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01. Equilibrium Thermodynamics I: Introduction

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Abstract

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Table of Contents [ttc]

1. Equilibrium Thermodynamics I: Introduction

2. Equilibrium Thermodynamics II: Engines

- Roads from 1 to 2: isothermal, isentropic, isochoric, isobaric. [tex25]
- Room heater: electric radiator versus heat pump. [tex13]
- Mayer's relation for the heat capacities of the classical ideal gas. [tex12]
- Positive and negative heat capacities. [tex26]
- Work extracted from finite heat reservoir in infinite environment. [tex9]
- Work extracted from finite heat reservoir in finite environment. [tex10]
- Heating the air in a room. [tex2]
- Gasoline engine. [tln65]
- Idealized gasoline engine(Otto cycle). [tex8]
- Diesel engine. [tln66]
- Idealized Diesel engine. [tex16]
- Escher-Wyss gas turbine. [tln75]
- Joule cycle. [tex108]
- Stirling engine. [tln76]
- Idealized Stirling cycle. [tex131]
- Ideal-gas engine with two-step cycle I. [tex106]
- Ideal-gas engine with two-step cycle II. [tex107]
- Circular heat engine I. [tex147]
- Circular heat engine II. [tex148]
- Square heat engine. [tex149]

3. Equilibrium Thermodynamics III: Free Energies
    - Fundamental equation of thermodynamics. [tln16]
    - Free energy. [tln3]
    - Retrievable and irretrievable energy put in heat reservoir. [tex6]
    - Legendre transform. [tln77]

- Thermodynamic potentials. [tln4]
- Alternative set of thermodynamic potentials. [tln9]
- Thermodynamic functions. [tln5]
- Maxwell's relations. [tln17]
- Free energy stored and retrieved. [tln18]
- Useful relations between partial derivatives. [tln6]
- Response functions (thermal, mechanical, magnetic). [tln7] (2)
- Isothermal and adiabatic processes in fluid systems and magnetic systems. [tln8]
- Conditions for thermal equilibrium. [tln19]
- Stability of thermal equilibrium. [tln20]
- Jacobi transformation. [tln21]
- Entropy of mixing. [tln25]
- Osmotic pressure. [tln26]

4. Equilibrium Thermodynamics IV: Applications
   - Entropy and internal energy of the classical ideal gas. [tex14]
   - Thermodynamic potentials of the classical ideal gas. [tex15]
   - Chemical potential of the classical ideal gas. [tex17]
   - Ideal gas heat capacity by design. [tex35]
   - Sound velocity in the classical ideal gas I. [tex18]
   - Sound velocity in the classical ideal gas II. [tex99]
   - Absolute temperature from measurements. [tex134]
   - Polytropic process of classical ideal gas. [tex138]
   - Heavy piston. [tex141]
   - Isothermal atmosphere. [tex150]
   - Adiabatic atmosphere. [tex151]
   - Homogeneous atmosphere. [tex152]
   - Van der Waals equation of state. [tln22]

- Cooling gases: Joule effect (free expansion) and Joule-Thomson effect (throttling). [tln23]
- Joule-Thomson inversion curves. [tsl1]
- Heat capacities of the van der Waals gas. [tex27]
- Internal energy and entropy of the van der Waals gas. [tex38]
- Joule coefficient of the van der Waals gas. [tex31]
- Joule-Thomson coefficient of the van der Waals gas. [tex32]
- Assembling thermodynamic information. [tex29]
- How not to modify the ideal gas equation of state. [tex11]
- Reconstructing the equation of state of a fluid system. [tex42]
- Reconstructing the equation of state of a gas. [tex43]
- Effects of first virial correction on ideal gas properties. [tex33]
- Entropy due to electronic spins in iron ammonium alum. [tsl2]
- Adiabatic demagnetization. [tln24]
- Thermodynamics of an ideal paramagnet I. [tex19]
- Thermodynamics of an ideal paramagnet II. [tex20]
- Thermodynamics of an ideal paramagnet III. [tex21]
- Thermodynamics of a real paramagnet. [tex36]
- Thermodynamics of a classical ideal paramagnetic gas I. [tex22]
- Thermodynamics of a classical ideal paramagnetic gas II. [tex133]
- Hydrostatic pressure. [tex132]
- Rubber band heat engine. [tex39]
- Equation of state and adiabate of an elastic band. [tex40]
- Determining C_V of condensed matter. [tex28]
- Thermodynamics of blackbody radiation. [tex23]
- Carnot cycle of thermal radiation. [tex24]

5. Thermodynamics of Phase Transitions I
    - Phase diagram of a “normal” substance. [tsl3]

- Phase diagram of H_2O. [tsl4]
- Ferrimagnetic phases. [tsl49]
- Liquid crystal phases. [tsl51]
- Ordering of surfactant molecules. [tsl50]
- Phase coexistence: Gibbs phase rule. [tln27]
- Classification of phase transitions. [tln28]
- Gibbs free energy and derivatives at discontinuous transition. [tsl7]
- Gibbs free energy and derivatives at continuous transition. [tsl8]
- Clausius-Clapeyron equation. [tln29]
- Entropy of a supercooled liquid. [tex30]
- Coexistence line of continuous phase transition. [tex37]
- Latent Heat and response functions. [tex124]
- Heat capacity of vapor in equilibrium with liquid phase. [tex41]
- Discontinuous transition: change in internal energy. [tex123]
- Dry ice. [tex125]
- Abnormal phase behavior. [tex54]
- Melting or freezing. [tex51]
- Triple-point phase changes. [tex52]
- Cooling down? Heating up? [tex153]
- Phase coexistence of ammonia. [tex55]

6. Thermodynamics of Phase Transitions II
    - Van der Waals equation of state with coexistence curve. [tsl10]
    - Law of corresponding states. [tln30]
    - Maxwell construction. [tln31]
    - Gibbs and Helmholtz free energies of the van der Waals fluid at $T < T_c$. [tsl11]
    - Condensation and evaporation. [tln32]
    - Dieterici equation of state. [tex34]

- Helium liquids. [tln33]
- Phase diagram of ^{4}He. [tsl13]
- Phase diagram of ^{3}He. [tsl14]
- Exotic properties of helium II. [tln34]
- Superconducting transition. [tln35]
- Thermodynamics of a ferromagnet. [tsl5]
- Structural transitions of iron. [tex53]
- Latent heat and heat capacities at superconducting transition. [tex44]
- Thermodynamics of the mean-field ferromagnet I. [tex45]
- Thermodynamics of the mean-field ferromagnet II. [tex46]

7. Kinetic Theory I
    - Statistical uncertainty and information. [tln37]
    - Statistical concept of uncertainty. [tex47]
    - Statistical uncertainty and information. [tln37]
    - Statistical uncertainty and information. [tex48]
    - Information of sequenced messages. [tex61]
    - Kinetics of classical ideal gas. [tsl28]
    - Pressure and mean square velocity in classical ideal gas. [tex49]
    - Maxwell velocity distribution. [tln38]
    - Maxwell velocity distribution (Maxwell's derivation). [tex50]
    - Maxwell distribution in D-dimensional space. [tex56]
    - Boltzmannn equation. [tln39]
    - Boltzmann's H-theorem. [tln40]
    - Energy distribution for N ideal gas atoms. [tex57]
    - Maxwell velocity distribution (Boltzmann's derivation). [mex58]
    - Ideal-gas entropy and Boltzmann's H-function. [tex59]
    - H-theorem and entropy. [tln41]

- Boltzmann's H-function simulated. [tsl27]
- Maxwell distribution derived from minimizing the H-function. [tex60]
- Doppler broadening of atomic spectral lines. [tex63]

8. Kinetic Theory II
    - Ideal gas atoms escaping from a container. [tex62]
    - Toward thermal equilibrium via particle transfer. [tex64]
    - Isotope separation via diffusion. [tex65]
    - Kinematic pressure and interaction pressure. [tln42]
    - Interaction pressure produced by Gaussian interparticle potential. [tex66]
    - Kinetic forces and mobility. [tln43]
    - Average force of particle beam on heavy hard sphere. [tex68]
    - Mobility of a hard sphere in a dilute gas. [tex69]
    - Collision rate and mean free path. [tln44]
    - Collision rate in classical ideal gas. [tex70]
    - Mean free path of particle in classical ideal gas. [tex71]
    - Rate of chemical reaction $A + A \to A_2$ in gas phase. [tex67]
    - Effect of escaping particles on temperature of 1D ideal gas. [tex72]

9. Microcanonical Ensemble
    - Classical Hamiltonian system. [tln45]
    - Classical Liouville operator. [tln46]
    - Quantum Liouville operator. [tln47]
    - Gibbs entropy. [tln48]
    - Microcanonical ensemble. [tln49]
    - Classical ideal gas (microcanonical ensemble). [tex73]
    - Array of classical harmonic oscillators (microcanonical ensemble). [tex74]
    - Quantum harmonic oscillators (microcanocal ensemble I). [tex75]

- Quantum harmonic oscillators (microcanocal ensemble II). [tex126]
- Quantum paramagnet (microcanonical ensemble). [tex127]
- Entropy of mixing revisited. [tln50]

