Equilibrium Statistical Physics

Physics Course Materials

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01. Equilibrium Thermodynamics I: Introduction

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Abstract

Part one of course materials for Statistical Physics I: PHY525, taught by Gerhard Müller at the University of Rhode Island. Documents will be updated periodically as more entries become presentable.

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Thermodynamics overview [tln2]
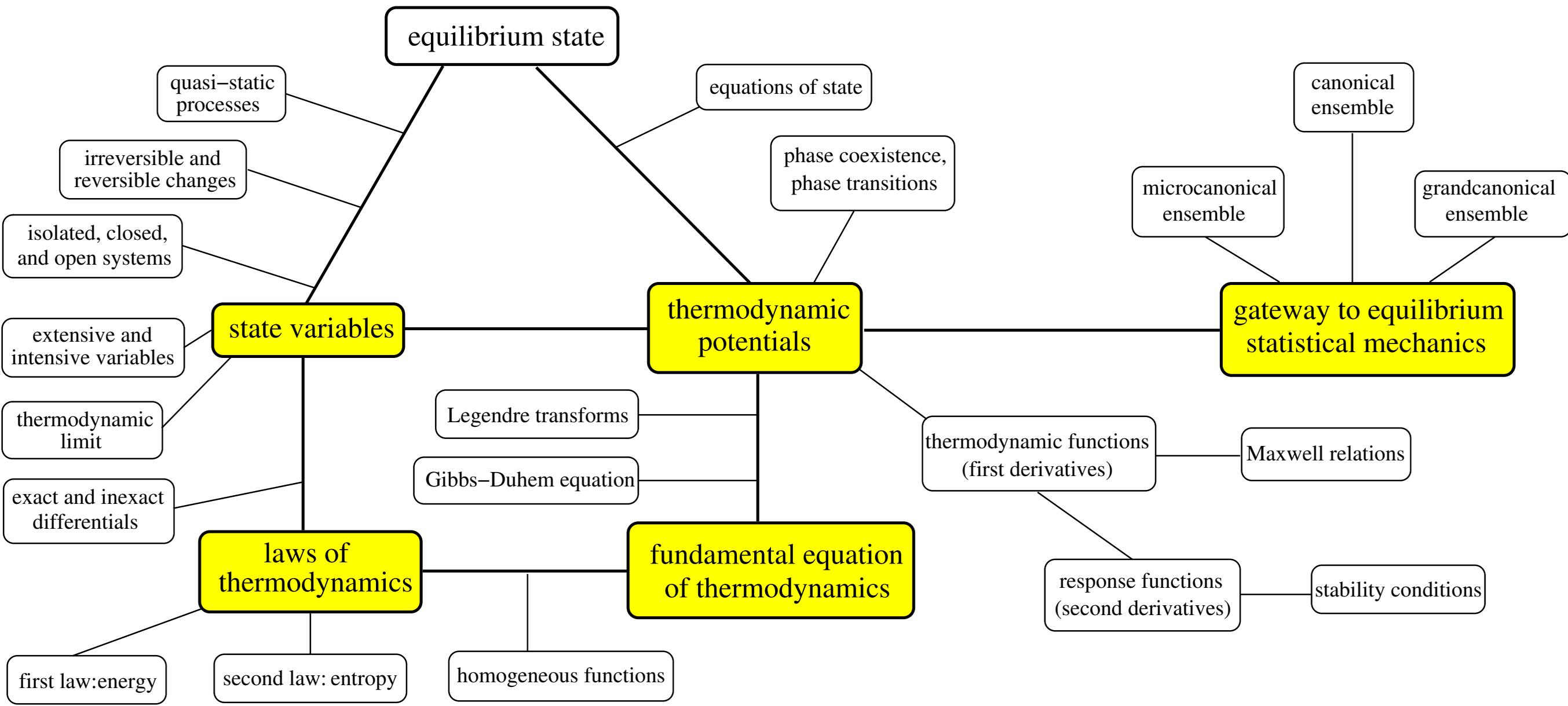
Preliminary list of state variables [tln1]

Thermodynamic functions

X: generic *extensive* variable Y: generic *intensive* variable
V: volume p: pressure
S: entropy T: temperature
M: magnetization H: magnetic field
N: number of particles μ: chemical potential
n: number of moles $\bar{\mu}$: 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_V: isochoric specific heat
C_p: isobaric heat capacity c_p: isobaric specific heat
χ_T: isothermal susceptibility
χ_S: adiabatic susceptibility

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$_2$O	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

Argon

$p_c = 48.00$ atm
$V_c = 1.8839 \text{cm}^3/\text{g}$
$T_c = 150.72 \ ^\circ\text{K}$
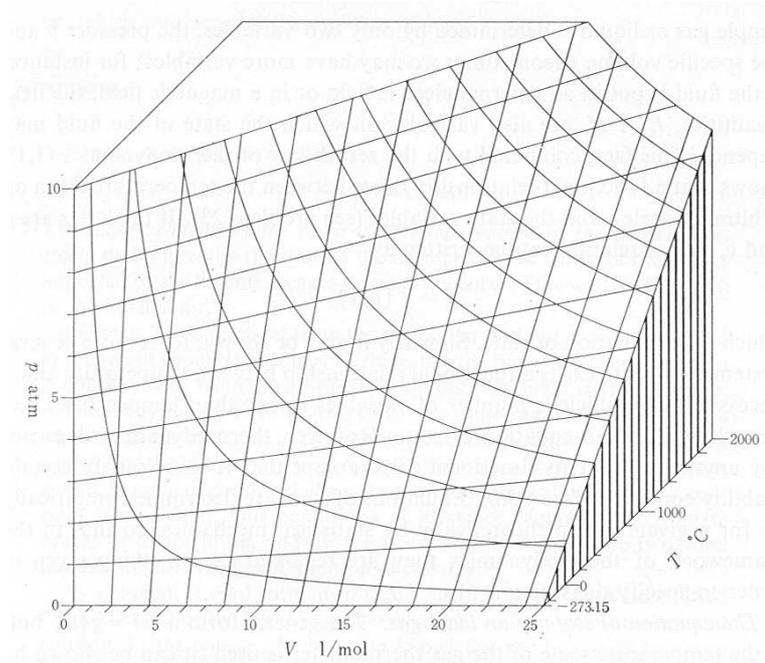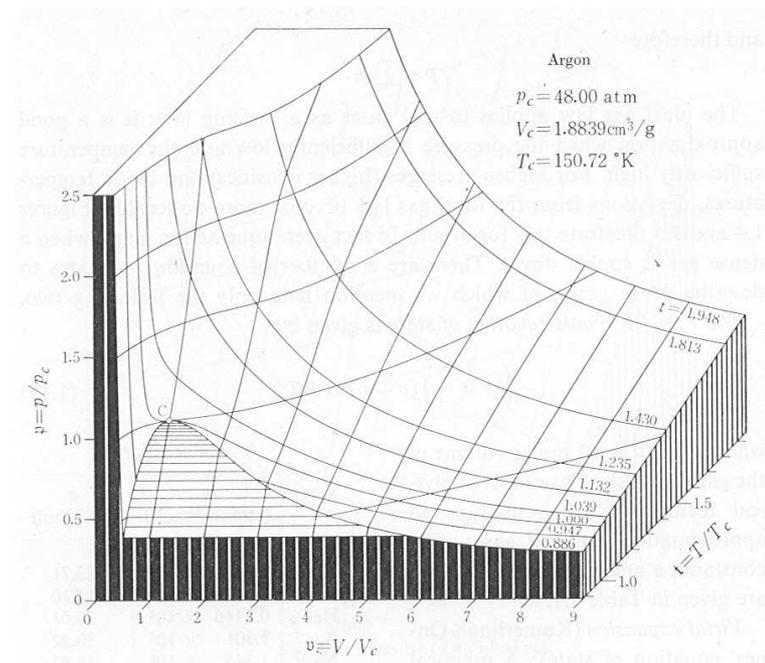
[from Kubo: Thermodynamics]

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

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

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

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

Internal energy U

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

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

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

Entropy S

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

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

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

S is a state variable.

Irreversible process:

$\eta = 1 - \dfrac{|\Delta Q_L|}{\Delta Q_H} < 1 - \dfrac{T_L}{T_H} \quad \Rightarrow \quad \dfrac{|\Delta Q_L|}{\Delta Q_H} > \dfrac{T_L}{T_H} \quad \Rightarrow \quad \dfrac{\Delta Q_L}{T_L} + \dfrac{\Delta Q_H}{T_H} < 0$.
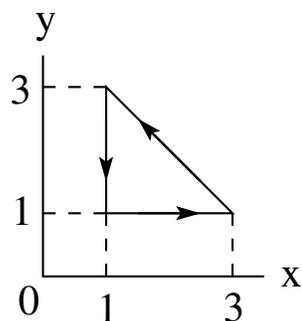
More general cyclic process: $\quad \displaystyle\oint \dfrac{\delta Q}{T} < 0, \quad \oint dS = 0 \quad \Rightarrow \quad dS > \dfrac{\delta Q}{T}$.

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

[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.
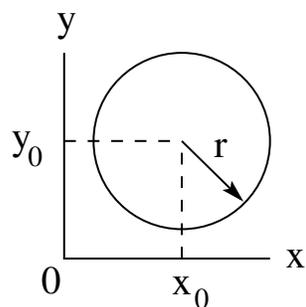
(b) Show that $dF_2 = (2y^2 - 3x)dx + 4xydy$ is an exact differential. Determine the function $F_2(x, y)$.

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: