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04. Equilibrium Thermodynamics IV: Applications

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Abstract

Part four 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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[tex14] Entropy and internal energy of the classical ideal gas

The classical ideal gas for a fixed number N of particles is specified by the equation of state $pV = Nk_BT$ and the constant heat capacity $C_V = \alpha Nk_B$ [$\alpha = \frac{3}{2}$ (monatomic), $\alpha = \frac{5}{2}$ (diatomic), $\alpha = 3$ (polyatomic)].
(a) Use this information to calculate the internal energy $U(T,V)$ and show that the result is, in fact, independent of V. Use the same information to calculate the entropy $S(T,V)$. Introduce reference values T_0, V_0, U_0, S_0 for the integrations.
(b) Determine the mechanical response functions α_p (thermal expansivity), κ_T (isothermal compressibility), and κ_S (adiabatic compressibility).

Solution:

[tex15] Thermodynamic potentials of the classical ideal gas

The classical ideal gas for a fixed number N of particles is specified by the equation of state $pV = Nk_BT$ and the constant heat capacity $C_V = \alpha N k_B$ [$\alpha = \frac{3}{2}$ (monatomic), $\alpha = \frac{5}{2}$ (diatomic), $\alpha = 3$ (polyatomic)]. From the functions $U(T)$ and $S(T,V)$ determined in [tex14] calculate the thermodynamic potentials $U(S,V)$ (internal energy), $E(S,p)$ (enthalpy), $A(T,V)$ (Helmholtz potential) and $G(T,p)$ (Gibbs potential). Use the reference values T_0, V_0, U_0, S_0 from [tex14].

Solution:

[tex17] Chemical potential of the classical ideal gas

Calculate the chemical potential $\mu(T,p)$ of the classical ideal gas by integrating the Gibbs-Duhem equation, $SdT - Vdp + Nd\mu = 0$, with $V(T,p)$ from the equation of state and $S(T,p)$ from [tex14]. Compare the result with the Gibbs free energy per particle, $G/N = \mu$, calculated in [tex15].

Solution:

[tex35] Ideal gas heat capacity by design

Consider 1mol of a classical ideal gas $[pV = RT, C_V = \frac{3}{2}R]$.
(a) If C_X is the heat capacity of a reversible process in which the thermodynamic variable X is kept constant, show that this process is described by a curve $pV^f = \text{const}$ in the (p, V)-plane with $f = (C_p - C_X)/(C_X - C_V)$.
(b) Discuss the result for three special cases: $X = p,\ X = V,\ X = S$.

Solution:

[tex18] Sound velocity in the classical ideal gas I

In a sound wave the classical ideal gas [$pV = nRT$, $C_V = \alpha nR =$ const, molar mass M] is *adiabatically* compressed and expanded.
(a) Show that the sound velocity is related to the adiabatic compressibility κ_S and the mass density ρ as follows:

$$c^2 = \frac{1}{\rho\kappa_S} = \left(\frac{\partial p}{\partial \rho}\right)_S .$$

(b) Use thermodynamic properties of the classical ideal gas to infer from this expression the result $c^2 = \gamma RT/M$, where $\gamma = 1 + 1/\alpha$.

Solution:

[tex99] Sound velocity in the classical ideal gas II

Show that the internal energy per unit mass and the enthalpy per unit mass of a classical ideal gas with heat capacity $C_V = \text{const}$ can be expressed as follows in terms of the sound velocity $c = \sqrt{(\partial p/\partial \rho)_S}$ and the ratio of heat capacities $\gamma = C_p/C_V$:

$$\bar{U} = \bar{U}_0 + \frac{c^2}{\gamma(\gamma-1)}, \quad \bar{E} = \bar{U}_0 + \frac{c^2}{\gamma-1},$$

where $\bar{U}_0$ is a constant.

Solution:

[tex134] Absolute temperature from measurements

Consider a compressible fluid in an insulating cylinder with a movable piston, a calibrated heat source, a pressure gauge, and a thermometer with arbitrary temperature scale θ. The experiment consists of measurements over a range of θ of the following quantities:

- rate $A(\theta) = (\delta V/\delta\theta)_p$ at which volume increases during isobaric heating up,
- rate $B(\theta) = (\delta Q/\delta p)_\theta$ at which heat is supplied during isothermal decompression.

Show that from the data of these two experiments we can infer the following differential relation between the thermometer reading θ and the absolute temperature T:

$$\frac{d\ln T}{d\theta} = -\frac{A(\theta)}{B(\theta)}.$$

The (undetermined) integration constant of $\ln T(\theta)$ can be used to fix the scale of the absolute temperature (e.g. by using the triple point of H_2O).

Solution:

[tex138] Polytropic process of classical ideal gas

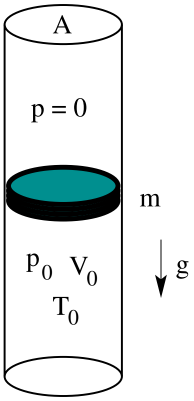
Consider an ideal monatomic gas $[pV = Nk_BT, C_V = \frac{3}{2}Nk_B]$ confined to a cylinder by a movable piston. The gas is compressed from volume V_1 to volume $V_2 < V_1$ under circumstances such that the relation $pV^x = a$ with $a = \text{const}$ is satisfied. In this polytropic process, determine the quantities ΔW (work done on the system), ΔU (change in internal energy), and ΔQ (heat added to the system) as functions of V_1 and V_2. Determine for which values of x $(0 < x < 2)$ each of these quantities is positive or negative.

Solution:

[tex141] Heavy piston

A cylinder of cross section A with insulating walls has two compartments separated by a disk of mass m. The axis of the cylinder is vertical. A uniform gravitational field g is present. The disk is initially held at a fixed position by an external agent. The upper compartment is evacuated and the lower compartment contains 1 mol of a monatomic, classical, ideal gas [$pV = RT$, $C_V = \frac{3}{2}R$] at temperature T_0, volume V_0, and pressure p_0. When the disk is released, it moves without (wall) friction and comes to rest at a lower position. Calculate the final values p_1, V_1, T_1 of pressure, volume, and temperature, respectively. The disk does not exchange heat. The only significant action of the gravitational field is on the disk.

Hint: Use energy conservation and Newton's third law. Assume thermal equilibrium for the inital and final states.



Solution:

[tex150] Isothermal atmosphere

Consider a column of air [molar mass $M = 29\text{g}$] treated as a classical ideal gas [$pV = nRT$] in a uniform gravitational field $g = 9.81\text{m/s}^2$. The column is assumed to be in thermal equilibrium.
(a) Calculate the dependence of pressure p on height z and (unifom) temperature T, assuming that the pressure is p_0 at $z = 0$.
(b) At what height z_1 (in meters) has the pressure fallen to half of p_0 and at what height z_2 to one percent of p_0 if the temperature is 20°C everywhere?
Hint: Start from the relation, $dp(z) = -\rho(z)d\mathcal{U}(z)$, between pressure p, mass density ρ, and gravitational potential $\mathcal{U}$ at height z. This relation expresses the increment of pressure caused by the weight of a thin layer of air. The ideal-gas equation of state is assumed to hold locally at all heights.

Solution:

[tex151] Adiabatic atmosphere

Consider a column of air [molar mass $M = 29\text{g}$] treated as a classical ideal gas [$pV = nRT$, $C_p/C_V = \gamma = 1.41$] in a uniform gravitational field $g = 9.81\text{m/s}^2$. The column is assumed to be in mechanical equilibrium but not (yet) in thermal equilibrium. The mechanical equilibrium is established by gravitational pressure and governed by the adiabatic relation pV^γ =const.
(a) Calculate the dependence on height z of the pressure p, the mass density ρ, and the temperature T, assuming that $p = p_0$ and $T = T_0$ at $z = 0$.
(b) Find the height z_m, expressed as a function of T_0, at which T, p, and ρ all reach zero. What is that height (in meters) if T_0 is room temperature?
Hints: (i) Infer from pV^γ =const the differential relation $dT/T = [(\gamma - 1)/\gamma]dp/p$. (ii) Use the relation $dp(z) = -\rho(z)d\mathcal{U}(z)$ from [tex150] linking pressure, mass density, and gravitational potential to infer differential equations for $T(z)$ and $p(z)$.

