Stat Mech (PHYS 370) Guide 13

Fall 2024 v2.0

Classes of problems for the final exam: The final will be cumulative but there will be an emphasis on material from Chapters 6 and 7.

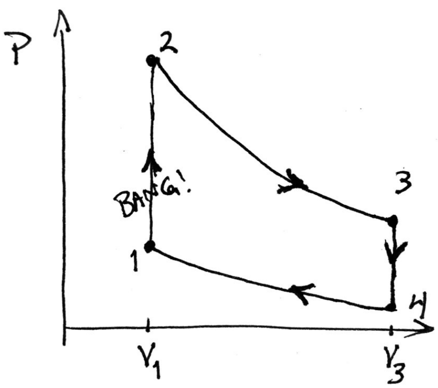
- Thermodynamics
  - Macro vs. microscopic descriptions and quantities including entropy
  - Fundamental understanding of temperature
  - Equipartition theorem
  - The 3 laws
  - Examples including ideal gas law, BOE calculation of climate change, black holes,
  - Thermodynamic potentials
- Methods of stat mech: Energy - partition function - average energy - heat capacity - compare to data
- Counting
- Results of quantum statistics:
  - Distributions: Fermi-Dirac, Boltzmann, Bose-Einstein
  - Degenerate Fermi gas at $T = 0$ and above (Sommerfeld expansion)
  - White dwarfs and neutron stars
  - Blackbody radiation
  - Debye model
- Phase transitions
- Mathematical methods: manipulating sums, fancy integration, Stirling's approximation, use of mathematica to compute partition functions, etc.
- Black Holes as an example of these methods

Problems: Possible final questions:

(1) **Heating water and doing work** You heat 1.2 kg of water in an electrical kettle for hot chocolate at the physics holiday party from 19°C to 99°C at atmospheric pressure. Find:
  - (a) The change in the energy of the water.
  - (b) The change in entropy of the water.
  - (c) The rough factor $\Omega_{99^\circ C}/\Omega_{19^\circ C}$ by which the multiplicity of et water has increased. Express your result as $e^{\text{a number}}$.
  - (d) The maximum mechanical work that could be achieved by using the water during heating process to run a engine that runs with a cold reservoir at 19°C .

(2) **Temperature of Sun** Sunlight arrives on the top of Earth's atmosphere at an intensity of about 1360 W/m^2. Find the temperature of the Sun. The radius of the Sun is about 6.96×10^5 km and the average Earth-Sun distance is about 1.5×10^8 km.

(3) **Heat engines**
  - (a) Sketch a heat engine and label W, Q_h, Q_c.
  - (b) Only using the first law of thermodynamics explain why perfect heat engines, with efficiencies of 1, might exist.
  - (c) Explain why perfect heat engines do not exist using the second law of thermodynamics.
  - (d) One familiar heat engine uses a gas comprised of a mixture of air and vaporized fuel.
    - (i) Here's the cycle, at least approximately,



At point 1 in the sketch of the cycle a (compressed) volume V_1 of this mixture is ignited yielding rapid increase in pressure and the system arrives at state 2. The gas expands adiabatically from 2 to 3, to volume V_3, typically by pushing on a piston. The hot gas is exhausted from 3 to 4. New fuel is added and the new mixture is compressed adiabatically back to state 1. Heat is added during the combustion. Let's call it Q_B, which replaces the traditional "Q_H" of heat engine fame. In what part of the cycle is work done? In what part of the cycle does the heat Q_C leave the system?

(ii) Using the equipartition theorem and ideal gas law, find Q_B and Q_C in terms of pressures and volumes.

(iii) Express the efficiency in terms of V_1, V_3, and γ, the adiabatic exponent.

(iv) Find the maximum efficiency for air and compression ratio 0f 8. Discuss how to increase efficiency of combustion engines.

(4) **Radiating physicists** In the physics carol "Energy" we sing, "There is still a light that shines from me, Thermal radiation, Energy". (Think Beetles if you haven't heard this one before.)

(a) Estimate the power of radiation coming from you in empty space, neglecting insulation such as sweaters. Humans are not very reflective and essential not at all reflective in the infra-red so our emissivity is essentially equal to 1.

(b) In everyday non-physically active conditions we actually radiate at about 70 W. What accounts for the discrepancy between this power and the result you just found?

(c) You invite 12 physics majors over on a cool fall evening when the outside temperature is 45°F $\simeq$ 7.2°C . Assume you have an efficient home with a surface area of 4340 ft^2 $\simeq$ 403 m^2, an average whole-house R-value of 4.0 m^{2}K/ W ($\simeq$ 23 in US units), and an initial interior temperature of 68°F $\simeq$ 20°C . Can you heat the house with your guests? Assume that the only relevant heat loss is through conduction.

(d) If you only heat your house with guests when the outside temperature is -5°C , what is the equilibrium interior temperature in °C ?

(5) **Harmonic oscillators** Consider a collection of a large number N of identical, non-interacting quantum oscillators, each one of which has an energy spectrum of

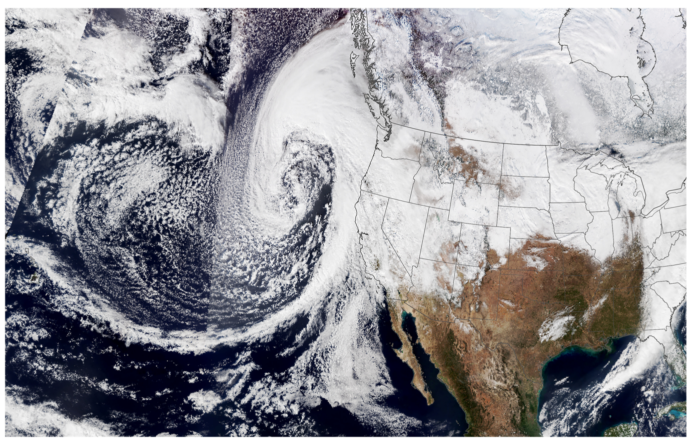
$$E_n = \hbar\omega \left(n + \frac{1}{2} \right)$$

where $n = 0, 1, 2, \ldots$.

(a) Find the partition function for a single oscillator.
(b) Find the log of the partition function for N indistinguishable oscillators. Let's assume that the density is such that we don't need to worry about quantum statistics.
(c) Find the average energy for the system.
(d) Find the heat capacity C for the system. Plot C/Nk vs. kT/ϵ, where $\epsilon = \hbar\omega$.
(e) Find the heat capacity in the limit of high, $\epsilon/kT \ll 1$, and low, $\epsilon/kT \gg 1$ temperatures.
(f) Explain why the high temperature result is correct.
(g) Explain why the low temperature result is incorrect.

(6) **An old metaphor** In his 'first-half biography' of Einstein, *Einstein in Love*, Dennis Overbye writes, "The first law of thermodynamics stated that energy was neither created nor destroyed: You couldn't win. The second law said you couldn't even break even. (There was, in time, a third law that said in effect that you couldn't get out of the game.)"[1] Is this correct? Why or why not? Refer to more precise formulations in your discussion.

(7) **Changes in "atmospheric rivers"** Recent rainfall events in the West, like this one from 2023, have had a higher amount of moisture.



NASA Earth Observatory images by Lauren Dauphin, using GEOS-5 data

One reason is derived from the Clausius-Clapeyron relation. As we saw, the slope of the phase boundary between gas a liquid phases was given by the Clausius-Clapeyron relation

$$\frac{dP}{dT} = \frac{Q_L}{T\Delta V},$$

where Q_L is the total latent heat and $\Delta V = V_g - V_l$, the difference in volumes between the phases. For water the latent heat of vaporization is $Q_L = 42$ kJ/mol at 1 atm.

(a) Under what conditions is the change in volume for one mole approximated as

$$\Delta V \simeq \frac{RT}{P}?$$

Show this and derive the new relation for the slope,

$$\frac{dP}{dT} = \frac{Q_L P}{RT^2},$$

for one mole.

[1] This turn of phrase as been used for some time so it is not original with Overbye.

(b) Integrate the relation to obtain a relation for the pressure P. This shows how the *saturation vapor pressure*, the maximum pressure of vapor before it condenses, changes with temperature.
(c) Explain why "warm air can hold more water vapor"[2]
(d) Show that "every extra degree Celsius of warming, air can hold [6]% more water. It would seem to suggest that with 2°C of global warming, the world could expect [12]% more moisture in the air." [D. Adam]
(e) Of course, it is not so simple and depends on whether there enough water to evaporate and whether rain drops form. When a weather forms over an ocean the effect can be strong, such as in the "atmospheric river" that arrived in the West not long ago.

(8) **An oscillator oops!** In our last week we saw that Einstein made a mistake - the heat capacity of materials such as gold do not follow the $C \propto e^{-\beta\epsilon}$ prediction of the model. We can fix this!

All matter is "floppy". We can think about the bonds between atoms as a bit like springs so perhaps it is not surprising that the oscillations in the structure of the material - the standing waves - are just like the modes we studied before, although instead of the waves traveling at the speed of light, they travel at the speed of sound in the material. In addition, on the atomic scale materials have some discrete lattice structure so that the wavelengths cannot become arbitrarily short, $\lambda > \ell$ where ℓ is the spacing between atoms.

(a) Show that in a simple box of length L the expected energies are

$$E(s) = \frac{hs\,c_s}{2L},$$

where c_s is the material's speed of sound and s is an integer. We'll express this energy as hf_i where the frequency $f_i = s_i c_s/2L$. The maximum such frequency is achieved when the wavelength is on the order of the lattice spacing in the material.

(b) For N oscillators in three dimensions, the partition function can be written as a product of sums over the occupation numbers of the different oscillators

$$Z = \sum_{n_1=0}^{\infty} \cdots \sum_{n_{3N}=0}^{\infty} e^{-\beta h \sum_{i=1}^{3N} f_i n_i}.$$

Show that the log of the partition function can be written as

$$\ln Z = -\sum_{i=1}^{3N} \ln\left(1 - e^{-\beta h f_i}\right).$$

In the next parts we'll think through this sum over oscillators i.

(c) In three dimensions assume that the material is in a cube of volume $V = L^3$, explain (or show) that the form of the frequency in three dimensions is

$$f_i = \frac{c_s}{2L} s_i \text{ where } s_i = \sqrt{s_{x_i}^2 + s_{y_i}^2 + s_{z_i}^2}$$

is the magnitude or 'radius' of the harmonic number in 3D. Clearly

$$f_{max} = \frac{c_s}{2L} s_{max}$$

is the highest frequency possible. (s_{max} is fixed by the latticing spacing, $s_{max} = L/\ell$.) In addition the (minimum) spacing between frequencies is

$$\Delta f_i = \frac{c_s}{2L} \Delta s_i = \frac{c_s}{2L}$$

[2] D. Adam, PNAS **120** (2023) e2304077120.

since the minimum spacing between modes is $\Delta s_i = 1$. By summing over all the allowed modes use these expressions to show that

$$\frac{4}{3}\frac{\pi f_{max}^3 V}{c_s^3} = N \text{ or } f_{max}^3 = \frac{3Nc_s^3}{4\pi V}.$$

(d) If the number of particles is very large the frequencies will be close to each other and we should be able to replace the sum in part (b) with an integral over f in the 1/8 of a sphere in (s_x, s_y, s_z) space so that (after a bit of work that you don't need to do)

$$\ln Z = -\frac{12\pi V}{c_s^3}\int_0^{f_{max}} f^2 \ln\left(1 - e^{-\beta h f}\right) df.$$

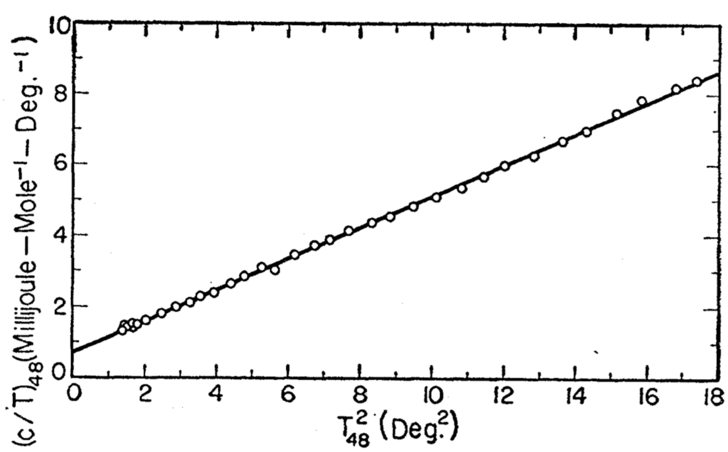
Find the energy U for this partition function. Your result will be in terms of an integral.

(e) Let $x = \beta h f$ and change variables in the integral. Find the energy U for cold temperatures when you can send $x_{max} \to \infty$. You'll find the integral

$$\int_o^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$$

helpful.

(f) Find the heat capacity for this corrected model and compare it to the data for gold in this plot of (molar heat capacity)/T vs. T^2.[3]



The speed of sound in gold is 3240 m/s and the volume of 1 mole of gold is 1.0×10^{-5} m^3.

(g) Find and explain the non-vanishing y-intercept in the above plot.

(9) **Quantum counting** Consider a system of two identical particles that occupy two possible energy levels

$$E_n = n\epsilon \text{ with } n = 0, 1$$

[3]From Corak et. al., Phys. Rev. **98** (1955) 1699

For each of the following (i) enumerate the possible configurations for a system in equilibrium at T, (ii) determine the partition function, and (iii) the energy:

- The particles are spin-1/2 fermions.
- The particles are spin-0 bosons.
- The particles are distinguishable particles satisfying Boltzmann statistics.

1. Handy Relations

$$
\begin{aligned}
N_A &= 6.02 \times 10^{23} \\
k &= 1.38 \times 10^{-23} \text{ J/K } = 8.62 \times 10^{-5} \text{ eV/K} \\
R &= 8.32 \times \text{ J/(mol K)} \\
h &= 6.63 \times 10^{-34} \text{ J s} = 4.14 \times 10^{-15} \text{ eV s} \\
G &= 6.67 \times 10^{-11} \frac{\text{m}^3}{\text{kg s}^2} \\
T \text{ (in K) } &= T \text{ (in } ^\circ\text{C) } + 273 \\
1 \text{ atm} &= 1.01 \text{ bar } = 1.01 \times 10^5 \text{ Pa} \\
kT_{room} &\approx \frac{1}{40} \text{ eV} \\
c &= 4.186 \text{J/g K for water} \\
kT &= \frac{1}{\beta} \\
\sigma &= \frac{2\pi^5 k^4}{15 h^3 c^2} \simeq 5.67 \times 10^{-8} \frac{W}{m^2 K^4} \\
\binom{N}{n} &= \frac{N!}{n!\,(N-n)!} \\
\Omega(N,q) &= \binom{q+N-1}{q} \text{ for Einstein solid} \\
N! &\approx N^N e^{-N} \sqrt{2\pi N} \\
f(x) &= f(0) + \left.\frac{df}{dx}\right|_{x=0} x + \frac{1}{2} \left.\frac{d^2 f}{dx^2}\right|_{x=0} x^2 + \frac{1}{6} \left.\frac{d^3 f}{dx^3}\right|_{x=0} x^3 + \dots \\
1 + x + x^2 + x^3 + \dots &= \frac{1}{1-x} \\
1 + x + x^2 + \cdots + x^N &= \frac{1 - x^{N+1}}{1-x}
\end{aligned}
$$

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-a)^2/(2\sigma^2)}$$

$$\cosh(x) = \frac{e^x + e^{-x}}{2}; \;\; \sinh(x) = \frac{e^x - e^{-x}}{2}$$

$$PV = NkT$$

$$W = -\int P dV$$

$$V^\gamma P = \text{constant and } VT^{f/2} = \text{constant' along adiabatics } (Q = 0) \text{ processes } \gamma = \frac{f+2}{f}$$

$$U_{thermal} = N\, f\, \frac{1}{2} kT$$

$$e = \frac{\text{benefit}}{\text{cost}} \leq 1 - \frac{T_c}{T_h} \text{ for heat engines}$$

$$\text{COP} \;\; = \frac{\text{benefit}}{\text{cost}} \leq \frac{T_c}{T_h - T_c} \text{ for heat pumps}$$

$$\Delta U = Q + W$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$Q = cm\Delta T, \text{ and } Q = mL$$

$$\frac{dQ}{dt} = -k_t A \frac{\Delta T}{\Delta x} = -\frac{A}{R} \Delta T$$

$$H = U + PV$$

$$F = U - TS = -kT \ln Z$$

$$G = U + PV - TS = N\mu$$

$$S = k \ln \Omega$$

$$\Delta S = \frac{dQ}{T}; \, \Delta S = \int \frac{C_V}{T} dT$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V}$$

$$P = T\left(\frac{\partial S}{\partial V}\right)_{N,U}$$

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{V,U}$$

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

$$dU = TdS - PdV + \mu dN$$

$$Z = \sum_s e^{-\beta E(s)}$$

$$\mathcal{Z} = \sum_s e^{-\beta(E(s) - \mu N(s))}$$

$$P(s) = \frac{e^{-\beta E(s)}}{Z}$$

$$U = -\frac{\partial \ln Z}{\partial \beta}$$

$$\frac{U}{V} = \frac{8\pi^5 (kT)^4}{15(hc)^3}$$

$$u(\epsilon) = \frac{8\pi}{(hc)^3}\frac{\epsilon^3}{e^{\beta\epsilon} - 1}$$

$$\mathcal{P} = e\sigma A T^4$$

$$\epsilon_{peak} = 2.82kT,\ \ \lambda_{peak} = 0.201\frac{hc}{kT}$$

$$\epsilon_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \text{ and } T_F = \frac{\epsilon_F}{k}$$

$$T_D = \frac{hc_s}{2k}\left(\frac{6N}{\pi V}\right)^{1/3}$$

$$R_S = \frac{2GM}{c^2}$$

$$S_{BH} = \frac{kc^3 A_H}{4Gh} \text{ with } A_{BH} = 4\pi R_S^2 = \frac{16\pi G^2}{c^4}M^2$$

$$T_{BH} = \frac{hc^3}{16\pi^2 kG}\frac{1}{M}$$