1. (Kittel 6.4) **Energy of gas of extreme relativistic particles.** Extreme relativistic particles have momenta \( p \) such that \( pc \gg Mc^2 \), where \( M \) is the rest mass of the particle. The de Broglie relation \( \lambda = h/p \) for the quantum wavelength continues to apply. Show that the mean energy per particle of an extreme relativistic ideal gas is \( 3\tau \) if \( \varepsilon \equiv pc \) in contrast to \( \frac{3}{2}\tau \) for the nonrelativistic problem. (An interesting variety of relativistic problems are discussed by E. Fermi in Notes on Thermodynamics and Statistics, University of Chicago Press, 1966, paperback.)

**Solution.**

\[
\langle \varepsilon \rangle = \frac{\int_0^\infty D(\varepsilon)e^{-\beta\varepsilon}d\varepsilon}{\int_0^\infty D(\varepsilon)e^{-\beta\varepsilon}d\varepsilon}
\]

For \( \varepsilon \equiv pc \), \( D(\varepsilon) \propto \varepsilon^2 \). Hence

\[
\langle \varepsilon \rangle = \frac{\int_0^\infty \varepsilon^2 e^{-\beta\varepsilon}d\varepsilon}{\int_0^\infty \varepsilon^2 e^{-\beta\varepsilon}d\varepsilon}
\]

Let \( x = \beta\varepsilon = \varepsilon k_B T \). Then

\[
\langle \varepsilon \rangle = k_B T \frac{\int_0^\infty x^3 e^{-x}dx}{\int_0^\infty x^2 e^{-x}dx} = k_B T \frac{3 \times 2}{2 \times 1} = 3k_B T
\]

2. (Kittel 6.5) **Integration of the thermodynamic identity for an ideal gas.** From the thermodynamic identity at a constant number of particles we have

\[
d\sigma = \frac{dU}{\tau} + \frac{pdV}{\tau} = \frac{1}{\tau} \left( \frac{\partial U}{\partial \tau} \right)_V d\tau + \frac{1}{\tau} \left( \frac{\partial U}{\partial V} \right)_\tau dV + \frac{pdV}{\tau}
\]

Show by integration that for an ideal gas the entropy is

\[
\sigma = C_v \log \tau + N \log V + \sigma_i
\]

where \( \sigma_i \) is a constant independent of \( \tau \) and \( V \).
Solution.

\[ d\sigma = \frac{1}{\tau} \left( \frac{\partial U}{\partial \tau} \right)_V d\tau + \frac{1}{\tau} \left( \frac{\partial U}{\partial V} \right)_\tau dV + \frac{p dV}{\tau} \]

For an ideal gas, \( pV = Nk_B T = \dot{N} \).

\[ \left( \frac{\partial U}{\partial V} \right)_\tau = T \left( \frac{\partial S}{\partial V} \right)_\tau - p = \frac{\partial p}{\partial T} \]

\[ d\sigma = \frac{1}{\tau} \left( \frac{\partial U}{\partial \tau} \right)_V d\tau + \frac{p dV}{\tau} = \frac{C_V}{\tau} d\tau + \frac{N}{V} dV \]

\[ \sigma = \int \frac{C_V}{\tau} d\tau + \frac{N}{V} dV = C_V \ln \tau + N \ln V + \sigma_i \]

3. (Kittel 6.7) **Relation of pressure and energy density.**

(a) Show that the average pressure in a system in thermal contact with a heat reservoir is given by

\[ p = -\frac{1}{Z} \sum \left( \frac{\partial \varepsilon_i}{\partial \mathcal{V}} \right)_N \exp(-\varepsilon_i/\tau) \]

where the sum is over all states of the system.

(b) Show for a gas of free particles that

\[ \left( \frac{\partial \varepsilon_i}{\partial \mathcal{V}} \right)_N = \frac{2 \varepsilon_i}{3 V} \]

as a result of the boundary conditions of the problem. The result holds equally well whether \( \varepsilon_i \) refers to a state of \( N \) noninteracting particles or to an orbital.

(c) Show that for a gas of free non-relativistic particles

\[ p = \frac{2}{3} U/V \]

where \( U \) is the thermal average energy of the system. The result is not limited to the classical regime; it holds equally well for fermion and boson particles, as long as they are nonrelativistic.
Solution.

\[ p = -\frac{1}{Z} \sum_s \left( \frac{\partial \epsilon_s}{\partial V} \right) N e^{-\epsilon_s / T} \]

\[ \epsilon_s = \frac{\hbar^2}{2m} k_s^2 \text{ with } k_s \approx \frac{1}{L} = \frac{1}{V^{1/3}} \]

\[ \epsilon_s \propto \frac{1}{V^{2/3}} \]

Let \( \epsilon_s \propto \frac{A_s}{V^{2/3}} \). Then

\[ \frac{\partial \epsilon_s}{\partial V} = \frac{2}{3 V^{2/3}} = -\frac{2}{3 V} \epsilon_s \]

\[ p = \frac{2}{3} \frac{1}{Z} \sum_s \frac{\epsilon_s}{V} e^{-\epsilon_s / T} = \frac{2}{3} \frac{1}{V} \sum_s \epsilon_s e^{-\epsilon_s / T} = \frac{2U}{3V} \]

4. (Kittel 6.9) **Gas of atoms with internal degrees of freedom.** Consider an ideal monatomic gas, but one for which the atom has two internal energy states, one an energy \( \Delta \) above the other. There are \( N \) atoms in volume \( V \) at temperature \( T \). Find the (a) chemical potential; (b) free energy; (c) entropy; (d) pressure; (e) heat capacity at constant pressure.

Solution.

\[ N = \lambda \sum e^{-\beta \epsilon} \]

\[ \epsilon = \frac{p^2}{2m} + \epsilon_{\text{int}} \]

\[ \epsilon_{\text{int}} = 0 \Rightarrow \sum e^{-\beta \epsilon} = Z = Vn_Q \]

\[ \epsilon_{\text{int}} = \Delta \Rightarrow \sum e^{-\beta \epsilon} = e^{-\beta \Delta} Z = Vn_Q e^{-\beta \Delta} \]
\[ N = \sum_{e} e^{-\beta e} = \lambda V n_q (1 + e^{-\beta t}) \]

\[ \lambda = \frac{n}{n_q} \frac{1}{1 + e^{-\beta t}} \]

\[ \lambda = e^{\mu t} \]

\[ \mu = \tau \ln \frac{n}{n_q} - \tau \ln (1 + e^{-\beta t}) \]

(b)

\[ Z_1 = \left(1 + e^{-\beta t}\right) Z_{\text{ideal}} = \left(1 + e^{-\beta t}\right) V n_q \]

\[ Z = \frac{Z_1^N}{N!} = \left(\frac{V n_q}{N!}\right)^N (1 + e^{-\beta t})^N \]

\[ F = -\tau \ln Z = -\tau \ln \left(\frac{V n_q}{N!}\right)^N - N \tau \ln (1 + e^{-\beta t}) = N \tau \left(\ln \frac{n}{n_q} - 1\right) - N \tau \ln (1 + e^{-\beta t}) \]

(c)

\[ \sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = N \left[ \ln \frac{n}{n_q} + \frac{5}{2} \right] + \tau \ln \left(1 + e^{-\beta t}\right) + \frac{\tau e^{-\beta t}}{1 + e^{-\beta t}} \frac{\Delta}{\tau^2} \]

ie. \[ \sigma = N \left[ \ln \frac{n}{n_q} + \frac{5}{2} \right] + N \ln \left(1 + e^{-\beta t}\right) + \frac{N \Delta}{\tau} \frac{1}{e^{\beta t} + 1} \]

(d)

\[ p = -\left(\frac{\partial F}{\partial V}\right)_\tau = \frac{N \tau}{V} \]

(e)

\[ C_p = \tau \left(\frac{\partial \sigma}{\partial T}\right)_p = k_b \tau \left(\frac{\partial \sigma}{\partial T}\right)_p = k_b \tau \frac{\partial}{\partial \tau} \left( N \ln \left(1 + e^{-\beta t}\right) + \frac{N \Delta}{\tau} \frac{1}{e^{\beta t} + 1} \right) \]

Hence,
5. (Kittel 6.11) Convective isentropic equilibrium of the atmosphere. The lower 10-15 km of the atmosphere - the troposphere - is often in a convective steady state at constant entropy, not constant temperature. In such equilibrium \( pV' \) is independent of altitude, where \( \gamma = C_p/C_v \). Use the condition of mechanical equilibrium in a uniform gravitational field to: (a) Show that \( dT/dz = \text{constant} \), where \( z \) is the altitude. This quantity, important in meteorology, is called the dry adiabatic lapse rate. (Do not use the barometric pressure relation that was derived in Chapter 5 for an isothermal atmosphere.) (b) Estimate \( dT/dz \), in degrees Celsius per km. Take \( \gamma = 7/5 \). (c) Show that \( p \propto \rho^\gamma \), where \( \rho \) is the mass density. If the actual temperature gradient is greater than the isentropic gradient, the atmosphere may be unstable with respect to convection.

Solution.

(a)

\[
[p(z) - p(z + dz)]A = nmAdzg \Rightarrow -\frac{dp}{dz} = nm\gamma g
\]

\[
\frac{dT}{dz} = \frac{dT}{dp} \frac{dp}{dz} = -\frac{dT}{dp} nm\gamma g \quad (\text{Eqn 1})
\]

\( pV' = \text{constant} \), with \( pV = Nk_BT \) gives \( \left( \frac{T}{p} \right)^\gamma = \text{constant} \) and so \( \frac{T^\gamma}{p^{\gamma-1}} = \text{constant} \)

\[
\ln \frac{T^\gamma}{p^{\gamma-1}} = \text{constant} \Rightarrow \gamma \ln T - (\gamma - 1) \ln p = \text{constant}
\]

\[
\frac{\gamma}{T} \frac{dT}{dp} - (\gamma - 1) \frac{dp}{p} = 0
\]

\[
\frac{dT}{dp} = \frac{(\gamma - 1)T}{\gamma p} \quad (\text{Eqn 2})
\]
Eqn 2 can also be obtained from
\[ d\sigma = dU + pdV = c_v dT + pdV \]

For isentropic processes \( d\sigma = 0 \) and so
\[ c_v dT + pdV = 0 \]
\[ pdV + Vdp = Nk_B dT \]
\[ c_v dT + Nk_B dT - Vdp = 0 \]
\[ c_p dT - \frac{Nk_B T}{p} dp = 0 \]

(since \( \gamma = \frac{C_p}{C_v} \) and \( Nk_B = C_p - C_v \)).

\[ \gamma dT - (\gamma - 1) \frac{Tdp}{p} = 0 \Rightarrow \frac{dT}{dp} = \frac{\gamma - 1}{\gamma} \frac{T}{p} \]

Substitute Eqn 2 into Eqn 1 to get
\[ \frac{dT}{dz} = -\frac{\gamma - 1}{\gamma} \frac{T}{p} mg \]

Now \( p = nk_B T \) and so
\[ \frac{dT}{dz} = -\gamma - 1 \frac{mg}{\gamma k_B} = \text{constant} \]

(b)
Take m the mass of \( N_2 \)
\[ m = 28 \times 1.67 \times 10^{-27} \text{kg} = 4.68 \times 10^{-26} \text{kg} \]

Now \( \gamma = \frac{7}{5} \) and so
\[
\frac{dT}{dz} = -\frac{7/5 - 1}{7/5} \times 10^{-26} 9.8 \frac{K}{m} = 9.5 \times 10^{-3} \frac{K}{m}
\]

T drops about 10 degrees Celsius every km.

(c)

\[pV^\gamma = \text{constant}, \quad \text{and} \quad \rho \propto V^{-1} \Rightarrow pp^{-\gamma} = \text{constant}, \quad \text{and so} \quad p \propto \rho^\gamma\]

6. (Kittel 6.12) **Ideal gas in two dimensions.** (a) Find the chemical potential of an ideal monatomic gas in two dimensions, with \(N\) atoms confined to a square of area \(A = L^2\). The spin is zero. (b) Find an expression for the energy \(U\) of the gas. (c) find an expression for the entropy \(\sigma\). The temperature is \(\tau\).

**Solution.**

(a) \(N = \lambda Z_1\) with \(Z_1 = \sum e^{-\beta \epsilon} = \int D(\epsilon)e^{-\beta \epsilon} d\epsilon\).

\[
D(\epsilon)d\epsilon = \frac{2\pi p dp}{\hbar^2} = \frac{2\pi A}{\hbar^2} \frac{1}{2} dp^2 = \frac{2\pi Am}{h^2} d\epsilon
\]

\[
Z_1 = \frac{2\pi Am}{h^2} \int_0^\infty e^{-\beta \epsilon} d\epsilon = \frac{2\pi Am}{h^2} \frac{1}{\tau}
\]

\[
N = e^{\mu \tau} \frac{2\pi Am}{h^2} \tau \Rightarrow \mu = \tau \ln \left( \frac{Nh^2}{2\pi Am} \right)
\]

(b)

\[
\bar{\epsilon} = \frac{1}{2} k_B T + \frac{1}{2} k_B T = k_B T
\]

\[
U = N\bar{\epsilon} = Nk_B T
\]

(c)

\[
Z = \frac{Z_1^N}{N!} \Rightarrow F = -\tau \ln Z = -\tau \left( N\ln \left( \frac{2\pi Am}{h^2} \frac{1}{\tau} \right) - N \ln N + N \right)
\]
\[ F = -\tau N \left( \ln \frac{2\pi Am \tau}{\hbar^2 N} + 1 \right) \]

\[ \sigma = -\left( \frac{\partial F}{\partial \tau} \right)_{A} = N \left( \ln \frac{2\pi Am \tau}{\hbar^2 N} + 1 \right) + N\tau \frac{1}{\tau} = N \left( \ln \frac{2\pi Am \tau}{\hbar^2 N} + 2 \right) \]

\[ U = F + \tau\sigma = N\tau \]