Solution:

[tex152] Homogeneous atmosphere

Meteorological modeling uses the concept of homogeneous atmosphere with constant density over some vertical distance. Consider a column of air [molar mass $M = 29\text{g}$] treated as a classical ideal gas [$pV = nRT$] in a uniform gravitational field $g = 9.81\text{m/s}^2$. The column is assumed to have constant mass density $\rho(z) = \rho_0 = \text{const}$.
(a) Calculate the dependence on height z of the pressure p and the temperature T, assuming that $p = p_0$ and $T = T_0$ at $z = 0$.
(b) Find the height z_h, expressed as a function of T_0, at which T and p both reach zero.
(c) What must be the temperature (in °C) at sea level so that the homogeneous atmosphere just reaches the tip of Mount Everest?
Hints can be gleaned from [tex150] and [tex151].

Solution:

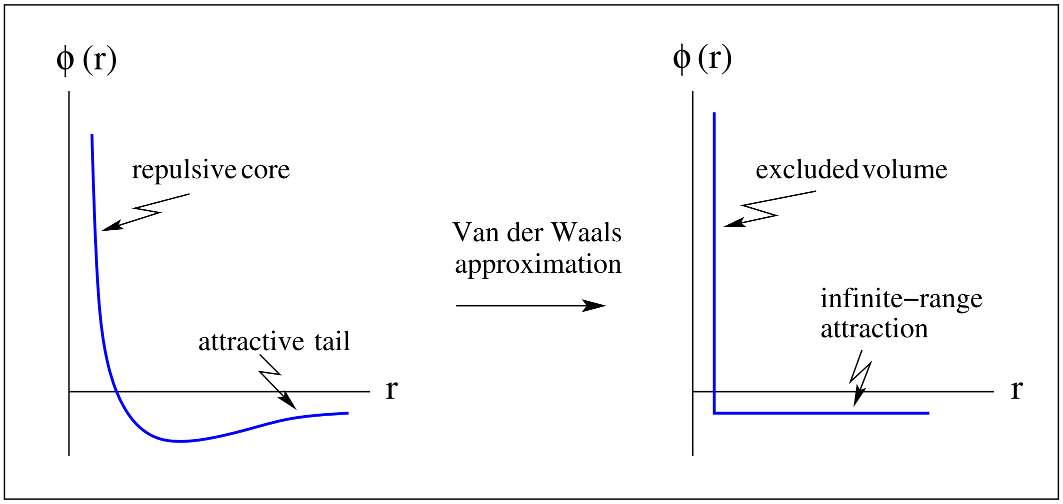
Van der Waals equation of state [tln22]

Atoms of gases interact via short-range force. The ideal gas equation of state, $pV = nRT$, neglects the interaction completely. The van-der Waals equation of state takes it into account summarily:

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

where a, b are empirical parameters.

- nb: excluded volume due to the repulsive core of the interaction at short distances,
- $-an^2/V^2$: pressure correction due to the attractive tail of the interaction at long distances.



Cooling of gases [tln23]

During expansion, a gas does work against attractive intermolecular forces. In the process, the average potential energy increases and, by virtue of energy conservation, the average kinetic energy decreases. The result is a drop in temperature. We discuss two processes to illustrate this effect.

Joule effect: free expansion

Free expansion involves no heat transfer and no work performance:
$\Delta Q = 0,\ \Delta U = 0,.$

Initial state: V_i, p_i, T_i; final state: V_f, p_f, T_f with $p_f < p_i$.

The temperature change in the expanding gas is calculated for a quasi-static process between the same equilibrium states.

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

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

Ideal gas: $T\left(\frac{\partial p}{\partial T}\right)_V = p \ \Rightarrow$ no effect.

Joule-Thomson effect: throttling

The gas is forced through a porous wall between two chambers. During the process the pressure is 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 $p_f < p_i$.

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

$$\Rightarrow\ U_i + p_i V_i = U_f + p_f V_f = \text{const.} \ \Rightarrow\ E = \text{const.} \ \Rightarrow\ dE = TdS + Vdp = 0.$$

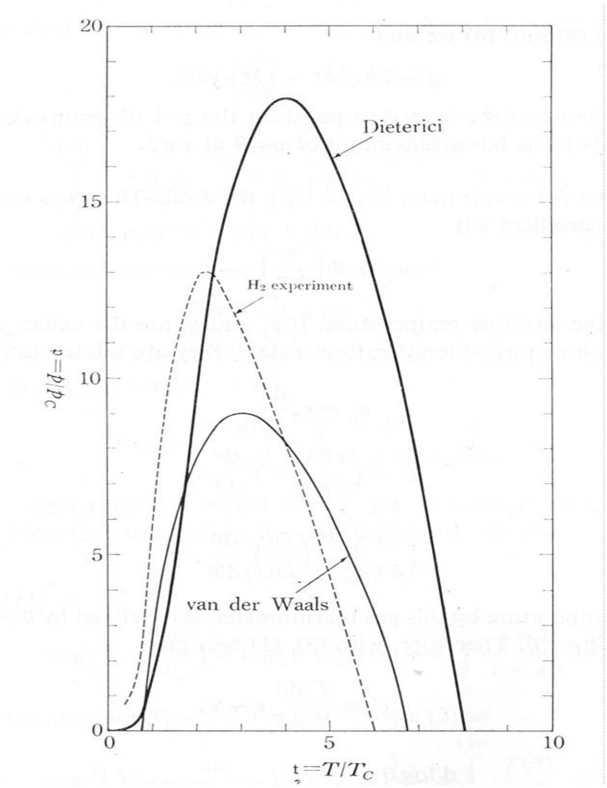
Use $\left(\frac{\partial E}{\partial T}\right)_p = C_p,\ \left(\frac{\partial E}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = -T\left(\frac{\partial V}{\partial T}\right)_p + V.$

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

Ideal gas: $T\left(\frac{\partial V}{\partial T}\right)_V = V \ \Rightarrow$ no effect.

Joule–Thomson inversion curves [tsl1]

- Hydrogen gas: experimental data.
- Van der Waals gas: $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$.
- Dieterici gas: $p = \frac{nRT}{V - nb}\exp\left(-\frac{an}{RTV}\right)$.



[from Kubo: Thermodynamics]

[tex27] Heat capacities of the van der Waals gas

Consider the van der Waals equation of state for $n = 1\text{mol}$ of a gas:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT.$$

(a) Show that the heat capacity C_V may depend on T but is independent of V.
(b) Calculate the quantity $C_p - C_V$ as a function of p and V. Verify that $C_p - C_V \to R$ in the ideal gas limit.

Solution:

[tex38] Internal energy and entropy of van der Waals gas

Calculate the internal energy $U(T,V)$ and the entropy $S(T,V)$ of the van der Waals gas, specified by the equation of state

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_BT$$

and the specific heat $C_V = \alpha N k_B$.

Solution:

[tex31] Joule coefficient of van der Waals gas

The cooling of a gas via free expansion is described by the Joule coefficient

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right].$$

(i) Determine the Joule coefficient for 1 mol of the ideal gas $[pV = RT, C_V = \alpha R]$ and for 1mol of the van der Waals gas $[(p + a/V^2)(V - b) = RT, C_V = \alpha R]$.
(ii) Calculate the temperature change $T_f - T_i$ when the van der Waals gas is freely expanded from V_i to $V_f > V_i$.

Solution:

[tex32] Joule–Thomson coefficient of van der Waals gas

The cooling of a gas via throttling is described by the Joule-Thomson coefficient

$$\left(\frac{\partial T}{\partial p}\right)_E = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right].$$

(i) Determine the Joule-Thomson coefficient for 1 mol of the van der Waals gas $[(p+a/V^2)(V-b) = RT, C_V = \alpha R]$.
(ii) Throttling results in cooling only if $(\partial T/\partial p)_E > 0$. In the (T,p)-plane, this region is bounded by the inversion curve, which is determined by the condition $(\partial T/\partial p)_E = 0$. Calculate the inversion condition $p^*(T)$ for the van der Waals gas.
(iii) Throttling is most efficient for cooling if it starts at the highest possible pressure. Find the temperature at which the inversion curve has a maximum.

Solution:

[tex29] Assembling thermodynamic information

The following thermodynamic information is known about $n = 1\text{mol}$ of a system:

- At constant temperature T_0, the work done on the system when it is compressed from V_0 to V is $\Delta W_0 = -RT_0 \ln(V/V_0)$.
- The entropy is $S(T,V) = R(V_0/V)(T/T_0)^a$, where V_0, T_0, a are constants.

Use this information to determine (i) the Helmholtz free energy $A(T,V)$, (ii) the equation of state $f(p,V,T) = 0$, and (iii) the work of compression ΔW done at an arbitrary temperature T.

Solution:

[tex11] How not to modify the ideal gas equation of state

Suppose we know empirically that for a real system with fixed n, the product of the pressure p and the volume V is a function of the temperature alone, $pV = f(T)$, and that the internal energy is also a function of the temperature alone, $U = U(T)$. These properties are realized in the classical ideal gas, where $f(T) = nRT$ and $U(T) = C_V T$ with $C_V = \alpha nR = \text{const}$. Show that the only function $f(T)$ in the equation of state of the above form which is compatible with $U = U(T)$, i.e. with $(\partial U/\partial V)_T = 0$ is linear in T with zero intercept: $f(T) = rT$ with $r = \text{const}$.

Solution:

[tex42] Reconstructing the equation of state of a fluid system

A fluid system is found to have a thermal expansivity $\alpha_p = (nR/pV) + (na/RT^2V)$ and an isothermal compressibility $\kappa_T = (n/V)[Tf(p) + b/p]$, where a, b are constants and $f(p)$ is an unknown function.
(a) Find the function $f(p)$ which makes the two response functions thermodynamically consistent.
(b) Reconstruct the equation of state $V = V(T, p)$ from the two response functions.

Solution:

[tex43] Reconstructing the equation of state of a gas

It is found for a gas that $\alpha_p = RV/np + aV/nT^2$ and $\kappa_T = T(V/n)f(p)$, where a is a constant and $f(p)$ is an unknown function.
(a) Find the function $f(p)$ which makes the two response functions thermodynamically consistent.
(b) Reconstruct the equation of state $g(V,T,p) = 0$ from the two response functions.

Solution:

[tex33] Effects of first virial correction on ideal gas properties

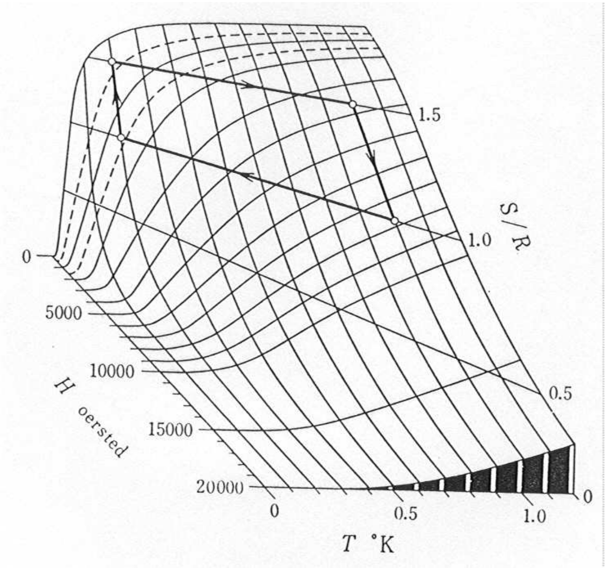
The ideal gas equation of state supplemented by the first virial correction reads $p = (nRT/V)[1 + (n/V)B(T)]$. The associated heat capacity at constant volume can be written in the form $C_V = \frac{3}{2}nR - (n^2R/V)F(T)$, where $F(T)$ and $B(T)$ are related by thermodynamic consistency conditions.
(a) Express $F(T)$ as a function of $B(T)$.
(b) Find the function $U(T, V)$ (internal energy) and $S(T, V)$ (entropy) for this system.
(c) Find the first virial correction $B(T)$ for the van der Waals gas, $[p + a(n/V)^2](V - nb) = nRT$, and calculate the associated virial correction $F(T)$ to the heat capacity C_V.

Solution:

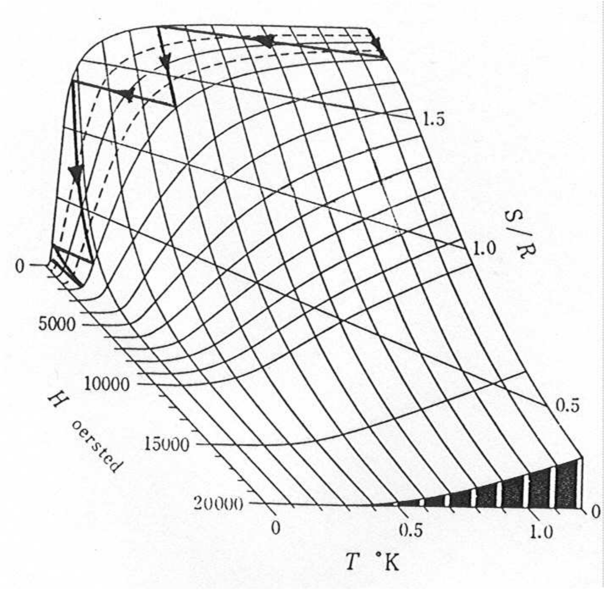
Entropy due to electronic spins in iron ammonium alum [tsl2]

Dependence of entropy on temperature and magnetic field for paramagnet.

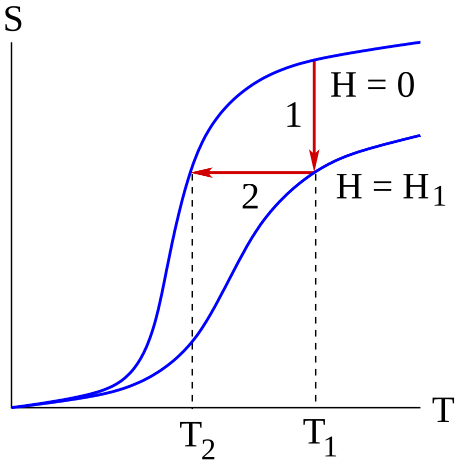
(a) Carnot cycle operating on this system.



(b) Cooling of this system via adiabatic demagnetization.



Adiabatic demagnetization [tln24]



Equation of state for paramagnetic salt in a weak magnetic field: $M(T,H) = \chi_T(T)H$.

Helmholtz free energy:

$$dA = -SdT + HdM, \quad \left(\frac{\partial A}{\partial M}\right)_T = H = \frac{M}{\chi_T}$$

$$\Rightarrow \; A(T,M) = A(T,0) + \frac{M^2}{2\chi_T}.$$

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

$$\Rightarrow \; S(T,H) = S(T,0) + \frac{1}{2}H^2\frac{d\chi_T}{dT}; \quad \chi_T > 0, \; \frac{d\chi_T}{dT} < 0 \; \text{ for paramagnet.}$$

Third law: $\lim_{T\to 0} S(T,H) = 0$ independent of H $\Rightarrow$ $\lim_{T\to 0}\frac{d\chi_T}{dT} = 0.$

1. Isothermal magnetization: $\Delta S = \frac{1}{2}\frac{d\chi_T}{dT}H_1^2 < 0.$

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

2. Adiabatic demagnetization: $\Delta S = 0 \;\Rightarrow\; S(T_1,H_1) = S(T_2,0).$

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

Consider the entropy function $S(T,H)$ for iron ammonium alum.

- The 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 heat reservoirs at various temperatures. They can be established by employing a Carnot engine consisting of steps 1 and 2 and their inverses.
- Magnetic refrigerators using paramagnetic salts attain ~ 0.2K. Adiabatic demagnetization attains mK temperatures.

[tex19] Thermodynamics of an ideal paramagnet I

For an ideal paramagnet specified by the equation of state $M = H/T$ (Curie law) and internal energy $U = 0$, find (a) the entropy $S(T, H)$, (b) the thermodynamic potentials $E(S, H)$, $A(T, M)$, $G(T, H)$, and (c) the response functions $C_M, C_H, \chi_T, \chi_S, \alpha_H$.

Solution:

[tex20] Thermodynamics of an ideal paramagnet II

For an ideal paramagnet specified by the equation of state $M = H/T$ (Curie law) and heat capacity $C_M = \text{const}$, find (a) the internal energy $U(T,H)$, the entropy $S(T,H)$, and the enthalpy $E(T,H)$; (b) the thermodynamic potentials $A(T,M)$, $G(T,H)$; (c) the response functions χ_T, χ_S, α_H, C_H.

Solution:

[tex21] Thermodynamics of an ideal paramagnet III

For an ideal Langevin paramagnet, which is specified by the equation of state $M = \tanh(H/T)$ (Langevin function) and the internal energy $U \equiv 0$, find (a) the entropy $S(T,H)$ and the enthalpy $E(T,H)$; (b) the thermodynamic potentials $A(T,M)$, $G(T,H)$; (c) the response functions χ_T, χ_S, α_H, C_H. Determine the integration constant S_0 in $S(T,H)$ such that $S \to 0$ for $T \to 0$ and $H \neq 0$ in accordance with the third law of thermodynamics.

Solution:

[tex36] Thermodynamics of a real paramagnet

The magnetization M of a paramagnetic system was measured over a certain temperature range, and it was found to depend only on the ratio H/T: $M = f(H/T)$.
(a) Show that the internal energy is then independent of H: $U = U(T)$.
(b) Show that the entropy then has the following functional form:

$$S(T,H) = S_1(T) - \frac{H}{T} f\left(\frac{H}{T}\right) + \int_0^{H/T} dx\, f(x), \quad \text{where} \;\; S_1(T) = S_0 + \int_{T_0}^{T} dT' \frac{U'(T')}{T'}.$$

Solution:

[tex22] Thermodynamics of a classical ideal paramagnetic gas I

Consider 1mol of a paramagnetic gas, specified by the equations of state $pV = RT$ (classical ideal gas) and $M = H/T$ (Curie paramagnet), and by a constant heat capacity $C_{VM} = \frac{3}{2}R$.
(a) Calculate the internal energy $U(T, V, M)$ by integration of the differential $dU = TdS - pdV + HdM$. Show that U only depends on T. (b) Calculate the entropy $S(T, V, M)$ by integration of the differential $dS = (1/T)dU + (p/T)dV - (H/T)dM$. (c) Calculate the Helmholtz potentials $A_M(T, V, M) \doteq U - TS$ and $A_H(T, V, H) \doteq U - TS - MH$. (d) Calculate the Gibbs potentials $G_M(T, p, M) \doteq U - TS + pV$ and $G_H(T, p, H) \doteq U - TS + pV - MH$.

Solution:

[tex133] Thermodynamics of a classical ideal paramagnetic gas II

Consider the fixed amount $n = 1\text{mol}$ of a paramagnetic gas, specified by the equations of state $pV = RT$, $M = H/T$, and by the heat capacity $C_{VM} = 3R/2$.
(a) Characterize a general adiabatic process by a functional relation of the form $f(T, p, H) = \text{const}$. Start from the function $S(T, V, M)$ derived in [tex22].
(b) Show that the heat transfer is path-independent for isothermal processes. Derive an expression for the heat transfer ΔQ_T of a general isothermal process between (p_0, H_0) and p_1, H_1.
(c) Show that the heat transfer for isobaric processes does depend on the path taken. Derive an expression for the heat transfer ΔQ_p of the isobaric process $(T_0, H_0) \to (T_0, H_1) \to (T_1, H_1) \to (T_1, H_0) \to (T_0, H_0)$ along straight segments in the (T, H)-plane.
(d) Consider a process $(T, P_0, H_0) \to (T, P_1, P_1)$ with $p_0 > p_1$ that is both isothermal (no change in energy) and adiabatic (no heat transfer). In this process mechanical work $\Delta W_p(T, p_0, p_1)$ done by the system is matched by the same amount of magnetic work $\Delta W_H(T, H_0, H_1)$ done on the system. Find $\Delta W_p(T, p_0, p_1)$ and $\Delta W_p(T, p_0, p_1)$.

Solution:

[tex132] Hydrostatic pressure

The chemical potential in a homogeneous fluid is a function $\mu = \mu_0(p, T)$ such as calculated in [tex17] for the classical ideal gas. What remains uniform throughout the fluid in the presence of a uniform gravitational field is the potential

$$\mu = \mu_0(p, T) + mgz = \text{const.},$$

where m is the mass of the fluid particle, g is the acceleration due to gravity, and the z-direction is against the field. For a fluid of negligible compressibility derive from the condition $d\mu/dz = 0$ the familiar result for the hydrostatic pressure,

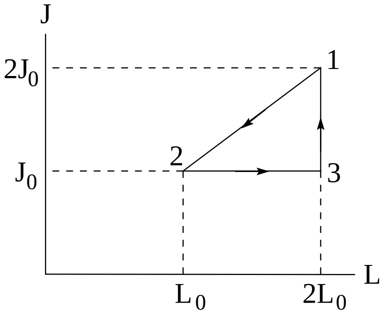
$$p(z) = p_0 - \rho g z,$$

where $\rho = Nm/V$ is the (average) mass density of the fluid.

Solution:

[tex39] Rubber band heat engine

Consider a heat engine that uses a rubber band in the three-step cycle shown. The equation of state $J = \alpha LT$ with $\alpha = \text{const}$ relates the tension J in the band to the length L of the band and to the absolute temperature T. The heat capacity of the band at constant length is $C_L = \text{const}$. Calculate the heat transfer ΔQ and the work performance ΔW in each of the three steps in the cyclic process shown:
$1 \to 2$ relaxation at $T = \text{const}$,
$2 \to 3$ expansion at $J = \text{const}$,
$3 \to 1$ heating up at $L = \text{const}$.
From these results calculate the efficiency η of the rubber band heat engine. Compare η with the efficiency of a Carnot engine operating between the same temperatures.



Solution:

[tex40] Equation of state and adiabate of an elastic band

Experimentally one finds the following response functions of a band of elastic material

$$\left(\frac{\partial J}{\partial L}\right)_T = \frac{aT}{L_0}\left[1 + 2\left(\frac{L_0}{L}\right)^3\right], \quad \left(\frac{\partial J}{\partial T}\right)_L = \frac{aL}{L_0}\left[1 - \left(\frac{L_0}{L}\right)^3\right],$$

where J is the tension, L is the length, T is the temperature, and a, L_0 are constants. The heat capacity at constant length is $C_L = \text{const}$.
(a) Use this empirical information to reconstruct the equation of state $J(T, L)$.
(b) Calculate the response function $(\partial L/\partial T)_J$ and discuss its physical meaning.
(c) If the band is stretched adiabatically from length L_0 at temperature T_0 to length $2L_0$, what is the final temperature?

Solution:

[tex28] Determining C_V of condensed matter

The direct measurement of the heat capacity at constant volume C_V for condensed matter is very difficult. Therefore, express C_V in terms of the following quantities, all of which are experimentally more accessible: the heat capacity at constant pressure C_p, the isothermal compressibility κ_T, the mass density ρ, and the sound velocity $c = \sqrt{(\partial p/\partial \rho)_S}$.

Solution:

[tex23] Thermodynamics of black-body radiation

Electromagnetic radiation inside a cavity is in thermal equilibrium with the walls at temperature T. The radiation has an energy density that depends only on the temperature, i.e. its internal energy has the form $U(T,V) = Ve(T)$. The radiation pressure is determined by the energy density alone: $p = \frac{1}{3}e(T)$. (a) Use the consistency equations for the total differential dS to show that the energy density has the form $e(T) = \sigma T^4$, where σ is a constant, now known as the *Stefan-Boltzmann constant*. In this argument, the additional assumption enters that $e(T) \to 0$ for $T \to 0$. (b) Determine the entropy $S(T,V)$ and the thermodynamic potentials $U(S,V)$, $E(S,p)$, $A(T,V)$, $G(T,p)$. (c) Determine the isotherms and adiabates in the (V,p)-plane. (d) Determine the response functions $C_V, C_p, \kappa_T, \kappa_S, \alpha_p$.

Solution:

[tex24] Carnot cycle of thermal radiation

Describe the four steps of a Carnot engine, where the operating material is black-body radiation. The internal energy is given by Stefan's law, $U(T,V) = \sigma T^4 V$. The equation of state is $p = \frac{1}{3}\sigma T^4$. Determine the work performance ΔW and the heat transfer ΔQ during each of the four steps and derive the Carnot efficiency from these results. Sketch the cycle in the (V,p)-plane.

Solution: