannot exchange mass but it can receive or lose energy
in the form of heat due to thermal contact with bath
or through work done on system

Adiabatic system is thermally isolated so it can't receive or lose heat
although work can be done on this system

Quasi-static compression and expansion are called adiabatic processes
Fast processes are adiabatic too because heat exchange through surface
requires a too long time and becomes inefficient during time of process

Isolated system cannot exchange neither mass nor energy
there is no contact between system and environment

EXTENSIVE, INTENSIVE, AND SPECIFIC PROPERTIES

Macroscopic physical properties can be **intensive** and **extensive**

Intensive properties do not depend on size (mass) of system

e.g. $P, \; T, \; \rho$

Extensive properties scale with system size

e.g. V

To make this definition more precise:
if we split system into two equal parts by an imaginary membrane

Intensive properties of the two resulting systems remain the same while extensive properties of each subsystem are half of that for whole system

Extensive properties can be converted to intensive properties:

$$\text{Specific value} \equiv \frac{\text{value of the extensive property}}{\text{mass of the system}}$$

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KILOMOLE

Kilomole is a unit of mass definied as:

$$1 \text{ kilomole} = \text{mass in kilograms equal to molecular weight}$$

1 kilomole of oxygen gas (O_2) is equal to $32\,\text{kg}$

The **mole** is a unit of mass familiar to chemists

1 mole is equal to the mass in grams ☛ a mole of oxygen is $32\,\text{g}$

AVOGADRO'S LAW

We assume that classical thermodynamics is a continuum theory that properties vary smoothly from point to point in the system

But if all systems are made up of atoms and molecules (as definition of kilomole implies) ☛ it is reasonable to ask:

How small a volume can we concerned with and still have confidence that our continuum theory is valid?

Answer by invoking Avogadro's Law:

At standard temperature and pressure ($0^\circ\mathrm{C}$ and atmospheric pressure)

1 kilomole of gas occupies $22.4\,\mathrm{m}^3$ and contains 6.02×10^{26} molecules

The latter is called Avogadro's number N_A

$$\frac{6.02\ \times\ 10^{26}\,\mathrm{molecules\,kilomole}^{-1}}{22.4\,\mathrm{m}^3\,\mathrm{kilomole}^{-1}} = 2.69\ \times\ 10^{25}\,\frac{\mathrm{molecules}}{\mathrm{m}^3}$$

This molecular density is sometimes called **Loschmidt's number (LNo)**

LIMITS OF THE CONTINUUM

Using LNo it is easily seen that a cube one millimeter on each side contains roughly 10^{16} molecules

whereas a cube one nanometer $(10^{-9}\,\mathrm{m})$ on a side has a very small probability of containing even one molecule

We can therefore be reasonably certain that classical thermodynamics is applicable down to very small macroscopic (& even microscopic) volumes but ultimately a limit is reached where the theory will break down

TEMPERATURE

Temperature is associated with notions **hot** and **cold**

➢ if hot and cold bodies are brought in contact
their temperatures would eventually equilibrate

Consider system in thermal contact with bath and make
quasi-static compression or expansion plotting its states in (P, V) diagram

As bath is large ☛ its temperature remains unchanged
as process is slow ☛ temperature of system will have same unchanged value

In this way ☛ we obtain isothermal curve (or isotherm) in (P, V) plot

Repeating this @ different temperatures of bath we obtain many isotherms

For most of substances (except water near $4^\circ\mathrm{C}$)
isotherms corresponding to different temperatures do not cross

We define empirical temperature T as a parameter labeling isotherms:

$$\phi\,(P, V) = T \qquad \textbf{(2)}$$

If $T = \mathrm{const} \succ$ P and V are related and belong to a particular isotherm

THERMOMETERS

Any monotonic function $f(T)$ can serve as empirical temperature as well so that choice of latter is not unique

(2) is the basis of thermometers using different substances such as alcohol or mercury

Fix P to atmospheric pressure and measure V (or height of alcohol or mercury column) that changes with temperature

It is convenient to choose empirical temperature in way that changes of volume and temperature are proportional to each other

$$\Delta T \propto \Delta V$$

Fix V and use P to define temperature changes as $\Delta T \propto \Delta P$

What remains is to choose proportionality coefficient in above formula and additive constant (offset) in T

This has been done historically in a number of different ways resulting in Fahrenheit, Celsius, Kelvin, and other defunct temperature scales

TEMPERATURE SCALES

Celsius scale uses very natural events (ice and steam points of water) to define basic temperature points $0^\circ\mathrm{C}$ and $100^\circ\mathrm{C}$

