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03. Equilibrium Thermodynamics III: Free Energies

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Abstract

Part three 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.

Contents of this Document [ttc3]

Fundamental equation of thermodynamics [tln16]

The first and second laws of thermodynamics imply that

$$dU = TdS + YdX + \mu dN \tag{1}$$

with

$$\left(\frac{\partial U}{\partial S}\right)_{X,N} = T, \quad \left(\frac{\partial U}{\partial X}\right)_{S,N} = Y, \quad \left(\frac{\partial U}{\partial N}\right)_{S,X} = \mu$$

is the exact differential of a function $U(S, X, N)$.

Here X stands for $V, M, \ldots$ and Y stands for $-p, H, \ldots$.

Note: for irreversible processes $dU < TdS + YdX + \mu dN$ holds.

U, S, X, N are extensive state variables.

$U(S, X, N)$ is a 1$^{\text{st}}$ order homogeneous function: $U(\lambda S, \lambda X, \lambda N) = \lambda U(S, X, N)$.

$$U[(1 + \epsilon)S, (1 + \epsilon)X, (1 + \epsilon)N] = U + \frac{\partial U}{\partial S}\epsilon S + \frac{\partial U}{\partial X}\epsilon X + \frac{\partial U}{\partial N}\epsilon N = (1 + \epsilon)U.$$

Euler equation:

$$U = TS + YX + \mu N. \tag{2}$$

Total differential of (2):

$$dU = TdS + SdT + YdX + XdY + \mu dN + Nd\mu \tag{3}$$

Subtract (1) from (3):

Gibbs-Duhem equation: $SdT + XdY + Nd\mu = 0$.

The Gibbs-Duhem equation expresses a relationship between the intensive variables T, Y, μ. It can be integrated, for example, into a function $\mu(T, Y)$.

Note: a system specified by m independent extensive variables possesses $m - 1$ independent intensive variables.

Example for $m = 3$: S, V, N (extensive); $S/N, V/N$ or p, T (intensive).

Complete specification of a thermodynamic system must involve at least one extensive variable.

Free energy

Mechanical system:

Consider a mechanical system in the form of a massive particle moving in a potential (e.g. harmonic oscillator, simple pendulum).

- Energy can be stored in a mechanical system when some agent does work on it.
- If the work involves exclusively *conservative* forces, then all energy added can be retrieved as work performed by the system.
- If the work done also involves *dissipative* forces, then only part of the energy added is retrievable as work performed by the system.
- The energy stored in and retrievable from the system is called *mechanical energy* (kinetic energy plus potential energy).

Thermodynamic system:

Consider a thermodynamic system in contact with a work source and (optionally) also with a heat reservoir and/or a particle reservoir.

- Energy can be stored in a thermodynamic system when some agent does work on it.
- If the work is done *reversibly*, then all the energy added can be retrieved as work performed by the system.
- If the work is done *irreversibly*, then only part of the energy added is retrievable as work performed by the system.
- The energy stored and retrievable as work is called *free energy*.
- The free energy stored in or retrieved from a thermodynamic system is expressed by some *thermodynamic potential*.
- The form of thermodynamic potential depends on the constraints imposed on the system during storage and retrieval of free energy.

[tex6] Retrievable and irretrievable energy put in heat reservoir

Consider the amount $n = 1$mol of a monatomic classical ideal gas inside a cylinder with a piston on one side. This system is in thermal contact with a heat bath at temperature $T_0 = 293K$. An external work source pushes the piston from position 1 ($V_1 = 5\text{m}^3$) in to position 2 ($V_2 = 3\text{m}^3$) and then back out to position 1. Calculate the work ΔW_{12} done by the source during step $1 \to 2$ and the (negative) work ΔW_{21} done during step $2 \to 1$ under three different circumstances: Compression and expansion of the gas take place (a) quasi-statically, i.e. isothermally; (b) rapidly, i.e. adiabatically, and in quick succession; (c) adiabatically again, but with a long waiting time between the two steps.

For each case calculate also the energy E_W wasted in the heat bath after one full cycle. Find the highest temperature T_H and the lowest temperature T_L reached by the gas in case (c).

The equation of state is $pV = nRT$, and the heat capacity is $C_V = \frac{3}{2}nR$. During the adiabatic process: $pV^\gamma = \text{const}$ with $\gamma = \frac{5}{3}$.

Solution:

Legendre transform [tln77]

Given is a function $f(x)$ with monotonic derivative $f'(x)$. The goal is to replace the independent variable x by $p = f'(x)$ with no loss of information.

Note: The function $G(p) = f(x)$ with $p = f'(x)$ is, in general, not invertible.

The Legendre transform solves this task elegantly.

- Forward direction: $g(p) = f(x) - xp$ with $p = f'(x)$.
- Reverse direction: $f(x) = g(p) + px$ with $x = -g'(p)$

Example 1: $f(x) = x^2 + 1$.

- $f(x) = x^2 + 1 \quad \Rightarrow \quad f'(x) = 2x \quad \Rightarrow \quad x = \dfrac{p}{2} \quad \Rightarrow \quad g(p) = 1 - \dfrac{p^2}{4}$.

- $g(p) = 1 - \dfrac{p^2}{4} \quad \Rightarrow \quad g'(p) = -\dfrac{p}{2} \quad \Rightarrow \quad p = 2x \quad \Rightarrow \quad f(x) = x^2 + 1$.

Example 2: $f(x) = e^{2x}$.

- $f(x) = e^{2x} \quad \Rightarrow \quad f'(x) = 2e^{2x} = p \quad \Rightarrow \quad x = \dfrac{1}{2} \ln \dfrac{p}{2}$
  $\Rightarrow \quad g(p) = \dfrac{p}{2} - \dfrac{p}{2} \ln \dfrac{p}{2}$.

- $g(p) = \dfrac{p}{2} - \dfrac{p}{2} \ln \dfrac{p}{2} \quad \Rightarrow \quad g'(p) = -\dfrac{1}{2} \ln \dfrac{p}{2} = -x$
  $\Rightarrow \quad p = 2e^{2x} \quad \Rightarrow \quad f(x) = e^{2x}$.

Thermodynamic potentials [tln4]

- All thermodynamic potentials of a system are related to each other via *Legendre transform*. Therefore, every thermodynamic potential has its distinct set of *natural independent variables*.

- All thermodynamic properties of a system can be inferred from any of the thermodynamic potentials. Any thermodynamic potential thus yields a *complete macroscopic description* of a thermodynamic system.

- Any quantity U, E, A, G, Ω which is not expressed as a function of its natural independent variables is not a thermodynamic potential and thus contains only partial thermodynamic information on the system.

- In *thermodynamics*, we determine thermodynamic potentials from *empirical macroscopic information* such as equations of state and response functions.

- In *statistical mechanics*, we determine thermodynamic potentials via partition functions from the *microscopic specification* (Hamiltonian) of the thermodynamic system.

- Any spontaneous i.e. irreversible process at constant values of the natural independent variables is accompanied by a *decrease* of the associated thermodynamic potential.

- The equilibrium state for fixed values of a set of natural independent variables is the state where the associated thermodynamic potential is a *minimum*.

- In the total differentials below, "=" holds for *reversible* processes and "<" for *irreversible* processes.

Internal energy: (set $X \equiv V, M$ and $Y \equiv -p, H$)
$$U(S, X, N) = TS + YX + \mu N, \qquad dU = TdS + YdX + \mu dN.$$

Enthalpy:
$$E(S, Y, N) = U - YX = TS + \mu N, \qquad dE = TdS - XdY + \mu dN.$$

Helmholtz free energy:
$$A(T, X, N) = U - TS = YX + \mu N, \qquad dA = -SdT + YdX + \mu dN.$$

Gibbs free energy:
$$G(T, Y, N) = U - TS - YX = \mu N, \qquad dG = -SdT - XdY + \mu dN.$$

Grand potential:
$$\Omega(T, X, \mu) = U - TS - \mu N = YX, \qquad d\Omega = -SdT + YdX - Nd\mu.$$

Alternative set of thermodynamic potentials

Intensive variables: $\alpha = -\dfrac{\mu}{T}, \; \beta = \dfrac{1}{T}, \; \gamma = \dfrac{p}{T}$

The following four thermodynamic potentials are related to each other via Legendre transform.

Entropy (microcanonical potential):

$$S(U, V, N) = \alpha N + \beta U + \gamma V, \quad dS = \alpha dN + \beta dU + \gamma dV$$

Massieu function (canonical potential):

$$\Phi(\beta, V, N) = S - \beta U = -A(T, V, N)/T, \quad d\Phi = \alpha dN - U d\beta + \gamma dV$$

Kramers function (grandcanonical potential):

$$\Psi(\beta, V, \alpha) = S - \beta U - \alpha N = -\Omega(T, V, \mu)/T, \quad d\Psi = -N d\alpha - U d\beta + \gamma dV$$

Planck function:

$$\Pi(\beta, \gamma, N) = S - \beta U - \gamma V = -G(T, p, N)/T, \quad d\Pi = \alpha dN - U d\beta - V d\gamma$$

Gibbs-Duhem relation: $N d\alpha + U d\beta + V d\gamma = 0$

Distinct properties:

- Any spontaneous i.e. irreversible process at constant values of the natural independent variables is accompanied by an *increase* of the associated thermodynamic potential.

- The equilibrium state for fixed values of a set of natural independent variables is the state where the associated thermodynamic potential is a *maximum*.

Entropy of mixing [tln25]

Consider two dilute gases in a rigid and insulating box separated by a mobile conducting wall: $n_1 = x_1 n$ (helium) and $n_2 = x_2 n$ (neon) with $x_1 + x_2 = 1$. Thermal equilibrium: p, T, $V_1 = x_1 V$, $V_2 = x_2 V$.

p T	p T
n₁ V₁	n₂ V₂

When the interior wall is removed, the gases mix spontaneously (irreversible process). By how much does the entropy increase?

To calculate ΔS, consider a reversible mixing process involving an isothermal expansion of semipermeable walls:

$$U = U_1 + U_2 \text{ with } U_i(T) = \text{const} \;\Rightarrow\; dU_i = TdS_i - p_i dV_i = 0.$$

$p_i = \dfrac{n_i RT}{V_i}$ are the partial pressures exerted on the semipermeable walls.

$$\Rightarrow\; dS_i = \frac{p_i}{T} dV_i = \frac{n_i R}{V_i} dV_i = nRx_i \frac{dV_i}{V_i}.$$

Entropy of mixing: $\;\Delta S = nR \sum_i x_i \int_{x_i V}^{V} \dfrac{dV_i}{V_i} = -nR \sum_i x_i \ln x_i > 0.$

Gibbs paradox: No entropy increase should result if the two gases happen to be of the same kind. This distinction is not reflected in the above derivation. The paradox is resolved by quantum mechanics, which requires that distinguishable and indistinguishable particles are counted differently.

To calculate the change in Gibbs free energy during mixing, we use the result for $G(T, p, N)$ of an ideal gas (see [tex15]) rewritten as $G(T, p, n) = -nRT \left[\ln(T/T_0)^{\alpha+1} - \ln(p/p_0) \right]$.

Initially: $\;p_1 = p_2 = p \;\Rightarrow\; G_{ini} = -\sum_i nx_i RT \left[\ln \left(\dfrac{T}{T_0} \right)^{\alpha+1} - \ln \dfrac{p}{p_0} \right].$

Finally: $\;p_i = px_i \;\Rightarrow\; G_{fin} = -\sum_i nx_i RT \left[\ln \left(\dfrac{T}{T_0} \right)^{\alpha+1} - \ln \dfrac{px_i}{p_0} \right].$

Change in Gibbs free energy: $\;\Delta G = nRT \sum_i x_i \ln x_i.$

Use $S = -\left(\dfrac{\partial G}{\partial T} \right)_p$ to recover $\Delta S = -nR \sum_i x_i \ln x_i.$

Change in chemical potential: use $G = \sum_i n_i \mu_i \;\Rightarrow\; \Delta \mu_i = RT \ln x_i.$

Thermodynamic functions [tln5]

First partial derivatives of thermodynamic potentials with respect to natural independent variables

Entropy:

$$S = -\left(\frac{\partial A}{\partial T}\right)_{X,N} = -\left(\frac{\partial G}{\partial T}\right)_{Y,N} = -\left(\frac{\partial \Omega}{\partial T}\right)_{X,\mu}$$

Temperature:

$$T = \left(\frac{\partial U}{\partial S}\right)_{X,N} = \left(\frac{\partial E}{\partial S}\right)_{Y,N}$$

Volume/magnetization $(X \equiv V, M)$:

$$X = -\left(\frac{\partial E}{\partial Y}\right)_{S,N} = -\left(\frac{\partial G}{\partial Y}\right)_{T,N}$$

Pressure/magnetic field $(Y \equiv -p, H)$:

$$Y = \left(\frac{\partial U}{\partial X}\right)_{S,N} = \left(\frac{\partial A}{\partial X}\right)_{T,N} = \left(\frac{\partial \Omega}{\partial X}\right)_{T,\mu}$$

Number of particles:

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,X}$$

Chemical potential:

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,X} = \left(\frac{\partial E}{\partial N}\right)_{S,Y} = \left(\frac{\partial A}{\partial N}\right)_{T,X} = \left(\frac{\partial G}{\partial N}\right)_{T,Y}$$

Osmotic pressure [tln26]

Consider a dilute solution. It consists of a solvent (e.g. water) and a solute (e.g. sugar). System A (pure solvent) is separated from system B (solution) by a membrane that is permeable to the solvent only. At thermal equilibrium, this causes an excess pressure in system B, which is called *osmotic pressure*.
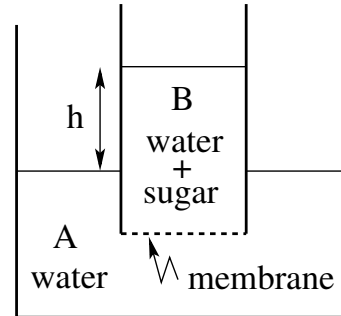
System A: pressure p_0, concentrations $x_S = 0$, $x_W = 1$.
System B: pressure $p = p_0 + \pi$, concentrations $x_S = 1 - x_W \ll 1$.

Observed osmotic pressure: $\pi = \rho_B g h$, where ρ_B is the mass density of B.

The osmotic pressure is a consequence of the requirement that the solvent on either side of the membrane must be in chemical equilibrium:

$$\mu_W(T, p, x_W) = \mu_W(T, p_0, 1).$$

(1) Effect of solute concentration on chemical potential:

$$\Delta\mu_W^{(1)} \equiv \mu_W(T, p, x_W) - \mu_W(T, p, 1) = RT \ln x_W = RT \ln(1 - x_S) \simeq -RT x_S.$$

(2) Effect of pressure on chemical potential: (use $n_W = n x_W$, $n_S = n x_S$)

$$
\begin{aligned}
\Delta\mu_W^{(2)} \equiv \mu_W(T, p, 1) - \mu_W(T, p_0, 1) &= \left(\frac{\partial \mu_W}{\partial p}\right)_{T, n_W} \Delta p = \left(\frac{\partial V}{\partial n_W}\right)_{T, p} \Delta p \\
&= \frac{V}{n_W} \Delta p \simeq \frac{V\pi}{n}.
\end{aligned}
$$

At thermal equilibrium: $\Delta\mu_W^{(1)} + \Delta\mu_W^{(2)} = 0 \Rightarrow \dfrac{V\pi}{n} - RT x_S = 0.$

Van't Hoff's law for osmotic pressure: $\pi = \dfrac{RT n_S}{V}$.

Maxwell's relations [tln17]

inferred from second partial derivatives of thermodynamic potentials with respect to two different natural independent variables

Fluid system:

$$dU = TdS - pdV \quad \Rightarrow \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$dE = TdS + Vdp \quad \Rightarrow \quad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$dA = -SdT - pdV \quad \Rightarrow \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$dG = -SdT + Vdp \quad \Rightarrow \quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Magnetic system:

$$dU = TdS + HdM \quad \Rightarrow \quad \left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial H}{\partial S}\right)_M$$

$$dE = TdS - MdH \quad \Rightarrow \quad \left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_H$$

$$dA = -SdT + HdM \quad \Rightarrow \quad \left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_M$$

$$dG = -SdT - MdH \quad \Rightarrow \quad \left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$$

Free energy stored and retrieved [tln18]

Consider a classical ideal gas confined to a cylinder with walls in thermal equilibrium with a heat reservoir at temperature T.

Reversible cyclic process:

1. Push the piston in from position 1 to position 2 quasi-statically.
   The work on the system is done reversibly.

$$\Delta W_{12} = \int_1^2 F dx = \int_1^2 dA = \int_1^2 (-SdT - pdV) \text{ with } dT = 0, \ dV < 0.$$

   $\Rightarrow \ \Delta W_{12} = A_2 - A_1 > 0.$
   The work done is equal to the excess Helmholtz potential (free energy).

2. Move the piston out from position 2 to position 1 quasi-statically.

$$\Delta W_{21} = \int_2^1 dA = \int_2^1 (-SdT - pdV) \text{ with } dT = 0, \ dV > 0.$$

   $\Rightarrow \ \Delta W_{21} = A_1 - A_2 = -\Delta W_{12} < 0.$
   All the energy stored (in the form free energy) is converted back into work done by the system.

Irreversible cyclic process:

1. Push the piston in from position 1 to position 2 rapidly.
   The initial and final equilibrium states are the same as previously, but the process requires more work. The gas heats up, which produces a larger pressure than in the quasi-static process.
   $\Rightarrow \ \Delta W_{12} > A_2 - A_1 > 0.$
   Only part of the work done on the system is stored as free energy.

2. (a) Move the piston out from position 2 to position 1 quasi-statically.
   $\Rightarrow \ |\Delta W_{21}| = |A_1 - A_2| < |\Delta W_{12}|.$
   All the free energy is converted back into work but that amount is smaller than the work previously done on the system.
   (b) Move the piston out from position 2 to position 1 rapidly.
   $\Rightarrow \ |\Delta W_{21}| < |A_1 - A_2| < |\Delta W_{12}|.$
   Only part of the available free energy is converted back into work, where the full amount of free energy is only part of the work previously done on the system.

Useful relations between partial derivatives [tln6]

Consider state variables x, y, z, w. Only two of the variables are independent.

#1 $\qquad \left(\dfrac{\partial x}{\partial y}\right)_z = \left(\dfrac{\partial y}{\partial x}\right)_z^{-1}$

#2 $\qquad \left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial z}\right)_x \left(\dfrac{\partial z}{\partial x}\right)_y = -1$

#3 $\qquad \left(\dfrac{\partial x}{\partial w}\right)_z = \left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial w}\right)_z$

#4 $\qquad \left(\dfrac{\partial x}{\partial y}\right)_z = \left(\dfrac{\partial x}{\partial y}\right)_w + \left(\dfrac{\partial x}{\partial w}\right)_y \left(\dfrac{\partial w}{\partial y}\right)_z$

Proof:

Start with total differential of $x(y, z)$: $\quad dx = \left(\dfrac{\partial x}{\partial y}\right)_z dy + \left(\dfrac{\partial x}{\partial z}\right)_y dz$.

Substitute total differential of $y(x, z)$: $\quad dy = \left(\dfrac{\partial y}{\partial x}\right)_z dx + \left(\dfrac{\partial y}{\partial z}\right)_x dz$.

$\Rightarrow \left[\left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial x}\right)_z - 1\right] dx + \left[\left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial y}{\partial z}\right)_x + \left(\dfrac{\partial x}{\partial z}\right)_y\right] dz = 0$.

Expressions in brackets must vanish independently $\Rightarrow$ #1 and #2.

Introduce parameter w: $x(y, z)$ with $y = y(w)$ and $z = z(w)$.

$dx = \left(\dfrac{\partial x}{\partial y}\right)_z dy + \left(\dfrac{\partial x}{\partial z}\right)_y dz \;\Rightarrow\; \dfrac{dx}{dw} = \left(\dfrac{\partial x}{\partial y}\right)_z \dfrac{dy}{dw} + \left(\dfrac{\partial x}{\partial z}\right)_y \dfrac{dz}{dw}$.

Specify path: $z =$const i.e. $dz = 0$: $\quad \Rightarrow$ #3.

Introduce parameter y: $x(y, w)$ with $w = w(y)$ and $z = z(y)$.

$dx = \left(\dfrac{\partial x}{\partial y}\right)_w dy + \left(\dfrac{\partial x}{\partial w}\right)_y dw \;\Rightarrow\; \dfrac{dx}{dy} = \left(\dfrac{\partial x}{\partial y}\right)_w + \left(\dfrac{\partial x}{\partial w}\right)_y \dfrac{dw}{dy}$.

Specify path: $z =$const i.e. $dz = 0$: $\quad \Rightarrow$ #4.

Response functions

Second partial derivatives of thermodynamic potentials with respect to natural independent variables. Response functions describe how one thermodynamic function responds to a change of another thermodynamic function under controlled conditions. Response functions are important because of their experimental accessibility. Consider a system with $N = \text{const}$.

Thermal response functions (heat capacities): $C \equiv \dfrac{\delta Q}{\delta T}$

$$
\delta Q = T dS =
\begin{cases}
T \left(\dfrac{\partial S}{\partial T} \right)_X dT + T \left(\dfrac{\partial S}{\partial X} \right)_T dX & \text{for } S(T, X) \\[2ex]
T \left(\dfrac{\partial S}{\partial T} \right)_Y dT + T \left(\dfrac{\partial S}{\partial Y} \right)_T dY & \text{for } S(T, Y)
\end{cases}
$$

$$
\Rightarrow \ C_X = T \left(\frac{\partial S}{\partial T} \right)_X = -T \left(\frac{\partial^2 A}{\partial T^2} \right)_X, \quad
C_Y = T \left(\frac{\partial S}{\partial T} \right)_Y = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_Y
$$

where $X \equiv V, M$ and $Y \equiv -p, H$.

Equivalent expressions of C_X, C_Y are derived from $\delta Q = dU - Y\, dX$:

$$
\delta Q = \left(\frac{\partial U}{\partial T} \right)_X dT + \left[\left(\frac{\partial U}{\partial X} \right)_T - Y \right] dX \quad \text{for } U(T, X)
$$

$$
\Rightarrow \ C_X \equiv \left. \frac{\delta Q}{\delta T} \right|_X = \left(\frac{\partial U}{\partial T} \right)_X
$$

$$
\Rightarrow \ C_Y \equiv \left. \frac{\delta Q}{\delta T} \right|_Y = C_X + \left[\left(\frac{\partial U}{\partial X} \right)_T - Y \right] \left(\frac{\partial X}{\partial T} \right)_Y
$$

Also, from $\delta Q = dE + X\, dY$ we infer $C_Y = \left(\dfrac{\partial E}{\partial T} \right)_Y$

Note that $U(T, X)$ and $E(T, Y)$ are not thermodynamic potentials.

Mechanical response functions

Isothermal compressibility: $\quad \kappa_T \equiv -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_T = -\dfrac{1}{V}\left(\dfrac{\partial^2 G}{\partial p^2}\right)_T$

Adiabatic compressibility: $\quad \kappa_S \equiv -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_S = -\dfrac{1}{V}\left(\dfrac{\partial^2 E}{\partial p^2}\right)_S$

Thermal expansivity: $\quad \alpha_p \equiv \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_p$

Relations with thermal response functions C_p, C_V:

$$\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S}, \quad C_p = \frac{TV\alpha_p^2}{\kappa_T - \kappa_S}, \quad C_V = \frac{TV\alpha_p^2 \kappa_S}{\kappa_T(\kappa_T - \kappa_S)}$$

$$\Rightarrow \quad C_p - C_V = \frac{TV\alpha_p^2}{\kappa_T} > 0$$

Magnetic response functions

Isothermal susceptibility: $\quad \chi_T \equiv \left(\dfrac{\partial M}{\partial H}\right)_T = -\left(\dfrac{\partial^2 G}{\partial H^2}\right)_T = \left(\dfrac{\partial^2 A}{\partial M^2}\right)_T^{-1}$

Adiabatic susceptibility: $\quad \chi_S \equiv \left(\dfrac{\partial M}{\partial H}\right)_S = -\left(\dfrac{\partial^2 E}{\partial H^2}\right)_S$

"You name it": $\quad \alpha_H \equiv -\left(\dfrac{\partial M}{\partial T}\right)_H$

Relations with thermal response functions C_H, C_M:

$$\frac{C_H}{C_M} = \frac{\chi_T}{\chi_S}, \quad C_H = \frac{T\alpha_H^2}{\chi_T - \chi_S}, \quad C_M = \frac{T\alpha_H^2 \chi_S}{\chi_T(\chi_T - \chi_S)}$$

$$\Rightarrow \quad C_H - C_M = \frac{T\alpha_H^2}{\chi_T}$$

Isothermal and adiabatic processes

Fluid system:

Start from $TdS = dU + pdV$ with $U = U(T, V)$

$$TdS = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]dV \overset{(a)}{=} C_V dT + \frac{1}{\alpha_p V}(C_p - C_V)dV$$

Isotherm: $dT = 0 \;\Rightarrow\; TdS = \frac{1}{\alpha_p V}(C_p - C_V)dV \overset{(b)}{=} -\frac{\kappa_T}{\alpha_p}(C_p - C_V)dp$

Adiabate: $dS = 0 \;\Rightarrow\; dT = -\frac{1}{\alpha_p V}\frac{C_p - C_V}{C_V}dV \overset{(c)}{=} \frac{\kappa_S}{\alpha_p}\frac{C_p - C_V}{C_V}dp$

(a) Use $C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p, \quad \left(\frac{\partial V}{\partial T}\right)_p = V\alpha_p$

(b) Use $dV = \left(\frac{\partial V}{\partial p}\right)_T dp = -V\kappa_T dp$

(c) Use $dV = -V\kappa_S dp$

Magnetic system:

Start from $TdS = dU - HdM$ with $U = U(T, M)$.

$$TdS = \left(\frac{\partial U}{\partial T}\right)_M dT + \left[\left(\frac{\partial U}{\partial M}\right)_T - H\right]dM = C_M dT - \frac{1}{\alpha_H}(C_H - C_M)dM$$

Isotherm: $dT = 0 \;\Rightarrow\; TdS = -\frac{1}{\alpha_H}(C_H - C_M)dM = -\frac{\chi_T}{\alpha_H}(C_H - C_M)dH$

Adiabate: $dS = 0 \;\Rightarrow\; dT = \frac{1}{\alpha_H}\frac{C_H - C_M}{C_M}dM = \frac{\chi_S}{\alpha_H}\frac{C_H - C_M}{C_M}dH$

Conditions for thermal equilibrium [tln19]

Consider a fluid system in a rigid and isolated container that is divided into two compartments A and B by a fictitious partition.

Conserved extensive quantities:
$$U = U_A + U_B = \text{const}, \quad V = V_A + V_B = \text{const}, \quad N = N_A + N_B = \text{const}.$$

Fluctuations in internal energy: $\Delta U_A = -\Delta U_B$
Fluctuations in volume: $\Delta V_A = -\Delta V_B$
Fluctuations in number of particles: $\Delta N_A = -\Delta N_B$

Entropy: $S(U, V, N), \quad dS = \dfrac{1}{T} \, dU + \dfrac{p}{T} \, dV - \dfrac{\mu}{T} \, dN$

$$
\begin{aligned}
\Delta S \;&=\; \sum_{\alpha = A, B} \left[\left(\frac{\partial S_\alpha}{\partial U_\alpha} \right)_{V_\alpha N_\alpha} \Delta U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha} \right)_{U_\alpha N_\alpha} \Delta V_\alpha + \left(\frac{\partial S_\alpha}{\partial N_\alpha} \right)_{U_\alpha V_\alpha} \Delta N_\alpha \right] \\
&=\; \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \Delta U_A + \left(\frac{p_A}{T_A} - \frac{p_B}{T_B} \right) \Delta V_A + \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B} \right) \Delta N_A
\end{aligned}
$$

At thermal equilibrium, the entropy is a maximum. Hence the entropy change due to fluctuations in U, V, N must vanish.

$\Rightarrow \; T_A = T_B, \quad p_A = p_B, \quad \mu_A = \mu_B$

If the fictitious wall is replaced by a real, mobile, conducting wall, then particle fluctuations in the two compartments are suppressed: $\Delta N_A = 0$. In this case, $\mu_A \neq \mu_B$ is possible at equilibrium.

If the mobile, conducting wall is replaced by a rigid, conducting wall, then volume fluctuations in the two compartments are also suppressed: $\Delta V_A = 0$. In this case, also $p_A \neq p_B$ is possible at equilibrium.

If the conducting wall is replaced by an insulating wall, then energy fluctuations in the two compartments are also suppressed: $\Delta U_A = 0$. In this case, also $T_A \neq T_B$ is possible at equilibrium.

Stability of thermal equilibrium [tln20]

Consider a fluid system with $N = \text{const}$ in thermal equilibrium at temperature T_0 and pressure p_0. Any deviation from that state must cause an increase in Gibbs free energy:

$$G(T_0, p_0) = U(S, V) - T_0 S + p_0 V.$$

Effects of fluctuations in entropy and volume:

$$
\begin{aligned}
\delta G \;=\; & \left[\left(\frac{\partial U}{\partial S} \right)_V - T_0 \right] \delta S + \left[\left(\frac{\partial U}{\partial V} \right)_S + p_0 \right] \delta V \\
& + \frac{1}{2} \left[\left(\frac{\partial^2 U}{\partial S^2} \right) (\delta S)^2 + 2 \left(\frac{\partial^2 U}{\partial S \delta V} \right) \delta S \delta V + \left(\frac{\partial^2 U}{\partial V^2} \right) (\delta V)^2 \right]
\end{aligned}
$$

Equilibrium condition: $\left(\dfrac{\partial U}{\partial S} \right)_V - T_0 = 0, \quad \left(\dfrac{\partial U}{\partial V} \right)_S + p_0 = 0$

Stability condition: $\left(\dfrac{\partial^2 U}{\partial S^2} \right) (\delta S)^2 + 2 \left(\dfrac{\partial^2 U}{\partial S \delta V} \right) \delta S \delta V + \left(\dfrac{\partial^2 U}{\partial V^2} \right) (\delta V)^2 > 0.$

Condition for positive definite quadratic form:

$$\frac{\partial^2 U}{\partial S^2} > 0, \quad \frac{\partial^2 U}{\partial V^2} > 0, \quad \frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \delta V} \right)^2 > 0.$$

Implications:

$$\left(\frac{\partial^2 U}{\partial S^2} \right)_V = \left(\frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V} > 0 \;\Rightarrow\; C_V > 0.$$

$$\left(\frac{\partial^2 U}{\partial V^2} \right)_S = - \left(\frac{\partial p}{\partial V} \right)_S = \frac{1}{V \kappa_S} > 0 \;\Rightarrow\; \kappa_S > 0.$$

$$\left(\frac{\partial^2 U}{\partial S^2} \right)_V \left(\frac{\partial^2 U}{\partial V^2} \right)_S > \left(\frac{\partial^2 U}{\partial S \delta V} \right)^2 \;\Rightarrow\; \frac{T}{V \kappa_S C_V} > \left(\frac{\partial T}{\partial V} \right)_S^2$$

Jacobi transformations [tln21]

Change of independent variables in a state function. Unlike in a Legendre transform, the state variable in question remains the same.

Task: Calculate $C_p = T\left(\dfrac{\partial S}{\partial T}\right)_p$ from entropy function $S(U,V)$.

Use $\left(\dfrac{\partial S}{\partial U}\right)_V = \dfrac{1}{T}$, $\left(\dfrac{\partial S}{\partial V}\right)_U = \dfrac{p}{T}$ and solve for $T(V,U), p(V,U)$.

Solving $T(V,U), p(V,U)$ for $V(T,p), U(T,p)$ to obtain $S(T,p)$ amounts to the simultaneous solution of two *nonlinear* equations for two variables.

Solving

$$dT = \left(\frac{\partial T}{\partial V}\right)_U dV + \left(\frac{\partial T}{\partial U}\right)_V dU$$

$$dp = \left(\frac{\partial p}{\partial V}\right)_U dV + \left(\frac{\partial p}{\partial U}\right)_V dU$$

for

$$dV = \frac{1}{J(V,U)}\left[\left(\frac{\partial p}{\partial U}\right)_V dT - \left(\frac{\partial T}{\partial U}\right)_V dp\right] \equiv \frac{J_1(V,U)}{J(V,U)}$$

$$dU = \frac{1}{J(V,U)}\left[-\left(\frac{\partial p}{\partial V}\right)_U dT + \left(\frac{\partial T}{\partial V}\right)_U dp\right] \equiv \frac{J_2(V,U)}{J(V,U)}$$

with Jacobian determinants

$$J(V,U) = \begin{vmatrix} \left(\dfrac{\partial T}{\partial V}\right)_U & \left(\dfrac{\partial T}{\partial U}\right)_V \\ \left(\dfrac{\partial p}{\partial V}\right)_U & \left(\dfrac{\partial p}{\partial U}\right)_V \end{vmatrix},$$

$$J_1(V,U) = \begin{vmatrix} dT & \left(\dfrac{\partial T}{\partial U}\right)_V \\ dp & \left(\dfrac{\partial p}{\partial U}\right)_V \end{vmatrix}, \quad J_2(V,U) = \begin{vmatrix} \left(\dfrac{\partial T}{\partial V}\right)_U & dT \\ \left(\dfrac{\partial p}{\partial V}\right)_U & dp \end{vmatrix},$$

amounts to the solution of two *linear* equations for two variables.

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

$$= \frac{1}{TJ}\left[-\left(\frac{\partial p}{\partial V}\right)_U + p\left(\frac{\partial p}{\partial U}\right)_V\right]dT + \frac{1}{TJ}\left[-p\left(\frac{\partial T}{\partial U}\right)_V + \left(\frac{\partial T}{\partial V}\right)_U\right]dp$$

$$\Rightarrow C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{J}\left[p\left(\frac{\partial p}{\partial U}\right)_V - \left(\frac{\partial p}{\partial V}\right)_U\right]$$