Equilibrium Thermodynamics IV: Applications [tsc4]

In this module we investigate a variety thermodynamic processes on the basis of empirical information such encoded in (caloric and thermodynamic equations of state and response functions.

We leave aside (for later modules) processes that involve phase transitions and coexisting phases.

Classical ideal gas:

A gas sufficiently dilute that particle interaction energies are negligible.

Thermodynamic equation of state: $pV = nRT$.

- $n = N/N_A$ (number of moles),
- $N_A = 6.022 \times 10^{23}$ (Avogadro's number),
- $R = 8.314 \mathrm{J\,mol^{-1}K^{-1}}$ (gas constant).
- Particle interactions are neglected, which is accurate for dilute gases.

Caloric equation of state: $C_V = \alpha n R = \text{const.}$

- monatomic gas: $\alpha = \frac{3}{2}$.
- diatomic gas: $\alpha = \frac{5}{2}$.
- polyatomic gas: $\alpha = 3$.
- The nonvanishing C_V for $T \to 0$ is inconsistent with the third law. Quantum statistics provide the remedy (to be discussed later).

Applications of classical ideal gas:

- Internal energy $U(T, V)$, entropy $S(T, V)$, and mechanical response functions α_p, κ_T, κ_S [tex14].
- Thermodynamic potentials $U(S, V)$, $E(S, p)$, $A(T, V)$, $G(T, p)$ [tex15].
- Chemical potential $\mu(T, p)$ [tex17].
- Polytropic processes [tex138].
- Heat capacity by design [tex35]
- Modifying equations of state requires caution [tex11]

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Van der Waals gas:

Atoms of gases interact via short-range forces.

The van-der Waals equation of state,

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT,$$

takes particle interactions into account summarily in the form of two corrections to the ideal-gas equation of state.

Each correction is controlled by an empirical parameter:

- ▷ $V \rightarrow V - nb$:
  The excluded volume correction accounts for the repulsive core of the interaction at short distances.
- ▷ $p \rightarrow p + \frac{an^2}{V^2}$:
  The pressure correction accounts for the attractive tail of the interaction at longer distances.
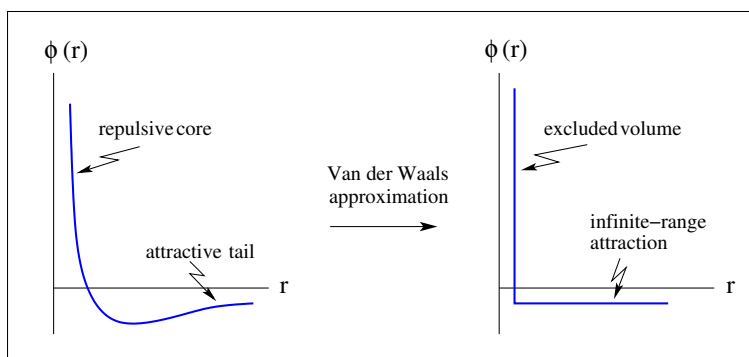
The short-range repulsion between the particles is replaced by a steric interaction and long-range attraction by a force of infinite range.

The caloric equation of state of the classical ideal gas is often used for the van der Waals gas. Modifications within certain constraints are permitted.

Applications:

- – Internal energy and entropy of van der Waals gas [tex38]
- – Heat capacities of the van der Waals gas [tex27]

Cooling a gas by free expansion (Joule effect):

It is useful to look ahead to kinetic theory for a better understanding.

> During expansion, a gas does work against attractive particle interactions. The average potential energy increases, which forces a decrease of the average kinetic energy. The consequence is a drop in temperature.

From here on the reasoning is purely thermodynamic.

Consider a process of free expansion of a gas in a container with two compartments and insulating walls.
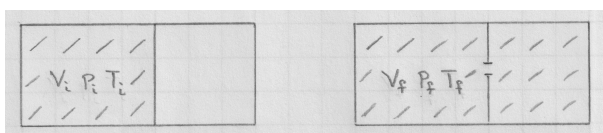
- initial state: V_i, p_i, T_i;
- final state: V_f, p_f, T_f with $V_f > V_i$ and $p_f < p_i$.

Free expansion means no heat transfer and no work performance, which implies that the internal energy is conserved:

$$dQ = 0, \quad dW = 0 \quad \Rightarrow \quad dU = 0.$$

Free expansion is an irreversible process even if it proceeds quasi-statically.[1] The Joule process is associated with an entropy increase:

$$dU = TdS - pdV = 0 \quad \Rightarrow \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T} > 0.$$

The temperature change in the gas expanding under constant internal energy is encoded in the Joule coefficient.

Use $\left(\frac{\partial U}{\partial T}\right)_V = C_V, \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p$

Joule coefficient: $\left(\frac{\partial T}{\partial V}\right)_U = -\frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V} = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right].$

No cooling effect is expected when a classical ideal gas is freely expanded:

$$p = \frac{nRT}{V} \quad \Rightarrow \quad p - T\left(\frac{\partial p}{\partial T}\right)_V = 0.$$

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[1]Quasi-static free expansion is a series of consecutive free expansions, each associated with infinitesimal volume increase (no moving walls).

Cooling a gas by throttling (Joule-Thomson effect):

Here the gas is forced through a porous wall between two chambers. During the process the (unequal) pressures are kept constant in both chambers. In the following we consider quasi-static throttling.
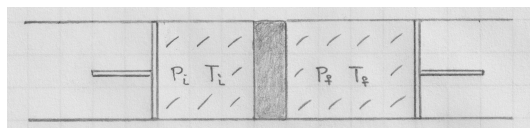
  – initial state: V_i, p_i, T_i;
  – final state: V_f, p_f, T_f with $V_f > V_i$ and $p_f < p_i$.

Throttling involves no heat transfer (walls and pistons are insulating). The moving pistons involve work performance:

$$dQ = 0 \quad \Rightarrow \quad dW = dU.$$

Quasi-static throttling (Joule-Thomson process) conserves the enthalpy.

$$\Delta U = \Delta W = -\int_0^{V_f} p_f dV - \int_{V_i}^0 p_i dV = -p_f V_f + p_i V_i$$

$$\Rightarrow \quad \underbrace{U_i + p_i V_i}_{E_i} = \underbrace{U_f + p_f V_f}_{E_f} \quad \Rightarrow \quad E = \text{const.}$$

The entropy increases, $dS > 0$, when the pressure drops, $dp < 0$:

$$dE = T dS + V dp = 0 \quad \Rightarrow \quad \left(\frac{\partial S}{\partial p}\right)_E = -\frac{V}{T} < 0.$$

The temperature change in the gas as it expands under constant enthalpy is encoded in the Joule-Thomson coefficient:

Use $\left(\dfrac{\partial E}{\partial T}\right)_p = C_p,$ $\left(\dfrac{\partial E}{\partial p}\right)_T = T\left(\dfrac{\partial S}{\partial p}\right)_T + V = -T\left(\dfrac{\partial V}{\partial T}\right)_p + V.$

Joule-Thomson coefficient: $\left(\dfrac{\partial T}{\partial p}\right)_E = -\dfrac{(\partial E/\partial p)_T}{(\partial E/\partial T)_p} = \dfrac{1}{C_p}\left[T\left(\dfrac{\partial V}{\partial T}\right)_p - V\right].$

No cooling effect is expected when a classical ideal gas is being throttled:

$$V = \frac{nRT}{p} \quad \Rightarrow \quad T\left(\frac{\partial V}{\partial T}\right)_V - V = 0.$$

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Applications of van der Waals gas:

- Internal energy $U(T, V)$ and entropy $S(T, V)$ [tex38].
- Heat capacities [tex27].
- Joule coefficient [tex31].
- Joule-Thomson coefficient [tex32].

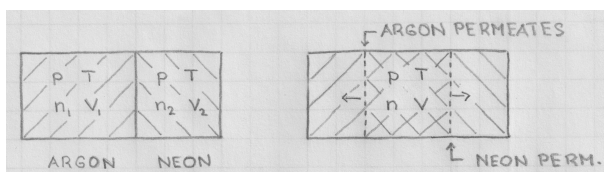**Entropy of mixing in classical ideal gases:**

Consider two dilute gases in a rigid conducting box, separated by a mobile conducting wall:

$$n_1 + n_2 = n, \quad V_1 + V_2 = V, \quad p_1 = p_2 = p, \quad T_1 = T_2 = T.$$

Equilibrium condition: $p_1 = p_2 \quad \Rightarrow \quad \dfrac{n_1 RT}{V_1} = \dfrac{n_2 RT}{V_2} \quad \dfrac{n_1}{V_1} = \dfrac{n_2}{V_2}.$

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

To calculate ΔS, consider a reversible mixing process involving an isothermal and quasi-static movement of semipermeable walls.

For classical ideal gases, $T = $ const means $U = $ const.

Wall exerts partial pressure $p_i = \dfrac{n_i RT}{V_i}$ on non-permeating gas.

$$dU_i = TdS_i - p_i dV_i = 0 \quad \Rightarrow \quad dS_i = \frac{p_i}{T} dV_i = \frac{n_i R}{V_i} dV_i.$$

Entropy of mixing: $\quad \Delta S = R \sum_{i=1,2} n_i \int_{V_i}^{V} \frac{dV_i'}{V_i'} = R \sum_{i=1,2} n_i \ln \left(\frac{V}{V_i} \right) > 0.$

No entropy increase should result if the two gases are of the same kind. The paradox (noted by Gibbs) is resolved by quantum mechanics, which requires that distinguishable and indistinguishable particles are counted differently.

Ideal paramagnet:

Models for ideal paramagnets are employed, for the most part, to describe the thermodynamics of a fixed quantity of solid paramagnetic material.

Differential of internal energy: $dU = TdS + HdM$ (for $N = \text{const}$).

The thermodynamics of ideal paramagnets typically uses equations of state from the following selections:

▷ Caloric equations of state:
  − $C_M \equiv 0$,
  − $C_M = \text{const} > 0$.

▷ Thermodynamic equations of state (in scaled units):
  − $M = H/T$,
  − $M = \tanh(H/T)$,
  − $M = f(H/T)$ with $f(0) = 0$,
  − $M = \chi_T(T)H$ with $\lim\limits_{T \to 0} \dfrac{d\chi_T}{dT} = 0$.

Applications: [tex19], [tex20], [tex21], [tex36].

Adiabatic demagnetization:

Pathways to very low temperatures in physics experiments use processes involving adiabatic demagnetization.

The key feature is that the entropy of a paramagnet is readily controllable with an external magnetic field.

Consider a paramagnetic salt in a weak magnetic field H. The thermodynamic equation of state is of the form,

$$M(T, H) = \chi_T(T)H,$$

where the isothermal susceptibility $\chi_T(T)$ satisfies the conditions,

$$\chi_T > 0, \quad \frac{d}{dT}\chi_T < 0.$$

Helmholtz free energy:

$$dA = -SdT + HdM = -SdT + \frac{MdM}{\chi_T} \quad \Rightarrow \quad A(T, M) = A(T, 0) + \frac{M^2}{2\chi_T}.$$

Entropy: $S(T, M) = -\left(\dfrac{\partial A}{\partial T}\right)_M = S(T, 0) - \dfrac{1}{2}M^2\left[\dfrac{d}{dT}\chi_T^{-1}\right]$

$\Rightarrow\ S(T, H) = S(T, 0) - \dfrac{1}{2}H^2\chi_T^2\left[\dfrac{d}{dT}\chi_T^{-1}\right] = S(T, 0) + \dfrac{1}{2}H^2\dfrac{d\chi_T}{dT}.$

Third-law condition: $\lim\limits_{T\to 0} S(T, H) = 0$ independent of H.

Consequence for susceptibility: $\lim\limits_{T\to 0}\dfrac{d\chi_T}{dT} = 0.$

Graphs of $S(T, H)$ for iron ammonium alum are shown in [tsl2].

Cooling processes that employ paramagnets involve the following two steps:
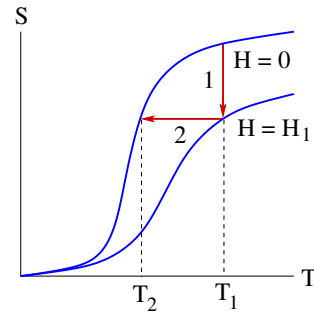
1. Isothermal magnetization:

   $\Delta S = \dfrac{1}{2}\dfrac{d\chi_T}{dT}H_1^2 < 0.$

   Heat expelled from system: $\Delta Q = T_1\Delta S.$

2. Adiabatic demagnetization:

   $\Delta S = 0\ \Rightarrow\ S(T_1, H_1) = S(T_2, 0).$

   $\Rightarrow\ S(T_2, 0) = S(T_1, 0) + \dfrac{1}{2}H_1^2\dfrac{d\chi_T}{dT}\bigg|_{T_1}\ \Rightarrow\ T_2 < T_1.$

Consider the entropy landscapes for iron ammonium alum shown in [tsl2].

– The alternating sequence of steps 1 and 2 approaches absolute zero. As $T \to 0$, adiabates and isotherms become increasingly parallel, implying a diminishing efficiency of the cooling process.

– The sequence of steps requires that heat reservoirs are present at various temperatures. They can be established by employing a Carnot engine run in reverse.

Ideal paramagnetic gas:

This is a system capable of two kinds of work performance dW:

  – mechanical work $-pdV$,
  – magnetic work $+HdM$.

Specifications for the simplest model:

  – two thermodynamic equations of state: $pV = nRT, \quad M = \dfrac{H}{T},$

  – one caloric equation of state: $C_{VM} \doteq T \left(\dfrac{\partial S}{\partial T} \right)_{VM} = \dfrac{3}{2} R.$

Differential of internal energy: $dU = TdS - pdV + HdM \quad$ (for $N = \text{const.}$)

The energy content can be changed by a combination of heat transfer, mechanical work, and magnetic work.

This system facilitates nontrivial processes that are both isothermal $(dU = 0)$ and adiabatic $(dS = 0)$.

The naming of thermodynamic potentials becomes ambiguous. Important is the set of natural independent variables for each type of free energy and the switch between them via Legendre transform.

Applications: [tex22], [tex133].

Photon gas:

Particles of light are unlike particles of a classical ideal gas. They travel fast under all circumstances, do not interact with each other even at high density, and interact differently with container walls.

Black body radiation is the name for a photon gas in thermal equilibrium with opaque container walls kept at a fixed temperature.

Empirical evidence suggests a pair of equations of state in the form,

$$U(T, V) = Ve(T), \quad p = \frac{1}{3}e(T).$$

The functional form of the energy density $e(T)$ can be determined from thermodynamic relations alone.

Applications: [tex23], [tex24].

Rubber band elasticity:

Consider a rubber band of contour length L_0 under tension J either insulated from or in contact with a heat bath (typically a surrounding fluid).

Differential of internal energy: $dU = TdS + JdL$.

Equations of state: $J = f(L, T), \quad U = g(L, T)$.

Experimentally accessible response functions:

- heat capacity: $C_J = T \left(\dfrac{\partial S}{\partial T} \right)_J$,

- tensile compliance: $\kappa_T = \dfrac{1}{L_0} \left(\dfrac{\partial L}{\partial J} \right)_T$,

- thermal expansivity: $\alpha_J = \dfrac{1}{L_0} \left(\dfrac{\partial L}{\partial T} \right)_J$.

Applications: [tex39], [tex40].

Inhomogeneous systems:

Thermodynamic systems at equilibrium may have profiles in pressure, density, chemical potential, and other intensive variables, but not temperature.

Any temperature gradients cause heat flows that diminish them until the temperature is uniform. The time scale of such heat flows may be long compared to certain phenomena of interest.

It is common practice to investigate systems with temperature inhomogeneities in the context of equilibrium thermodynamics, e.g. sound waves or layers of adiabatic atmosphere.

The most familiar inhomogeneities are caused by the Earth's gravitational field on the pressure in layers of liquid (e.g. lakes) and gas (e.g. atmosphere). Electrolytes (ionic fluids) develop profiles in ion concentrations caused by electric fields, turning chemical potentials into functions of position. Such situations are ubiquitous in biological physics, for example.

Applications:

- Atmospheres [tex132], [tex150], [tex151], [tex152].
- Sound waves [tex18], [tex99]