Kelvin scale ➢ $T = 0$ where volume (or pressure) of ideal gas vanishes and one degree of temperature difference is same as in Celsius scale

Relation between two scales is

$$T(^\circ\mathrm{C}) = \mathrm{T}(^\circ\mathrm{K}) + 273.15 \qquad (3)$$

Farenheit scale ➢ $$T(^\circ\mathrm{F}) = \frac{9}{5}\,T(^\circ\mathrm{C}) + 32$$

THE ZEROTH LAW OF THERMODYNAMICS

Existence of temperature as new (non-mechanical) quantity that equilibrates systems in thermal contact encompass

zeroth law of thermodynamics

If two systems are separately in thermal equilibrium with a third system, they are in equilibrium with each other

EQUATION OF STATE

We rewrite (2) symmetric with respect to thermodynamic quantities

$$f(P, V, T) = 0 \qquad (4)$$

This relation between three quantities is called **equation of state**

If two of quantities are known ☛ third can be found from (4)

If $T = \text{const}$ ➢ P and V lie on curve called **isotherm**

If $P = \text{const}$ ➢ V and T lie on curve called **isobar**

If $V = \text{const}$ ➢ P and T lie on curve called **isocore**

(4) is written for a fixed amount of substance in a closed system

$$f(P, v, T) = 0 \qquad v \equiv V/M = \rho^{-1}$$

MAGNETIC SYSTEMS

Considerations thus far pertain to simplest thermodynamic systems such as gasses or liquids that are characterized by P and V

There are many systems described by other macroscopic quantities

e.g. magnetic systems are additionally described by:
magnetic induction B (intensive quantity)
and magnetic moment $\mathcal{M}$ (extensive quantity)

Usually magnetic systems are solid and their P and V do not change

Thus equation of state for magnetic systems has form

$$f\left(B, \mathcal{M}, T\right) = 0$$

EQUATION OF STATE OF IDEAL GAS

Equation of state of system composed of m kg of a gas whose molecular weight is M is given approximately by

$$PV = \frac{m}{M} RT$$

$R = 8.314 \times 10^3 \,\mathrm{J}/(\mathrm{kilomole\,K})$ ➢ **universal gas constant**

Since $n \equiv m/M$ is number of kilomoles of gas we can write

$$PV = nRT \qquad \textbf{(5)}$$

This equation is called equation of state of an ideal gas or perfect gas
It includes the laws of Boyle, Gay-Lussac, Charles and Avogadro
which were discovered over a period of 200 years

BRIDGE FROM MACROSCOPIC TO MICROSCOPIC PHYSICS

(5) can be rewritten as $PV = m\bar{R}T$

Downside of this form is that $\bar{R} = R/M$ is not universal

(depends on particular gas)

To make connection with molecular theory we rewrite (5) as

$$PV = N\,k_B T \qquad (6)$$

N ☛ number of particles (atoms or molecules) in gas

$k_B = 1.38 \times 10^{-23}\,\mathrm{J/K}$ ☛ Boltzmann constant

The lhs of (6) ☛ macroscopic amount of pressure-volume energy representing state of the bulk gas

The rhs of (6) divides this energy into N units (1 for each gas particle) each of which has an average kinetic energy of k_BT

ABSOLUTE ZERO

Isotherm of ideal gas is a hyperbole

while isochore and isobar are straight lines

Temperature in (5) and (6) is in Kelvin

P and V turn to zero at $T = 0$

The beginning of Kelvin temperature scale has a deep physical meaning:
At $T = 0$ molecules of ideal gas freeze and stop to fly inside container falling down into their state of lowest energy

As the pressure is due to the impact of the molecules onto the walls

it vanishes at $T = 0$

Equation of state of the ideal gas loses its applicability at low T

because any actual gas becomes non-ideal

THERMODYNAMIC COEFFICIENTS

Writing $V = V(P,T)$ we obtain for infinitesimal changes full differential

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \qquad (7)$$

Partial derivatives above enter the thermodynamic coefficients:

isothermal compressibility $$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad (8)$$

thermal expansivity $$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad (9)$$

To mantain mechanical stability all materials have $\kappa_T > 0$

There is no general principle that could limit the range of β

Most materials expand upon heating $\beta > 0$

Materials that consist of long polymer molecules such as rubber contract upon heating $\beta < 0$

(this can be explained by their molecular motion)

THERMODYNAMIC COEFFICIENTS (cont'd)

Using $P = P(V, T)$ we obtain the differential

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT \qquad (10)$$

Both partial derivatives in (10) can be reduced to those in (7) with the help of two formulas from the calculus:

the reciprocal relation
$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{(\partial V/\partial P)_T} \qquad (11)$$

and the triple product rule
$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1 \qquad (12)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\beta}{\kappa_T} \qquad (13)$$

MATHEMATICAL INTERLUDE

Consider function of 3 variables $f(x,y,z)=0$

Only 2 variables are independent ➢ $x=x(y,z)$ and $y=y(x,z)$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \qquad\qquad dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

Substituting right into left

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz$$

If we choose x and z as independent variables

previous Eq. holds for all values of dx and dz

If $dz=0$ and $dx \neq 0$ ☛ **reciprocal relation**

If $dz \neq 0$ and $dx = 0$ ➢ $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y$

Using reciprocal relation ☛ **triple product rule**

THERMODYNAMIC COEFFICIENTS FOR IDEAL GAS

Substituting $V = nRT/P$ in (8) and (9) we obtain

$$\kappa_T = -\frac{P}{nRT}\left(\frac{nRT}{P^2}\right) = \frac{1}{P} \qquad (14)$$

and

$$\beta = \frac{P}{nRT}\left(\frac{nR}{P}\right) = \frac{1}{T} \qquad (15)$$

Now (13) yields

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T} \qquad (16)$$

EXACT AND INEXACT DIFFERENTIALS

Differential is called exact if there is function $F(x_1, \cdots, x_n)$ satisfying

$$dF = \sum_{i=1}^{k} A_i \, dx_i \qquad \text{with} \qquad A_i = \frac{\partial F}{\partial x_i} \Leftrightarrow \frac{\partial A_i}{\partial x_j} = \frac{\partial A_j}{\partial x_i} \quad \forall i, j$$

For exact differential ☛ integral between fixed endpoints is path-independent

$$\int_A^B dF = F(x_1^B, \cdots, x_k^B) - F(x_1^A, \cdots, x_k^A)$$

It follows that ☛

$$\oint dF = 0$$

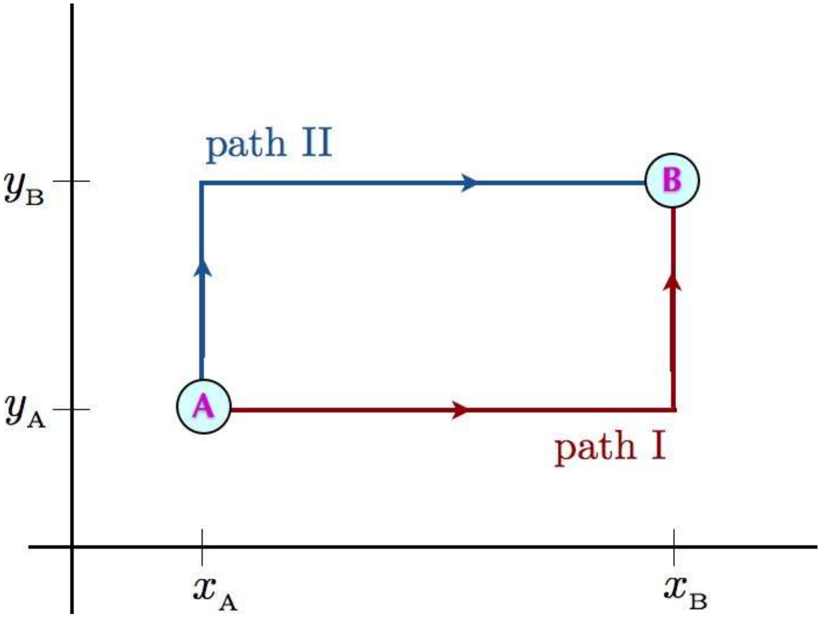
When the cross derivatives are not identical ☛ $\frac{\partial A_i}{\partial x_j} \neq \frac{\partial A_j}{\partial x_i}$

δF differential is inexact

Integral of δF is path dependent and does not depend solely on endpoints

TWO DISTINCT PATHS WITH IDENTIAL END POINTS

$$\delta F = K_1 \ y \ dx + K_2 \ x \ dy$$



$$W^{(\mathrm{I})} = K_1 \int_{x_A}^{x_B} dx \ y_A + K_2 \int_{y_A}^{y_B} dy \ x_B = K_1 y_A (x_B - x_A) + K_2 x_B (y_B - y_A)$$

$$W^{(\mathrm{II})} = K_1 \int_{x_A}^{x_B} dx \ y_B + K_2 \int_{y_A}^{y_B} dy \ x_A = K_1 y_B (x_B - x_A) + K_2 x_A (y_B - y_A)$$

In general ☛ $W^{(\mathrm{I})} \neq W^{(\mathrm{II})}$

WORK

The system and environment can exchange energy with each other

One of the ways to exchange energy is doing work that can be understood in mechanical terms

According to Newton’s third law ➢ work done on system by environment and work done by system on environment differ by the sign

Consider system characterized by P, V, T contained in cylinder of area S with moving piston

$$\delta W = Fdl = PSdl = PV \qquad \textbf{(17)}$$

(17) is general and can also be obtained for any type of deformations of system’s surface

We write δW instead of dW to emphesize ☛ W is not **state variable**

δW is a small increment but not an exact differential

STATE VARIABLE

State variable is any thermodynamic quantity
that has a well-defined value in any particular state of the system

In particular ☛ for **cyclic processes** system returns to same state at end of cycle so that all state variables assume their initial values

Nonzero work can be done in cyclic processes
(the area circumscribed by the cycle in the P, V diagram)
so we can't ascribe amount of work to any particular state of system

Finite work done on the way from initial state 1 to final state 2

$$W_{12} = \int_1^2 P \, dV \tag{18}$$

depends on the whole way from initial to final states

That is ☛ work is a way function rather than a state function

CALCULUS OF W_{12} FOR IDEAL GAS

For isochoric process obviously $W_{12} = 0$ because volume does not change

For isobaric process integrand P in **(18)** is constant

$$W_{12} = \int_1^2 P\, dV = P(V_2 - V_1) \tag{19}$$

For isothermal process with help of equation of state **(5)** we obtain

$$W_{12} = nRT \int_1^2 \frac{dV}{V} = nRT \ln \frac{V_2}{V_1} \tag{20}$$

Positive work is done by system in isobaric and isothermal expansion

CONFIGURATIONAL AND DISSIPATIVE WORK

Configurational work is the work in a reversible process given by product of some intensive variable and change in some extensive variable In thermodynamics it is often called "$P\,dV$" work (for obvious reasons)

Dissipative work is the work done in irreversible process
It is understood that dissipative work cannot be described by (17)-(18)

Total work is sum of both:

$$\delta W = \delta W_{\rm configurational} + \delta W_{\rm dissipative} \qquad (21)$$

Next class I'll show you that dissipative work is always done on system

$$\delta W_{\rm dissipative} \leq 0 \qquad (22)$$

INTERNAL ENERGY

Similarly to mechanics one can define internal energy U of system through work on way from 1 to 2

To do this one has to thermally insulate system from the environment

Experiment shows that total amount of work on adiabatic system

$$(\text{configurational} + \text{dissipative})\, W_{12}$$

is entirely determined by initial and final states 1 and 2

We then define internal energy for any state 2 of system

$$U_2 = U_1 - W_{12} \tag{23}$$

CALORIC EQUATION OF STATE

To reach state 2 from state 1 we make (in general)
both configurational and dissipative work

Order in which these works are done is arbitrary
so that there are many paths leading from 1 to 2

Still W_{12} is same for all these paths

U_2 (or simply U) is a state quantity

$$U = U(T, V) \tag{24}$$

Within thermodynamics
only way to obtain (24) is to take it from the experiment

Statistical mechanics provides analytic form of caloric equation of state
in many cases

THE FIRST LAW OF THERMODYNAMICS

Having defined the internal energy U for any state P, V of system
we can relax the condition that the system is adiabatic

After allowing thermal contact between system and environment
the energy balance in mechanical form is no longer satisfied

To restore energy conservation
we include heat Q received by the system from the environment

In infinitesimal form energy conservation reads

$$dU = \delta Q - \delta W \tag{25}$$

Energy conservation law written in form of (25)
constitutes **the first law of thermodynamics**

HEAT

calory = amount of heat needed to increase of $1\ \mathrm{g}$ water by $1^\circ\mathrm{C}$

mechanical equivalent of calory

$$1\mathrm{cal} = 4.19\,\mathrm{J} \tag{26}$$

The heat received in a finite process is given by

$$Q_{12} = \int_1^2 (dU + \delta W) = U_2 - U_1 + \delta W_{12} \tag{27}$$

Since W_{12} depends on path between 1 and 2

heat is a path function rather than a state function