10. Canonical Ensemble I
    - Canonical ensemble. [tln51]
    - Classical ideal gas (canonical ensemble). [tex76]
    - Ultrarelativistic classical ideal gas (canonical idela gas). [tex77]
    - Ultrarelativistic classical ideal gas in two dimensions. [tex154]
    - Array of classical harmonic oscillators (canonical ensemble). [tex78]
    - Irreversible decompression. [tex136]
    - Irreversible heat exchange. [tex137]
    - Reversible decompression. [tex139]
    - Reversible heat exchange. [tex140]
    - Heavy piston. [tex141]
    - Ensemble averages. [tln52]
    - Classical virial theorem. [tln83]
    - Systems of noninteracting particles. [tln54]
    - Further ensemble averages. [tln55]
    - Classical ideal gas in a uniform gravitational field. [tex79]
    - Gas pressure and density inside centrifuge. [tex135]
    - Relative momentum of two ideal gas particles. [tex80]
    - Partition function and density of states. [tln56]
    - Ideal gas partition function and density of states. [tex81]
    - Vibrational heat capacities of solids. [tln57]
    - Array of quantum harmonic oscillators (canonical ensemble). [tex82]
    - Vibrational heat capacities of solids (Debye theory). [tsl29]
    - Thermodynamic perturbation expansion. [tln80]
    - Vibrational heat capacity of a solid. [tex83]

- Anharmonic oscillator and thermodynamic perturbation. [tex104]

11. Canonical Ensemble II
    - Paramagnetism. [tln58]
    - Paramagnetic salts. [tsl30]
    - Fluctuations in a magnetic system. [tln53]
    - Fluctuations in a magnetic system. [tex109]
    - Classical paramagnet (canonical ensemble). [tex84]
    - Quantum paramagnet (two-level system). [tex85]
    - Quantum paramagnet (Brillouin function). [tex86]
    - Ising trimer. [tex142]
    - Negative temperatures. [tsl31]
    - Gases with internal degrees of freedom. [tln59]
    - Classical rotational free energy of NH_3 gas. [tex87]
    - Classical rotational entropy of HCl and N_2 gas. [tex88]
    - Quantum rotational heat capacity of a gas at low temperature. [tex89]
    - Quantum rotational heat capacity of a gas at high temperature. [tex90]
    - Rotational and vibrational heat capacities. [tsl32]
    - Orthohydrogen and parahydrogen. [tln81]
    - Relativistic classical ideal gas (canonical partition function). [tex91]
    - Relativistic classical ideal gas (entropy and internal energy). [tex92]
    - Relativistic classical ideal gas (heat capacity). [tex93]
    - Relativistic classical ideal gas (heat capacity). [tsl34]

12. Grandcanonical Ensemble
    - Grandcanonical ensemble. [tln60]
    - Classical ideal gas (grandcanonical ensemble). [tex94]
    - Density fluctuations and compressibility. [tln61]

- Density fluctuations in the grand canonical ensemble. [tex95]
- Density fluctuations and compressibility in the classical ideal gas. [tex96]
- Energy fluctuations and thermal response functions. [tex103]
- Microscopic states of quantum ideal gases. [tln62]
- Partition function of quantum ideal gases. [tln63]
- Ideal quantum gases: grand potential and thermal averages. [tln64]
- Ideal quantum gases: average level occupancies. [tsl35]
- Occupation number fluctuations. [tex110]
- Density of energy levels for ideal quantum gas. [tex111]
- Maxwell-Boltzmann gas in D dimensions. [tex112]

13. Ideal Quantum Gases I: Bosons
    - Bose-Einstein functions. [tsl36]
    - Ideal Bose-Einstein gas: equation of state and internal energy. [tln67]
    - BE gas in D dimensions I: fundamental relations. [tex113]
    - Reference values for T, V/N, and p. [tln71]
    - Bose-Einstein condensation. [tsl38]
    - Ideal Bose-Einstein gas: isochores. [tsl39]
    - BE gas in D dimensions II: isochore. [tex114]
    - BE gas in D dimensions III: isotherm and isobar. [tex115]
    - Bose-Einstein gas: isotherms. [tsl40]
    - Bose-Einstein gas: isobars. [tsl48]
    - Bose-Einstein gas: phase diagram. [tln72]
    - Bose-Einstein heat capacity. [tsl41]
    - BE gas in D dimensions IV: heat capacity at high temperature. [tex97]
    - BE gas in D dimensions V: heat capacity at low temperature. [tex116]

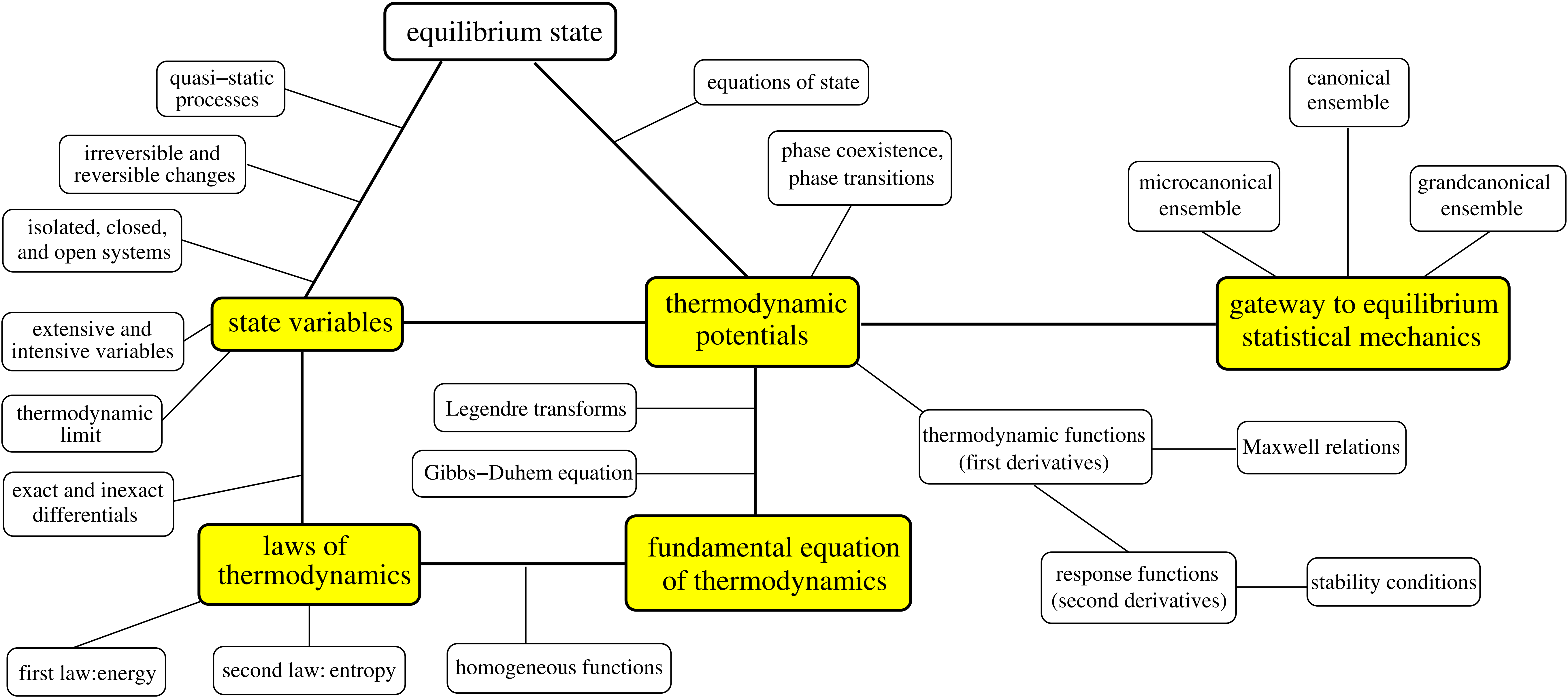
- BE gas in D dimensions VI: isothermal compressibility. [tex128]
- BE gas in D dimensions VII: isobaric expansivity. [tex129]
- BE gas in D dimensions VIII: speed of sound. [tex130]
- Ultrarelativistic Bose-Einstein gas. [tex98]
- Blackbody radiation. [tln68]
- Statistical mechanics of blackbody radiation. [tex105]

14. Ideal Quantum Gases II: Fermions
    - Fermi-Dirac functions. [tsl42]
    - Ideal Fermi-Dirac gas: equation of state and internal energy. [tln69]
    - Ideal Fermi-Dirac gas: chemical potentia.l [tsl43]
    - FD gas in D dimensions: chemical potential I. [tex117]
    - FD gas in D dimensions: chemical potential II. [tex118]
    - Ideal Fermi-dirac gas: average level occupancy. [tsl44]
    - Ideal Fermi-Dirac gas: isochores I. [tsl46]
    - FD gas in D dimensions: statistical interaction pressure. [tex119]
    - Ideal Fermi-Dirac gas: isotherms. [tln70]
    - FD gas in D dimensions: isotherm and adiabate. [tex120]
    - FD gas in D dimensions: ground-state energy. [tex102]
    - Ideal Fermi-Dirac gas: heat capacity. [tsl45]
    - FD gas in D dimensions: heat capacity at high temperature. [tex100]
    - FD gas in D dimensions: heat capacity at low temperature. [tex101]
    - Ideal Fermi-Dirac gas: isochores II. [tln73]
    - Ideal Fermi-Dirac gas: phase diagram in infinite dimensions. [tln74]
    - Stable white dwarf. [tex121]
    - Unstable white dwarf. [tex122]

Contents of this Document [ttc1]

1. Equilibrium Thermodynamics I: Introduction

Thermodynamics overview [tln2]



equilibrium state

quasi–static processes

irreversible and reversible changes

isolated, closed, and open systems

equations of state

phase coexistence, phase transitions

canonical ensemble

microcanonical ensemble

grandcanonical ensemble

state variables

thermodynamic potentials

gateway to equilibrium statistical mechanics

extensive and intensive variables

thermodynamic limit

exact and inexact differentials

Legendre transforms

Gibbs–Duhem equation

thermodynamic functions (first derivatives)

Maxwell relations

laws of thermodynamics

fundamental equation of thermodynamics

response functions (second derivatives)

stability conditions

first law:energy

second law: entropy

homogeneous functions

Preliminary list of state variables [tln1]

Thermodynamic functions

X: generic *extensive* variable
V: volume
S: entropy
M: magnetization
N: number of particles
n: number of moles

Y: generic *intensive* variable
p: pressure
T: temperature
H: magnetic field
μ: chemical potential
$\bar{\mu}$: chemical potential

Thermodynamic potentials

U: internal energy
E: enthalpy
A: Helmholtz free energy
G: Gibbs free energy
Ω: grand potential

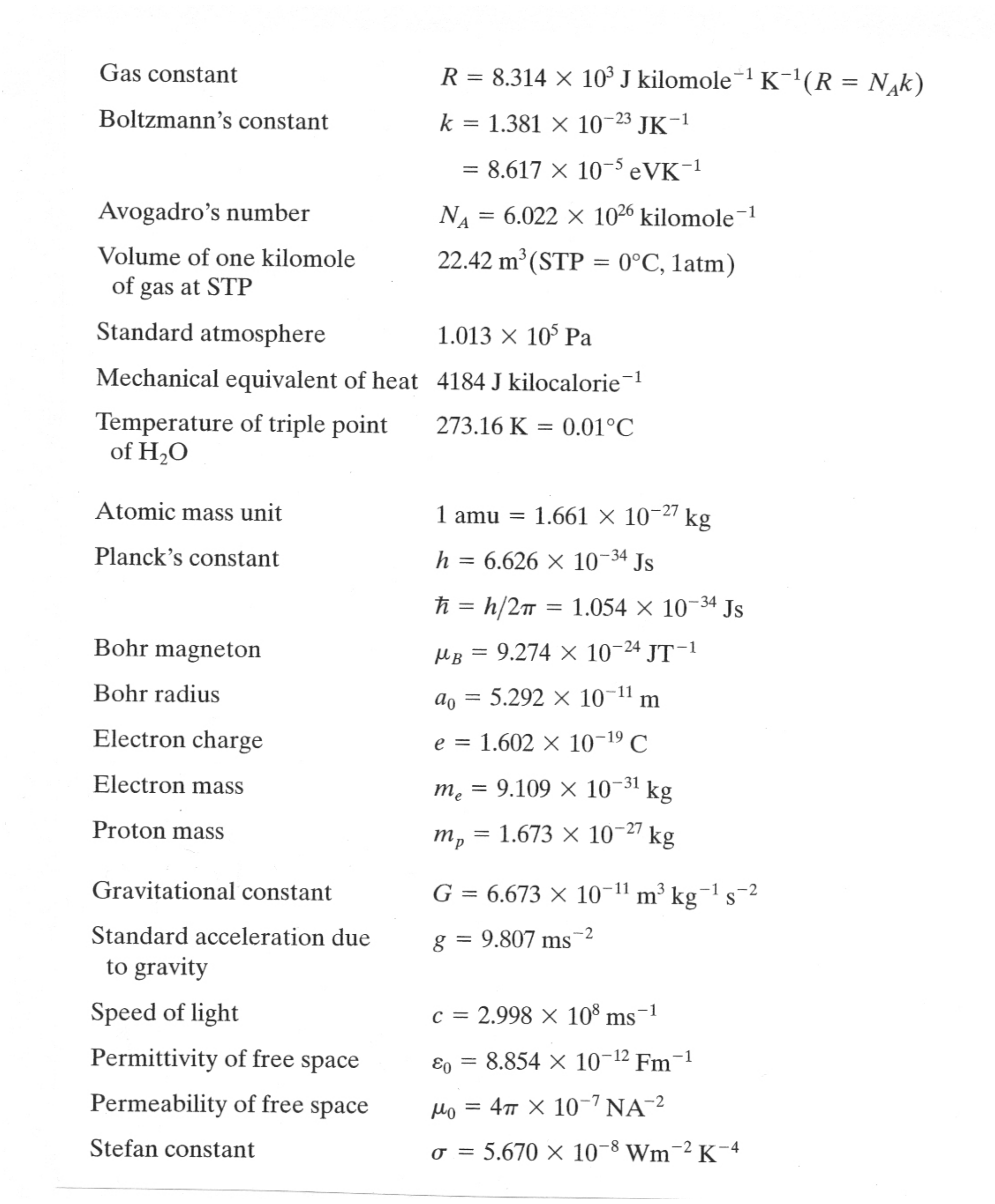
Thermodynamic response functions

C_V: isochoric heat capacity
C_p: isobaric heat capacity
χ_T: isothermal susceptibility
χ_S: adiabatic susceptibility

c_V: isochoric specific heat
c_p: isobaric specific heat

κ_T: isothermal compressibility
κ_S: adiabatic compressibility
α_p: thermal expansivity

Physical Constants [tsl47]



Gas constant	$R = 8.314 \times 10^3$ J kilomole^{-1} K^{-1} $(R = N_A k)$
Boltzmann's constant	$k = 1.381 \times 10^{-23}$ JK^{-1}
	$= 8.617 \times 10^{-5}$ eVK^{-1}
Avogadro's number	$N_A = 6.022 \times 10^{26}$ kilomole^{-1}
Volume of one kilomole of gas at STP	22.42 m^3 (STP = 0°C, 1atm)
Standard atmosphere	1.013×10^5 Pa
Mechanical equivalent of heat	4184 J kilocalorie^{-1}
Temperature of triple point of H_2O	273.16 K = 0.01°C
Atomic mass unit	1 amu $= 1.661 \times 10^{-27}$ kg
Planck's constant	$h = 6.626 \times 10^{-34}$ Js
	$\hbar = h/2\pi = 1.054 \times 10^{-34}$ Js
Bohr magneton	$\mu_B = 9.274 \times 10^{-24}$ JT^{-1}
Bohr radius	$a_0 = 5.292 \times 10^{-11}$ m
Electron charge	$e = 1.602 \times 10^{-19}$ C
Electron mass	$m_e = 9.109 \times 10^{-31}$ kg
Proton mass	$m_p = 1.673 \times 10^{-27}$ kg
Gravitational constant	$G = 6.673 \times 10^{-11}$ m^3 kg^{-1} s^{-2}
Standard acceleration due to gravity	$g = 9.807$ ms^{-2}
Speed of light	$c = 2.998 \times 10^8$ ms^{-1}
Permittivity of free space	$\varepsilon_0 = 8.854 \times 10^{-12}$ Fm^{-1}
Permeability of free space	$\mu_0 = 4\pi \times 10^{-7}$ NA^{-2}
Stefan constant	$\sigma = 5.670 \times 10^{-8}$ Wm^{-2} K^{-4}

[A. H. Carter 2001]

Equations of state [tln78]

The empirical specification of a thermodynamic system is traditionally expressed in the form of two kinds of equations of state.

- **Thermodynamic equation of state:**
  Functional relation between thermodynamic variables.
  For example: $pV = nRT$ (classical ideal gas).
- **Caloric equation of state:**
  Temperature dependence of internal energy or heat capacity.
  For example: $U = C_V T$ with $C_V = \text{const}$ (classical ideal gas).

The complete thermodynamic information about a system is encoded in this dual specification. In more complex systems the thermodynamic equation of state consists of multiple relations.

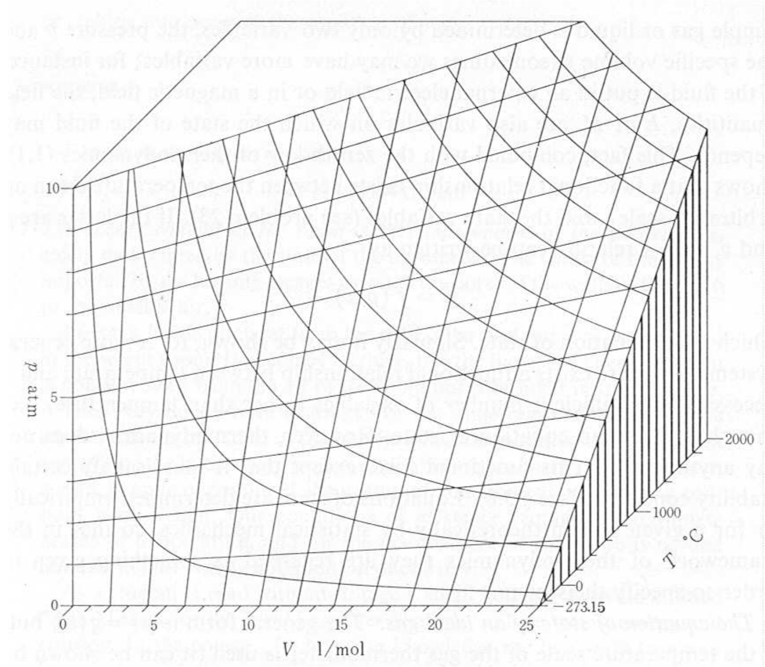
The most concise way of encoding the complete specification of a thermodynamic system is in the form of a *thermodynamic potential*. All thermodynamic quantities of interest about a given system can directly be derived from a thermodynamic potential.

Strategies commonly pursued:

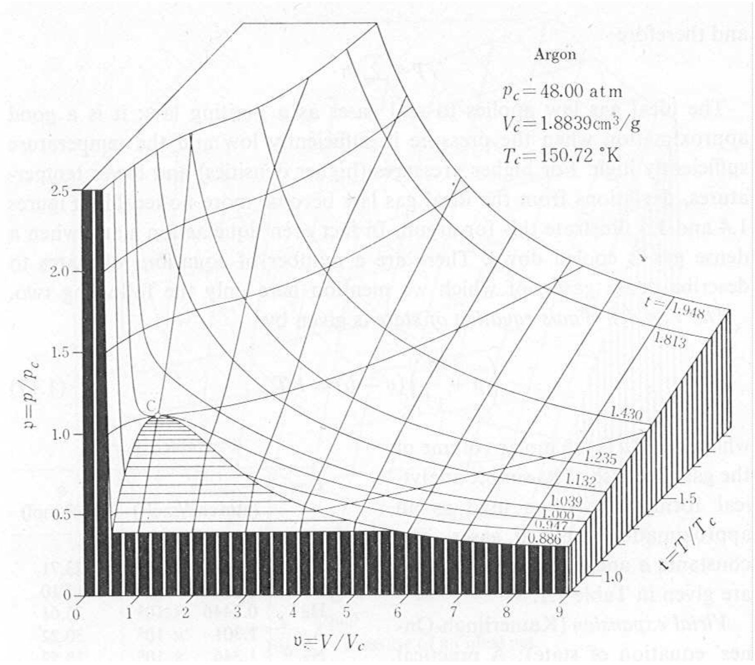
- **Equilibrium thermodynamics:**
  Construct a thermodynamic potential from the empirical information contained in the thermodynamic and caloric equations of state. Then derive any thermodynamic quantity of interest from the thermodynamic potential.
- **Equilibrium statistical mechanics:**
  Derive a thermodynamic potential (or partition function) from the microscopic specification of the system in the form of a many-body Hamiltonian. Then derive any thermodynamic quantity of interest from the thermodynamic potential.

Equations of state for ideal gas and real fluid [tsl12]

classical ideal gas



argon



[from Kubo: Thermodynamics]

Classification of thermodynamic systems [tln10]

Criterion: Thermodynamic contact.

1. Mechanical interaction (with work source).
   Exchange of energy via work performance.
2. Thermal interaction (with heat reservoir).
   Exchange of energy via heat transfer.
3. Mass interaction (with particle reservoir).
   Exchange of energy via matter transfer.

Isolated system: contact 1.
Closed system: contacts 1, 2.
Open system: contacts 1, 2, 3.

Laws of thermodynamics

Zeroth law: Two systems, each in thermal equilibrium with a third system, are in thermal equilibrium with each other.

- Prerequisite for measurement of thermodynamic properties.
- Thermal equilibrium implies uniform temperature.
- Mechanical equilibrium implies uniform pressure.
- Chemical equilibrium implies uniform chemical potential.

First Law: Energy is conserved.

- Internal energy U is a state variable.
- Heat and work are not state variables.

Second Law: Heat flows spontaneously from high to low temperatures.

- Entropy S is a state variable.
- Efficiency of heat engines.
- Reversibility and irreversibility.
- Definition of absolute temperature T.

Third Law: $\Delta S \to 0$ as $T \to 0$ for any process.

- No cooling to $T = 0$ in a finite number of steps.

Thermodynamic processes [tln79]

The study of equilibrium thermodynamics cannot do without processes that connect equilibrium states. Processes necessarily disturb the equilibrium.

Generic process:

- During a generic process between equilibrium states some of the thermodynamic variables may not be defined.
- Information about changes in all thermodynamic variables during a generic process can be obtained if we connect the same initial and final equilibrium states by a quasi-static process.

Quasi-static process:

- A quasi-static process involves infinitesimal steps between equilibrium states along a definite path in the space of state variables.
- The equations of state remain satisfied as the thermodynamic variables change during a quasi-static process.

Adiabatic process:

- During an adiabatic process the system is thermally isolated. There is no heat transfer. Changes are caused by work performance.
- An adiabatic process must not be too fast in order not to produce entropy within the system.
- In some practical applications, an adiabatic process must not be too slow in order to prevent significant heat exchange between the system and the environment.

Reversible and irreversible processes:

- In an isolated system the entropy (to be defined) stays constant during a reversible process and increases during an irreversible process.
- Quasi-static processes can be reversible or irreversible.

[tex143] Fast heat

A lead bullet of 20g mass traveling at 784mph is being lodged into a block of wood.
(a) How many calories of heat are generated in the process?
(b) If half that heat goes into the bullet, what rise in temperature will it experience?

Solution:

[tex144] Expansion and compression of nitrogen gas

One mol of N_2 at 25°C undergoes isothermal expansion from 1.0bar to 0.132bar pressure.
(a) How much work does the gas perform during expansion?
(b) If the gas is then adiabatically compressed by the same amount of work, what will be its final temperature?
Assume that both processes are quasistatic.

Solution:

[tex145] Bathtub icebreaker

How long does it take a heater coil operating at 500W to melt 1kg of ice initially at 0°F?

Solution:

Exact differentials [tln14]

Total differential of a function $F(x_1,x_2)$: $dF = \dfrac{\partial F}{\partial x_1}dx_1 + \dfrac{\partial F}{\partial x_2}dx_2$.

The differential $dF = c_1(x_1,x_2)dx_1 + c_2(x_1,x_2)dx_2$ is exact if dF is the total differential of a function $F(x_1,x_2)$.

Condition: $\dfrac{\partial^2 F}{\partial x_1 \partial x_2} = \dfrac{\partial^2 F}{\partial x_2 \partial x_1} \;\Rightarrow\; \dfrac{\partial c_1}{\partial x_2} = \dfrac{\partial c_2}{\partial x_1}$.

Consequences: $\displaystyle\int_{(a_1,a_2)}^{(b_1,b_2)} dF = F(b_1,b_2) - F(a_1,a_2), \qquad \oint dF = 0.$

Internal energy U

U is a state variable. $\oint dU = 0$ for reversible cyclic processes.

$dU = \delta Q + \delta W + \delta Z = TdS + YdX + \mu dN$ is an exact differential.

$\delta Q = TdS$: heat transfer
$\delta W = YdX$: work performance $(-pdV + HdM + \ldots)$
$\delta Z = \mu dN$: matter transfer

Entropy S

Carnot cycle: $\dfrac{|\Delta Q_L|}{\Delta Q_H} = \dfrac{T_L}{T_H} \;\Rightarrow\; \dfrac{\Delta Q_L}{T_L} + \dfrac{\Delta Q_H}{T_H} = 0$.

Any reversible cyclic process is equivalent to an array of Carnot cycles running in parallel.

$\Rightarrow \displaystyle\oint \frac{\delta Q}{T} \equiv \oint dS = 0$ for reversible cyclic processes.

S is a state variable.

Irreversible process:

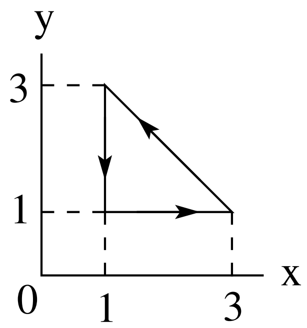
$$\eta = 1 - \frac{|\Delta Q_L|}{\Delta Q_H} < 1 - \frac{T_L}{T_H} \;\Rightarrow\; \frac{|\Delta Q_L|}{\Delta Q_H} > \frac{T_L}{T_H} \;\Rightarrow\; \frac{\Delta Q_L}{T_L} + \frac{\Delta Q_H}{T_H} < 0.$$

More general cyclic process: $\displaystyle\oint \frac{\delta Q}{T} < 0, \;\; \oint dS = 0 \;\Rightarrow\; dS > \frac{\delta Q}{T}$.

Irreversible process in isolated system: $\delta Q = 0 \;\Rightarrow\; dS > 0$.

[tex5] Exact and inexact differentials I

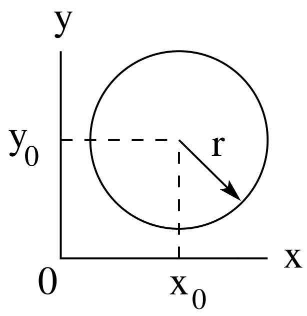
(a) Show that the differential $dF_1 = xydx + x^2dy$ is inexact. Determine the value of the integral $\oint dF_1$ along the closed path shown.
(b) Show that $dF_2 = (2y^2 - 3x)dx + 4xydy$ is an exact differential. Determine the function $F_2(x, y)$.



Solution:

[tex146] Exact and inexact differentials II

(a) Show that the differential $dF_1 = (x+y)dx + ydy$ is inexact. Determine the value of the integral $\oint dF_1$ along the circular path shown in counterclockwise direction.
(b) Show that $dF_2 = (x+y)dx + xdy$ is an exact differential. Determine the function $F_2(x,y)$.



Solution: