

You are graded on your work (with partial credit where it is deserved) so please do not just write down answers with no explanation (or skip important steps)!

Please give clear, well-organized, understandable solutions.

$$\begin{array}{llll}
 h = 6.63 \times 10^{-34} \text{ J s} & \text{[Planck's constant]} & k = 1.38 \times 10^{-23} \text{ J/K} & \text{[Boltzmann constant]} \\
 c = 3.00 \times 10^8 \text{ m/s} & \text{[speed of light]} & m_e = 9.11 \times 10^{-31} \text{ kg} & \text{[mass of electron]} \\
 \sigma_B = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \cdot \text{K}^4} & \text{[Stefan-Boltzmann constant]} & G = 6.67 \times 10^{-11} \frac{\text{N m}^2}{\text{kg}^2} & \text{[gravitational constant]} \\
 1 \text{ eV} = 1.60 \times 10^{-19} \text{ J} & \text{and} & \frac{1 \text{ eV}}{k} = 11,600 \text{ K} & 0 \text{ }^\circ\text{C} = 273 \text{ K}
 \end{array}$$

The variables have their usual meanings: E = energy, S = entropy, V = volume, N = number of particles, T = temperature, P = pressure, μ = chemical potential, B = applied magnetic field, C_V = heat capacity at constant volume, k = Boltzmann constant. Also, $\langle \dots \rangle$ represents an average.

You should know this, but:

$$\langle n(\epsilon_i) \rangle = \frac{1}{e^{(\epsilon_i - \mu)/kT} \pm 1} \quad ; \quad dE = TdS - PdV + \mu dN \quad ; \quad E = TS - PV + \mu N$$

$$PV^\gamma = \text{constant} \quad \text{for process in which entropy is constant} \quad PV = NkT$$

1. **Stefan-Boltzmann law from thermodynamics alone.** Here we will employ only the *thermodynamics* of a classical radiation field, with no reference to statistical mechanics.

(a) (4) Use the first law of thermodynamics,

$$dE = dq - dw ,$$

with dq and dw written in terms of dS and dV respectively, to obtain the familiar relation between dE , dS , and dV .

(b) (4) Recall that the Helmholtz free energy is defined by $F = E - TS$. Use this definition and the result of part (a) to obtain dF in terms of dT and dV .

(c) (4) Using the result of part (b), obtain the Maxwell relation that relates $\left(\frac{\partial S}{\partial V}\right)_T$ to $\left(\frac{\partial P}{\partial T}\right)_V$.

(d) (4) Use the result of part (a) and the Maxwell relation in part (c) to obtain a relation between

$\left(\frac{\partial E}{\partial V}\right)_T$, $\left(\frac{\partial P}{\partial T}\right)_V$, and P .

(e) (1) It is conventional to write $E = V u(T)$, where the energy density $u(T)$ is a function of only the temperature T . Rewrite the result of (d) in terms of $u(T)$, $\left(\frac{\partial P}{\partial T}\right)_V$, and P .

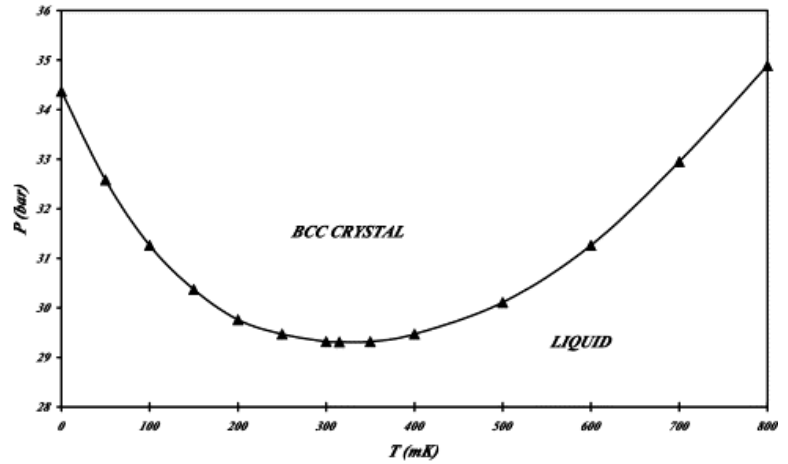
(f) (4) From Maxwell's equations of electromagnetism, it can be shown that $P = \frac{1}{3}u$ for radiation. Use this relation and the result of part (e) to get a relation between u and $\left(\frac{\partial u}{\partial T}\right)_V$.

(f) (4) Integrate this equation of part (f) (at constant volume) to obtain $u = aT^n$, while at the same time determining the constant n . This is essentially the Stefan-Boltzmann law, derived through a thermodynamic rather than a statistical-mechanics argument.

2. **The Pomeranchuk refrigerator.** On the right you will see the experimentally determined melting curve for ^3He , in the neighborhood of its pressure minimum at $T = 0.32\text{ K}$ and $P = 29.3\text{ atm}$.

(From <https://www.princeton.edu/~fhs/kcurve/kcurve.htm>, adapted from E.R. Dobbs. *Helium Three* (Oxford University Press, 2002).)

Let us start with general ideas and then consider this solid-liquid coexistence curve from 320 mK down to a few mK, temperatures that can be reached with the cooling technique below. ($1\text{ mK} = 10^{-3}\text{ K}$ of course)



(a) (3) Give a qualitative explanation of the fact that ^3He remains a liquid at low temperature and $P = 1\text{ atm}$. How many other substances have this property?

(b) (3) For a general system, use Euler's theorem and the expression for dE on the front page of this exam to obtain the (Gibbs-Duhem) relation between $d\mu$, dT , and dP , or small $\Delta\mu$, ΔT , and ΔP , in terms of the entropy s per particle and the volume v per particle.

(c) (3) Now consider two closely-separated points A and B along a coexistence curve like the one shown in the figure above, and let $\Delta\mu = \mu_B - \mu_A$. Use the result of part (b), together with the condition for thermal equilibrium between two phases with the same kind of particles, to obtain the Clausius-Clapeyron equation – which relates the slope dP/dT along the coexistence curve to the differences Δs and Δv between the quantities s and v in the two phases.

(d) (4) Let us specialize to the case that the particles are **^3He atoms in a SOLID**, with spin $\frac{1}{2}$ and thus 2 possible spin states per atom. (We neglect other contributions to the entropy, which become negligibly small at the temperatures considered here, between a few mK and 320 mK.) Based on Boltzmann's expression for the entropy S , what is $s = S/N$ in **solid ^3He** if each of the N atoms independently has the 2 spin states (up and down)?

(e) (4) On the other hand, if the particles are **^3He atoms in a LIQUID**, and we model this liquid as a quantum ideal gas of spin $\frac{1}{2}$ fermions, the heat capacity at low temperatures is given by

$$C_V = \frac{\pi^2}{2} Nk \frac{T}{T_F} .$$

Using the fact that $C_X = T \left(\frac{\partial S}{\partial T} \right)_X$ (with $X = V$ here) and that $C_V \rightarrow 0$ as $T \rightarrow 0$ by the third law of

thermodynamics, integrate to obtain $S(T)$ and then $s(T) = \frac{S(T)}{N}$ in **liquid ^3He** .

(f) (4) Let $\Delta s = s_{\text{liq}} - s_{\text{sol}}$, where s_{sol} and s_{liq} are the values of s in parts (d) and (e) respectively. For

$$\frac{T}{T_F} < \text{constant}$$

we will have

$$\Delta s < 0 .$$

Calculate this constant using your results from parts (d) and (e).

(g) (4) Now let Δv be the change in volume per atom when ${}^3\text{He}$ goes from solid to liquid: $\Delta v = v_{\text{liq}} - v_{\text{sol}}$. It turns out that

$$\Delta v > 0 .$$

Clearly explain why the temperature will fall along the coexistence curve, for $T < \text{constant} \times T_F$, as the pressure is increased. I.e., why does $\Delta P > 0$ imply that $\Delta T < 0$ at low T ? (We thus cool the system by squeezing it.)

3. Adiabatic compression. A Diesel engine requires no spark plug. Instead the air is compressed so much that the fuel ignites spontaneously. Recall that air is composed 99% of the diatomic molecules N_2 and O_2 and that we can ignore the contribution of molecular vibrations to the energy and heat capacity in a problem like the one below.

(a) (5) In preparation, use the equipartition theorem to determine the energy E of a diatomic ideal gas with N molecules at temperature T , bearing in mind that there are 3 translational and 2 relevant rotational degrees of freedom per molecule.

(b) (5) Use the result of part (a), plus the fact that $C_p = C_v + Nk$, to obtain C_v , C_p , and the approximate value of the ratio $\gamma = C_p / C_v$ for air.

(c) (10) The air in a cylinder of a Diesel engine starts at a temperature of 20°C and a pressure of 1 atm. It is then adiabatically compressed by a factor of 15. (I.e., the final volume is $1/15$ of the initial volume.) What is the final pressure, in atm?

(d) (5) What is the final temperature?

4. **Minimum free energy.** Let us demonstrate that the appropriate free energy is minimized in thermodynamic equilibrium by considering a system at constant temperature T and pressure P , for which the Gibbs free energy $G = E - TS + PV$ is appropriate. (The proof for other cases is very similar.)

(a) (5) Write down the first law of thermodynamics, relating q to ΔE and w , where q is the heat added, ΔE is the change in internal energy, and w is the work done by the system.

(b) (5) Write down an inequality relating $T\Delta S$ to q , where ΔS is the change in entropy. Why is $T\Delta S$ not equal to q when an ideal gas undergoes a free expansion?

(c) (5) Use the results of parts (a) and (b) to write down an inequality relating $T\Delta S$ to ΔE and $P\Delta V$.

(d) (5) Use the result of part (c) to obtain an inequality for ΔG when the system is released out of equilibrium and undergoes spontaneous random changes.

(e) (5) Explain **clearly** why your result in part (d) implies that the system has reached a state of thermal equilibrium if G has reached a minimum.

Merry Christmas and Happy Holidays!