Various quantum effect will be discussed, but mainly about internal degrees of freedom.

1. [Internal degrees of freedom of heavy hydrogen]
The potential energy function describing the chemical bond in a heavy hydrogen D$_2$ may be approximately described by

\[ \phi(r) = \epsilon \left[ e^{-(r-d)/a} - 2e^{-(r-d)/a} \right], \quad (\text{DH11.1}) \]

where \( \epsilon = 7 \times 10^{-19} \) J, \( d = 8 \times 10^{-11} \) m and \( a = 5 \times 10^{-11} \) m. Deuterium mass \( M \) is \( 1.66 \times 10^{-27} \) kg.

(1) Evaluate the smallest energy required to excite the rotational motion, and estimate the temperature \( T_r \) for which the rotation contribution becomes significant.

(2) Evaluate the smallest energy required to excite the vibrational motion, and estimate the temperature \( T_v \) for which the vibration contribution becomes significant.

**Soln.**

(1) The moment of inertia is

\[ I = \frac{1}{2}Md^2 = \frac{1}{2} \times (1.66 \times 10^{-27}) \times (8 \times 10^{-11})^2 = 5.31 \times 10^{-48} \text{ kg m}^2, \quad (\text{DH11.2}) \]

so the rotational energy levels are given by

\[ \epsilon_J = \frac{\hbar^2}{2I} J(J+1). \quad (\text{DH11.3}) \]

Thus, the representative temperature for rotational excitation is

\[ \Theta_r = \frac{\hbar^2}{2k_B I} = \frac{(1.055 \times 10^{-34})^2}{2 \times (1.38 \times 10^{-23}) \times (5.31 \times 10^{-48})} \]

\[ = \frac{1.113 \times 10^{-68}}{1.466 \times 10^{-70}} \approx 76 \text{ K}. \quad (\text{DH11.4}) \]

(2) The minimum point of the potential \( \phi(r) \) is \( r = d \) with \( \phi(d) = -\epsilon \). Since

\[ e^{-2x} - 2e^{-x} = 1 - 2x + 2x^2 + \cdots - 2(1 - x + x^2/2 + \cdots) = -1 + x^2 + \cdots, \quad (\text{DH11.6}) \]
\[ \phi(r) = -\epsilon + \frac{\epsilon}{a^2} (r - d)^2 + \cdots. \]  
\text{(DH11.7)}

The vibrational equation of motion is (here \( M/2 \) is the reduced mass)

\[ \frac{M}{2} \ddot{x} = -2 \frac{\epsilon}{a^2} x + \cdots. \]  
\text{(DH11.8)}

Therefore,

\[ \omega = \sqrt{\frac{4\epsilon}{Ma^2}} = \frac{2}{a} \sqrt{\frac{\epsilon}{M}} = \frac{2}{5 \times 10^{-11}} \sqrt{\frac{7 \times 10^{-19}}{1.66 \times 10^{-27}}} = 8.21 \times 10^{14} \text{ rad/s.} \]  
\text{(DH11.9)}

The vibrational quantum is

\[ \Theta_v = \frac{\hbar \omega}{k_B} = \frac{1.055 \times 10^{-34} \times 8.21 \times 10^{14}}{1.38 \times 10^{-23}} = 6276 \text{ K.} \]  
\text{(DH11.10)}

Therefore, around 6000 K the vibration becomes significant.

2. [Specific heat of various hydrogen gases]

Consider a 1 mole of ideal gas at 10 K consisting of pure HD, pure HT or pure DT (H: hydrogen, D: deuterium, T: tritium; you should know their masses). Whose specific heat \( C_V \) is the largest? Give your answer without detailed computation. You may assume that the length of the chemical bonds are all the same. You may take the fact into account that the rotational contribution reaches its peak beyond 40 K.

