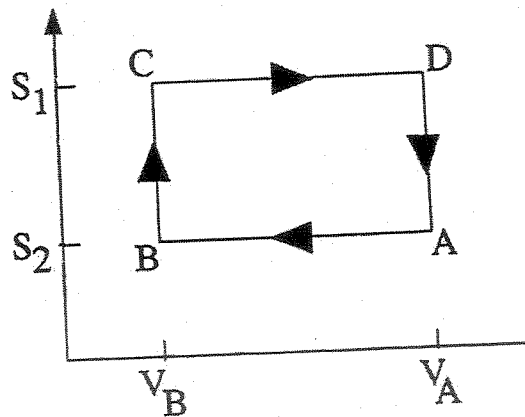


Rutgers - Physics Graduate Qualifying Exam

Thermodynamics & Statistical Mechanics: January 12, 2007

TA

The operation of a gasoline engine is (roughly) similar to the Otto cycle (Figure):



A → B Gas compressed adiabatically

B → C Gas heated isochorically (constant volume; corresponds to combustion of gasoline)

C → D Gas expanded adiabatically (power stroke)

D → A Gas cooled isochorically.

Compute the efficiency of the Otto cycle for an ideal gas (with temperature-independent heat capacities) as a function of the compression ratio V_A/V_B , and the heat capacity per particle C_V .

Solution: TA

From the standard thermodynamic relation

$$dU = T dS - P dV,$$

we note that the work done by the engine during one cycle is

$$\begin{aligned} W_{tot} &= W_{A \rightarrow B} + W_{C \rightarrow D} \\ &= \int_{A \rightarrow B} P dV + \int_{C \rightarrow D} P dV, \end{aligned} \quad (1)$$

and the energy absorbed by the engine is

$$\begin{aligned} Q_{in} &= Q_{B \rightarrow C} \\ &= \int_{B \rightarrow C} T dS. \end{aligned} \quad (2)$$

(The heat lost by the engine between D and A is wasted energy.) The efficiency we wish to find is defined in terms of these quantities by

$$\epsilon \equiv \frac{W_{tot}}{Q_{in}}.$$

Using the two ideal gas relations $PV = NkT$ and $C_V dT = dU$, equation (13.42) can be recast as

$$dS = C_V \frac{dT}{T} + Nk \frac{dV}{V},$$

where k is the Boltzmann constant. We integrate this to find the entropy:

$$S = C_V \ln T + Nk \ln V + \text{constant}.$$

Solving this for the temperature, we find

$$T = \alpha e^{S/C_V} V^{-Nk/C_V}, \quad (3)$$

where α is a constant with the appropriate dimensions. We can now find the work done by the system between A and B . Since we are compressing the gas, we are actually doing work on the system and $W_{A \rightarrow B}$ is negative:

$$\begin{aligned} W_{A \rightarrow B} &= \int_{V_A}^{V_B} P dV \\ &= -NK \int_{V_B}^{V_A} \frac{T}{V} dV \\ &= -\alpha Nk \int_{V_B}^{V_A} e^{S_2/C_V} V^{-(1+Nk/C_V)} dV \\ &= -\alpha \left(V_B^{-Nk/C_V} - V_A^{-Nk/C_V} \right) e^{S_2/C_V} C_V. \end{aligned} \quad (4)$$

We get a similar expression (with opposite sign) for $W_{C \rightarrow D}$. Putting these together, we find that the total work done in one cycle is

$$W_{tot} = \alpha C_V \left(V_B^{-Nk/C_V} - V_A^{-Nk/C_V} \right) \left(e^{S_1/C_V} - e^{S_2/C_V} \right) \quad (5)$$

The heat of combustion can be found similarly:

$$Q_{B \rightarrow C} = \int_{S_2}^{S_1} T dS \quad (6)$$

$$= \alpha \int_{S_2}^{S_1} V_B^{-Nk/C_V} e^{S/C_V} dS \quad (7)$$

$$= \alpha C_V V_B^{-Nk/C_V} \left(e^{S_1/C_V} - e^{S_2/C_V} \right). \quad (8)$$

From equation (13.45) we can now find the efficiency of the engine,

$$\epsilon = 1 - \left(\frac{V_A}{V_B} \right)^{-k/c_V}, \quad (9)$$

where we have written $c_V = C_V/N$. We note that in the special case of a monatomic ideal gas, for which $c_V = 3k/2$, we have

$$\epsilon = 1 - \left(\frac{V_A}{V_B} \right)^{-2/3}. \quad (10)$$

TB

Two identical perfect gases with the same pressure P and the same number of particles N , but with different temperatures T_1 and T_2 , are confined in two vessels, of volume V_1 and V_2 , which are then connected. Find the change in entropy after the system has reached equilibrium.

Solution: TB

Since the final entropy does not depend on how the final state is reached it will be calculated as if it were reached isobarically. This is possible because the final pressure is $P_f = P$. Then, for each side separately,

$$T dS = C_p dT,$$

Hence

$$\Delta S_1 = C_p \log \frac{T_f}{T_1} \quad \text{and} \quad \Delta S_2 = C_p \log \frac{T_f}{T_2}.$$

But $T_f = (T_1 + T_2)/2$ and $C_p = (5/2)Nk$. Therefore

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 = \frac{5}{2} Nk \log \left(\frac{T_f^2}{T_1 T_2} \right) \\ &= 5Nk \log \left\{ \sqrt{\frac{T_f^2}{T_1 T_2}} \right\} \end{aligned} \quad (11)$$

which vanishes if $T_1 = T_2$ as it should.

$$S(N, V, U) = Nk_B \ln \left[\frac{V}{N} \left(\frac{4\pi m}{3h^2} \frac{U}{N} \right)^{3/2} \right] + \frac{5}{2} Nk_B$$

$$S_f = 2Nk_B \ln \left[\left(\frac{V_1 + V_2}{2N} \right) (\propto T_f)^{3/2} \right] + \frac{5}{2} 2Nk_B$$

$$S_1 = Nk_B \left[\frac{V_1}{N} (\propto T_1)^{3/2} \right] + \frac{5}{2} Nk_B$$

$$S_2 = Nk_B \left[\frac{V_2}{N} (\propto T_2)^{3/2} \right] + \frac{5}{2} Nk_B$$

$$\frac{\Delta S}{Nk_B} = \ln \left\{ \frac{(V_1 + V_2)^2 N_2}{4N_2 V_1 V_2} \right\} + \frac{3}{2} \ln \left\{ \frac{T_f^2}{T_1 T_2} \right\} = \left[T_f = \frac{T_1 + T_2}{2} \right] =$$

$$= \ln \left\{ \frac{(V_1 + V_2)^2}{4V_1 V_2} \right\} + \frac{3}{2} \ln \left\{ \frac{(T_1 + T_2)^2}{4T_1 T_2} \right\} = \left\{ \begin{array}{l} P(V_1 + V_2) = 2Nk_B \frac{T_1 + T_2}{2} \\ PV_1 = Nk_B T_1 \\ PV_2 = Nk_B T_2 \end{array} \right\} =$$

$$= \frac{5}{2} \ln \left\{ \frac{(T_1 + T_2)^2}{4T_1 T_2} \right\}$$

TC1

Consider a system of N particles with only 3 possible energy levels separated by ϵ (let the energies be 0 , ϵ , 2ϵ and 3ϵ). The system occupies a fixed volume V and is in thermal equilibrium with a reservoir at temperature T . Ignore interactions between particles and assume that Boltzmann statistics applies.

- (a) What is the partition function for a single particle in the system?
- (b) What is the average energy per particle?
- (c) What is probability that the 2ϵ level is occupied in the high temperature limit, $k_B T \gg \epsilon$? Explain your answer on physical grounds.
- (d) What is the average energy per particle in the high temperature limit, $k_B T \gg \epsilon$?
- (e) Find the heat capacity of the system, C_V , analyze the low- T ($k_B T \ll \epsilon$) and high- T ($k_B T \gg \epsilon$) limits, and sketch C_V as a function of T . Explain your answer on physical grounds.

Tcl

Consider a system of N particles with only 3 possible energy levels separated by ϵ (let the ground state energy be 0). The system occupies a fixed volume V and is in thermal equilibrium with a reservoir at temperature T . Ignore interactions between particles and assume that Boltzmann statistics applies.

- (a) (2) What is the partition function for a single particle in the system?
- (b) (5) What is the average energy per particle?
- (c) (5) What is probability that the 2ϵ level is occupied in the high temperature limit, $k_B T \gg \epsilon$?
- (d) (5) Explain your answer on physical grounds.
- (e) (5) What is the average energy per particle in the high temperature limit, $k_B T \gg \epsilon$?
- (f) (3) At what temperature is the ground state 1.1 times as likely to be occupied as the 2ϵ level?

(f) (25) Find the heat capacity of the system, C_V , analyze the low- T ($k_B T \ll \epsilon$) and high- T ($k_B T \gg \epsilon$) limits, and sketch C_V as a function of T . Explain your answer on physical grounds.

(a)
$$Z = \sum_i d_i \exp(-\beta \epsilon_i) = 1 + e^{-\beta \epsilon} + e^{-2\beta \epsilon}$$

(b)
$$\langle \epsilon \rangle = - \frac{1}{Z} \frac{\partial Z}{\partial \beta} = - \frac{(-\epsilon)e^{-\beta \epsilon} + (-2\epsilon)e^{-2\beta \epsilon}}{1 + e^{-\beta \epsilon} + e^{-2\beta \epsilon}} = \epsilon \frac{e^{-\beta \epsilon} + 2e^{-2\beta \epsilon}}{1 + e^{-\beta \epsilon} + e^{-2\beta \epsilon}}$$

(c)
$$P = \frac{e^{-2\beta \epsilon}}{1 + e^{-\beta \epsilon} + e^{-2\beta \epsilon}} \approx \frac{1 - 2\beta \epsilon}{1 + 1 - \beta \epsilon + 1 - 2\beta \epsilon} \approx \frac{1}{3}$$
 all 3 levels are populated with the same probability

(d)
$$\langle \epsilon \rangle = \epsilon \frac{e^{-\beta \epsilon} + 2e^{-2\beta \epsilon}}{1 + e^{-\beta \epsilon} + e^{-2\beta \epsilon}} \approx \epsilon \frac{1 + 2}{1 + 1 + 1} = \epsilon$$

$$(e) \quad \exp(-2\beta\varepsilon) = \frac{1}{1.1} \quad 2\beta\varepsilon = \ln 1.1 \quad T = \frac{2\varepsilon}{k_B \ln 1.1}$$

$$(f) \quad C_V = \frac{dU}{dT} = N \frac{d\langle \varepsilon \rangle}{dT} = N \frac{d\langle \varepsilon \rangle}{d\beta} \frac{d\beta}{dT}$$

$$= N\varepsilon \left(-\frac{1}{k_B T^2} \right) \left\{ \frac{(-\varepsilon)e^{-\beta\varepsilon} + (-2\varepsilon)2e^{-2\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}} - \frac{(e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon}) \left[(-\varepsilon)e^{-\beta\varepsilon} + (-2\varepsilon)e^{-2\beta\varepsilon} \right]}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2} \right\}$$

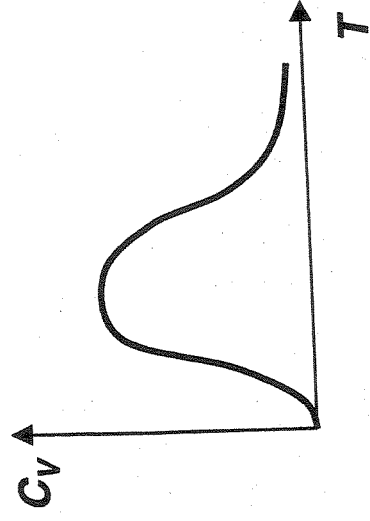
$$= \left(\frac{N\varepsilon^2}{k_B T^2} \right) \left\{ \frac{[e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon}] [1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}] - (e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon}) (e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon})}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2} \right\}$$

$$= \frac{N\varepsilon^2}{k_B T^2} \left\{ \frac{e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon} + e^{-2\beta\varepsilon} + 4e^{-3\beta\varepsilon} + e^{-3\beta\varepsilon} + 4e^{-4\beta\varepsilon} - e^{-2\beta\varepsilon} - 4e^{-3\beta\varepsilon} - 4e^{-4\beta\varepsilon}}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2} \right\}$$

$$= \frac{N\varepsilon^2}{k_B T^2} \frac{e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2}$$

$$\text{Low } T (\beta > \varepsilon): \quad C_V = \frac{N\varepsilon^2}{k_B T^2} \frac{e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2} \approx \frac{N\varepsilon^2}{k_B T^2} e^{\frac{\varepsilon}{k_B T}}$$

$$\text{high } T (\beta < \varepsilon): \quad C_V = \frac{N\varepsilon^2}{k_B T^2} \frac{e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}}{[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}]^2} \approx \frac{2 N\varepsilon^2}{3 k_B T^2}$$



TC2

- (a) The black body radiation fills a cavity of volume V . The radiation energy is:

$$U(V, T) = \frac{4\sigma}{c} VT^4 \quad (12)$$

The radiation pressure is:

$$P = \frac{4\sigma}{3c} T^4 \quad (13)$$

$[\sigma = 5.7 \times 10^{-8} \text{W}/(\text{m}^2 \cdot \text{K}^4)]$. Consider an isentropic (quasi-static and adiabatic) process of the cavity expansion. The radiation pressure performs work during the expansion and the temperature of radiation will drop. Find how T and V are related for this process.

- (b) Assume that the cosmic microwave background radiation (CMBR) was decoupled from the matter when both were at 3000 K. Currently, the CMBR temperature is 2.7 K. What was the radius of the universe at the moment of decoupling, compared to now? Consider the process of expansion as isentropic.
- (c) Estimate by an order of magnitude the number of CMBR photons hitting the earth per second per square meter [i.e. photons/(s · m²)]?

You might need the following integral:

$$\int_0^{\infty} \frac{x^2}{e^x - 1} dx \approx 2.4 \quad (14)$$

Solution: ~~7C2~~ 7C2

(a) The equation that describes the isentropic (quasi-static adiabatic) process for the

photon gas: $dS = 0$ $TdS = dU + PdV$ $dU = -PdV$

$$\frac{4\sigma}{c} V 4T^3 dT + \frac{4\sigma}{c} T^4 dV = -\frac{4\sigma}{3c} T^4 dV$$

$$\frac{dT}{T} = -\frac{1}{3} \frac{dV}{V} \quad VT^3 = const$$

$$16 \frac{\sigma}{c} VT^3 dT = -\frac{16\sigma}{3c} T^4 dV$$

(b) $\frac{V_i}{V_f} = \left(\frac{R_i}{R_f} \right)^3 = \left(\frac{T_f}{T_i} \right)^3$

Thus, at the moment of decoupling, the radius of the universe was ~ 1000 time smaller

or $TR = const$

(c) $N \left(\frac{\text{photons}}{s \cdot m^2} \right) = \frac{J \left(\frac{W}{m^2} \right)}{\bar{\epsilon}(J)}$

where $\bar{\epsilon}(J)$ is the average energy of photons

$$J = \sigma T_{CMBR}^4 = 5.7 \cdot 10^{-8} (W/K^4 \cdot m^2) \times (2.7)^4 K^4 = 3 \cdot 10^{-6} W/m^2$$

An estimate of a photon energy based on the Wien's law. The energy of a photon that corresponds to the maximum of $u(\epsilon)$:

$$\bar{\epsilon} \approx h \nu_{max} \approx 2.8 k_B T$$

TCZ

More accurately, the total number of photons per unit volume:

$$\bar{n} \equiv \frac{\bar{N}}{V} = \int_0^{\infty} \bar{n}(\varepsilon) g(\varepsilon) d\varepsilon = \frac{8\pi}{c^3} \int_0^{\infty} \frac{v^2}{\exp\left(\frac{hv}{k_B T}\right) - 1} dv = \frac{8\pi}{c^3} \left(\frac{k_B T}{h}\right)^3 \int_0^{\infty} \frac{x^2 dx}{e^x - 1} = 8\pi \left(\frac{k_B}{hc}\right)^3 T^3 \times 2.4$$

$$\bar{\varepsilon} = \frac{u(T)}{\bar{N}} = \frac{8\pi^5 (k_B T)^4 (hc)^3}{15 (hc)^3 8\pi (k_B T)^3 \times 2.4} = \frac{\pi^4}{15 \times 2.4} k_B T \approx 2.7 k_B T$$

$$N \left(\frac{\text{photons}}{s \cdot m^2} \right) = \frac{J \left(\frac{W}{m^2} \right)}{\bar{\varepsilon} (J)} \approx \frac{3 \cdot 10^{-6}}{2.7 \times 1.38 \cdot 10^{-23} \times 2.7} \approx 3 \cdot 10^{16} \frac{\text{photons}}{s \cdot m^2}$$

TD1

Consider a system of two particles, each of which can be in any one of three quantum states of energies 0, e , and $5e$, respectively. The system is in thermal equilibrium at a temperature $T = (k\beta)^{-1}$.

- (a) Write an expression for the partition function and the entropy of the system, assuming that the particles are distinguishable and obey Maxwell-Boltzmann statistics.
- (b) Write an expression for the partition function and the entropy of the system, assuming that the particles obey Bose-Einstein statistics.
- (c) Write an expression for the partition function and the entropy of the system, assuming that the particles obey Fermi-Dirac statistics.

~~SOLUTION 4a~~

D1

THERMAL SOL'N

$$F = \bar{E} - TS$$

$$S = \frac{1}{T} [\bar{E} - F] = k \ln Z - \frac{1}{T} \frac{\partial \ln Z}{\partial \beta}$$

$$(a) \ln Z = \ln \left[\sum_{n_1, n_2, n_3} \frac{z!}{n_1! n_2! n_3!} e^{-\beta(n_2 e + 5n_3 e)} \right]$$

$$k \ln Z = k \ln (1 + e^{-\beta e} + e^{-5\beta e})$$

$$-\frac{1}{T} \frac{\partial \ln Z}{\partial \beta} = \frac{ze}{T} \frac{[e^{-\beta e} + 5e^{-5\beta e}]}{[1 + e^{-\beta e} + e^{-5\beta e}]}$$

$$(b) k \ln Z = k \ln [1 + e^{-\beta e} + e^{-2\beta e} + e^{-5\beta e} + e^{-6\beta e} + e^{-10\beta e}]$$

$$-\frac{1}{T} \frac{\partial \ln Z}{\partial \beta} = \frac{e}{T} \frac{[e^{-\beta e} + 2e^{-2\beta e} + 5e^{-5\beta e} + 6e^{-6\beta e} + 10e^{-10\beta e}]}{[1 + e^{-\beta e} + e^{-2\beta e} + e^{-5\beta e} + e^{-6\beta e} + e^{-10\beta e}]}$$

$$(c) k \ln Z = k \ln [e^{-\beta e} + e^{-5\beta e} + e^{-6\beta e}]$$


$$-\frac{1}{T} \frac{\partial \ln Z}{\partial \beta} = \frac{e}{T} \frac{[e^{-\beta e} + 5e^{-5\beta e} + 6e^{-6\beta e}]}{[e^{-\beta e} + e^{-5\beta e} + e^{-6\beta e}]}$$

TD2

Consider a non-relativistic ideal gas of N free particles of mass m confined to a cubical box of side L and volume $V = L^3$.

- (a) What is the energy of the quantum states of the particles $e_n(V)$ as a function of the volume V ?
- (b) What is the pressure of this quantum mechanical ideal gas in equilibrium as a function of E/V , where E is the total energy of the gas particles?
- (c) What would be the pressure as a function of E/V of a gas of photons in this same volume?
- (d) Calculate the pressure as a function of E/V of an ideal gas of N particles, using semiclassical kinetic theory, i.e. the pressure due to molecular impacts with the walls of the cube. How does this result compare to that of part (b) above?

Solutions 4/6
DZ THERMAL SOLN

a)  $\frac{n\lambda}{2} = L, \lambda = \frac{2L}{n}$

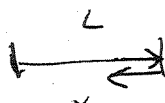
$$E_n = \frac{p^2}{2m} = \frac{h^2}{2m} \left(\frac{1}{\lambda}\right)^2 = \frac{h^2}{8m} \frac{n^2}{V^{2/3}}$$

b) $\bar{E} = \frac{N h^2}{8m} \frac{n^2}{V^{2/3}}$

$$P = -\frac{\partial E}{\partial V} = -\frac{2}{3} \left(\bar{E} / V\right)$$

c) $E = N h f = N h c \left(\frac{1}{\lambda}\right) = \frac{N h c n}{2 V^{1/3}}$

$$P = -\frac{\partial E}{\partial V} = \frac{1}{3} \left(\bar{E} / V\right) \Rightarrow \text{half that of (b)}$$

d)  $\Delta p = 2m v_x$

$$P = \frac{F}{A} = \frac{1}{A} \left(\frac{\Delta p}{\Delta t}\right) = \frac{2m v_x v_x}{2LA} = \frac{m \overline{v_x^2}}{V}$$

$$= \frac{2}{3} \frac{\left(\frac{1}{2} m \overline{v^2}\right)}{V} = \frac{2}{3} \bar{E} / V, \text{ same as (b)}$$