**Soln.**

We may totally ignore the contribution of oscillations. There is no difference in the contribution of translational motions. These are all heteronuclear molecules, so we need not worry about spin-rotation coupling.\(^1\) Therefore, we have only to pay attention to the rotational contributions. The molecules with the largest moment of inertia is the easiest to excite, so their rotational specific heat is the largest (notice that the 10K is still away from the peak of the rotational specific heat). Therefore, around 10 K the specific heat of DT must be the largest among the three. This is indeed the case.

3. [Black body box expansion]

\(^1\)which we do not discuss in this course.
A cavity of volume $V$ is filled with electromagnetic wave in equilibrium with temperature $T_i$ initially. If the volume is doubled adiabatically and quasistatically, what is the final temperature $T_f$?

**Soln.**

(1) Since $S$ is constant and since $PV = E/3$, we get

$$dE = -PdV = -\frac{E}{3V}dV.$$  \hspace{1cm} (DH11.11)

Therefore, $EV^{1/3}$ is constant, or $PV^{4/3}$ is constant.

On the other hand, Planck’s law tells us $E \propto VT^4$; if you wish to proceed from scratch, we get the one particle density $D \propto V^2 p^2 dp/d\omega \propto p^2 \propto \omega^2$ (cf. $p = \hbar \omega/c$), so ‘power counting’ is enough to conclude

$$E = \int d\omega D(w) \frac{\omega}{e^{\beta \hbar \omega} - 1} \propto VT^4.$$  \hspace{1cm} (DH11.12)

Thus, $P \propto T^4$. This with $PV^{4/3}$ implies that $T^4V^{4/3}$ or $VT^3$ is constant. Therefore, $T_f = T^i/2^{1/3}$.

4. **[Quantum gas with internal degrees of freedom]**

Let us consider a quantum gas consisting of $N$ particles. Individual particles have internal states consisting of two levels: the ground state and the non-degenerate excited state with energy $\epsilon$ $(>0)$.

(1) Suppose the particles are fermions. How does the Fermi energy $\mu_F$ (i.e., the chemical potential at $T = 0$) change as $\epsilon$ is increased?

(2) Suppose the particles are bosons. How does the Bose-Einstein critical temperature $T_c$ depends on $\epsilon$ qualitatively?

For both cases, you must state your supporting logic clearly.

**Soln.**

(1) The Fermi energy $\mu_F$ is determined by

$$N = \int_0^{\mu_F} dE D(E).$$  \hspace{1cm} (DH11.13)

Here, $D$ is the one-particle energy level density including the internal energy. If $\epsilon$ is increased, then the total occupation number of the one-particle states with internal
excitation decreases. The 'spilt particles' from the states with the internal excitation must be accommodate by the states without internal excitations. Therefore, $\mu_F$ is an increasing function of $\epsilon$.

(2) Consider the total number of the particles in the non-condensate (note that $\mu = 0$):

$$N_1 = \int_0^\infty dE \mathcal{D}(E) \frac{1}{e^{\beta E} - 1}. \quad \text{(DH11.14)}$$

If $\epsilon$ is increased, $N_1$ decreases, so this favors the formation of condensate. That is, $T_c$ increases with $\epsilon$. Or, you can say that increasing $\epsilon$ makes particles to evaporate from the condensate into internally excited non-condensate becomes harder, so $T_c$ goes up.

5. [The classical-quantum specific heat difference of insulating solid]

Let $C_V(T)$ be the true quantum-mechanical specific heat of a non-conducting solid that obeys asymptotically the $T^3$-law at low temperatures. We know $C_V(\infty)$ is obtained by the equipartition of energy for harmonic oscillators (i.e., the Dulong-Petit law).

Let $\Delta C_V = C_V(\infty) - C_V(T)$. Then, we happen to obtain

$$\int_0^\infty dT \Delta C_V(T) = \text{the zero-point energy of the solid.} \quad \text{(DH11.15)}$$

This is just the area of A in Fig. DH11.1.

Let us demonstrate this result.

Let $D(\omega)$ be the true (not the Debye approximate version) mode density (i.e., the actual single phonon energy level density or the phonon spectrum).

(1) Find the total phonon (i.e., oscillation) internal energy of the solid $E(T)$ in terms of $D(\omega)$.

(2) Find its classical approximation $E_C(T)$.

(3) By differentiating $E_C(T) - E(T)$ with respect to $T$, we can get $\Delta C$. Then calculate the integral in (DH11.15) to demonstrate the desired equality.

**Soln.**

(1) This is just we did for the Debye model (but without his approximation):

$$E(T) = \int d\omega D(\omega) \left[ \frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right]. \quad \text{(DH11.16)}$$
(2) This is the classical limit: for sufficiently large $T$

\[ E_C(T) = \int d\omega D(\omega) k_B T. \]  

\[(DH11.17)\]

(3)

\[ \Delta C = \frac{d}{dT} \int d\omega D(\omega) \left[ k_B T - \frac{\hbar \omega}{2} - \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right] \]  

\[(DH11.18)\]

\[ = \int d\omega D(\omega) \frac{d}{dT} \left[ k_B T - \frac{\hbar \omega}{2} - \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right] \]  

\[(DH11.19)\]

\[ = \int d\omega D(\omega) \frac{d}{dT} \left[ k_B T - \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right]. \]  

\[(DH11.20)\]

The exchange of differentiation and integration is legitimate.\(^2\) Now,

\[ \int_0^\infty dT \Delta C(T) = \int d\omega D(\omega) \int_0^\infty dT \left[ k_B T - \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right] \]  

\[ = \int d\omega D(\omega) \left[ k_B T - \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right]_{T=0}^\infty. \]  

\[(DH11.21)\]

\[(DH11.22)\]

\(^2\)The exchange of integrals in the following line is also legitimate. Every physicist must learn Lebesgue integration theory to be reasonable.
There is no contribution from the $T = 0$ end. Setting $x = \hbar \omega / k_B T$, we have

\[
\lim_{T \to \infty} \left[ k_B T - \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right] = \hbar \omega \lim_{x \to 0} \left[ \frac{1}{x} - \frac{1}{e^x - 1} \right] = \hbar \omega \lim_{x \to 0} \frac{e^x - 1 - x}{x(e^x - 1)} = \hbar \omega \lim_{x \to 0} \frac{x^2/2 + x^3/6 + \cdots}{x^2 + x^3/2 + \cdots} = \frac{\hbar \omega}{2},
\]

(DH11.23)

which happens to be the zero-point energy of the mode with $\omega$. Thus, we have arrived at the desired result:

\[
\int_0^\infty dT \left[ C_{\text{classical}} - C(T) \right] = \int d\omega D(\omega) \frac{\hbar \omega}{2}.
\]

(DH11.25)

Does this have a deep meaning? I am very sceptical.

6. [Electron-positron-photon equilibrium]

Assume the whole system is charge neutral. Electrons ‘e’ and positrons ‘p’ are in equilibrium with the photon field (electromagnetic field) through the pair creation/annihilation:

\[
e + p \leftrightarrow \gamma.
\]

(DH11.26)

Let us assume the temperature $T$ is much higher than the rest mass of the electron (i.e., $k_B T \gg m c^2$), so there is an equilibrium between the electromagnetic field (i.e., black-body radiation) and the positron/electron plasma.

(1) Show that the chemical potential $\mu_e$ of electrons and that $\mu_p$ of positrons are identical and zero $\mu_e = \mu_p = 0$. Do not forget that the chemical potential of photons is not definable. You may ignore the interactions among particles except for pair creation/annihilation.

(2) Let us consider a finite domain of volume $V$ in the system filled with the high temperature radiation field. Assuming particles are super relativistic, find the numbers of electrons ($N_e$) and positrons ($N_p$) [You need not perform the integrals, but pay attention to the degeneracy due to spins].

**Soln.**

(1) Let us minimize the Helmholtz free energy of the whole system under the condition that $N_e = N_p$, since $T$ is uniform.\(^3\) We use the Helmholtz free energy for

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\(^3\)Following Akira Shimizu (U Tokyo), who emphasizes (as quoted in the lecture notes and in my lectures) that chemical potential is coupled (basically) to conserved quantities.
photons $A_{h\nu}$, that for electrons $A_e$ and that for positrons $A_p$:
\[ A = A_{h\nu}(T) + A_e(T, N_e) + A_p(T, N_p). \] (DH11.27)

Let us minimize $A + \lambda (N_e - N_p)$, where $\lambda$ is Lagrange’s multiplier to impose the charge neutrality. We get
\[ \frac{\partial A_e}{\partial N_e} T + \lambda = \mu_e + \lambda = 0, \] (DH11.28)
\[ \frac{\partial A_p}{\partial N_p} T - \lambda = \mu_p - \lambda = 0. \] (DH11.29)

Therefore, we have
\[ \mu_e + \mu_p = 0. \] (DH11.30)

This is due to the electrical charge conservation.

Since $N_e = N_p$, $\mu_e = \mu_p$. Therefore, $\mu_e = \mu_p = 0$.

**Remark.** The ‘standard’ textbooks including Landau-Lifshitz claim that photons indeed have zero chemical potential, because the number $N$ of phonons is determined when $T$ is fixed by an equilibrium condition:
\[ \left( \frac{\partial A}{\partial N} \right)_T = 0. \] (DH11.31)

Therefore, the chemical equilibrium means $\mu_e + \mu_p = 0$, because the sum of chemical potentials of the reactants and products are identical. As you see below this argument is totally wrong.

You might think the situation is just like the following logic introducing $T$ to a microcanonical calculation:
\[ \left( \frac{\partial S}{\partial E} \right)_V = \frac{1}{T}. \] (DH11.32)

(DH11.31) just looks like this argument to introduce a new thermodynamic variable $\mu$. However, there is a fundamental difference: $E$ in (DH11.32) is one of the thermodynamic coordinates, and you can change it independently with $V$.

In contrast, for photons $E$ and $N$ are not independent variables, so the following derivative is meaningless:
\[ \left( \frac{\partial S}{\partial N} \right)_E = -\frac{\mu}{T}. \] (DH11.33)

Just as illegitimate as this, in (DH11.31), you cannot change $N$ while keeping $T$, since they are not independent variables.
Therefore, $\mu$ is not defined for photons in the ‘standard way’ (under true equilibrium conditions). □

(2) Since the particles are superrelativistic, the dispersion relation is $\epsilon = c|p|$. Therefore, the density $D$ of one-particle (translational) states may be obtained as

$$
\int_0^{\epsilon} d\epsilon \, D(\epsilon) = \frac{4\pi V}{h^3} \int_0^{\epsilon/c} p^2 dp = \frac{4\pi V}{3h^3c^3} \epsilon^3 ; \quad (\text{DH}11.34)
$$

or

$$
D(\epsilon) = \frac{4\pi V}{h^3c^3} \epsilon^2 . \quad (\text{DH}11.35)
$$

Therefore, taking the spin degrees of freedom into account by multiplying the degeneracy factor 2, we get

$$
N_e = 2 \times \frac{4\pi V}{h^3c^3} \int_0^{\infty} d\epsilon \frac{\epsilon^2}{e^{\beta \epsilon} + 1} = N_p . \quad (\text{DH}11.36)
$$

Its temperature dependence is $\propto T^3$ (use power counting).

7. [Effective interaction due to statistics]  
Fig. 21.6 illustrates how we can intuitively understand the effective interactions between particles: compared with classical particles, between bosons there is an effective attraction, and between fermions there is an effective repulsion. Let us make this understanding slightly quantitative. Here, we proceed step by small step, reviewing elementary quantum mechanics.

We wish to consider a two-particle system in terms of canonical ensemble theory. The system Hamiltonian reads

$$
H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} , \quad (\text{DH}11.37)
$$

and the canonical partition function is

$$
Z = \text{Tr} \, e^{-\beta H} , \quad (\text{DH}11.38)
$$

where the trace is with respect to the microstates specified by two momenta $|p, p'|$.

To compute this trace semi-classically, we introduce a single-particle momentum

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4Without elementary QM, this may be a bit too hard to understand, but the result Fig. DH11.2 is intuitively appealing.
state $|p\rangle$.

(1) Express $|p, p'\rangle$ both for the boson and fermion cases in terms of single particle kets $|p\rangle$. You may regard two momenta are distinct, but the obtained states must be properly normalized. Recall that boson wave functions are totally symmetric with respect to the permutation of particle numberings; fermion wave functions are totally antisymmetric.

(2) Assuming that the space is unbounded (for simplicity), find the position representation $\langle r | p \rangle$ (i.e., the wave function) of the momentum ket $|p\rangle$ (use the $\delta$-function normalization).

(3) Let $r_i$ be the position vector of the $i$-th particle. Find the position representation of $|p, p'\rangle$. [This is of course virtually the same question as (1).]

For an $N$-particle system in the semi-classical limit, the calculation of trace in $Z$ may be performed as follows:

$$
\text{Tr} \rightarrow \frac{1}{N!} \int_{\mathbb{R}^{3N}} d\{r_k\} \prod_{k=1}^{N} \langle r_k | \cdots \prod_{k=1}^{N} | r_k \rangle
$$

$$
= \frac{1}{N!} \int_{\mathbb{R}^{3N}} d\{r_k\} \prod_{k=1}^{N} \langle r_k | \left[ \left( \int_{\mathbb{R}^{3N}} d\{p_k\} |\{p_i\}\rangle \langle \{p_i\}| \right) \cdots \left( \int_{\mathbb{R}^{3N}} d\{p_k\} |\{p_i\}\rangle \langle \{p_i\}| \right) \right] \prod_{k=1}^{N} | r_k \rangle.
$$

(4) Write $Z$ down using $h^{-3/2} e^{ir \cdot p/h} = \langle r | p \rangle$.

(5) The outcome of (4) must have the following form:

$$
\frac{1}{2h^6} \int dr_1 dr_2 dp dp' e^{-\beta(p^2 + p'^2)/2m} \cdot \cdot \cdot
$$

Perform the integrations with respect to $p$ and $p'$ in this expression and find $F(r_1, r_2)$ in the following formula:

$$
Z = \frac{1}{2h^6} \int dr_1 dr_2 dp dp' e^{-\beta(p^2 + p'^2)/2m} F(r_1, r_2).
$$

(6) $F$ may be interpreted as the Boltzmann factor coming from the effective interaction originating from particle statistics. Sketch the potential $(\times \beta)$ of this effective interaction for bosons and fermions.

Soln

(1) The ket $|p\rangle|p'\rangle$ must be correctly symmetrized; $+$ is for bosons and $-$ for
fermions:

\[ |p, p'\rangle = \frac{1}{\sqrt{2}} (|p\rangle|p'\rangle \pm |p'\rangle|p\rangle). \quad (DH11.43) \]

(2) \(|p\rangle\) describes a plane wave of wave vector \(k = p/\hbar\):

\[ \langle r|p\rangle \propto e^{i p \cdot r/\hbar}. \quad (DH11.44) \]

The normalization condition is

\[ \delta(p - p') = \frac{1}{\hbar^3} \int_{\mathbb{R}^3} d^3r \langle p'|r\rangle \langle r|p\rangle. \quad (DH11.45) \]

Therefore,

\[ \langle r|p\rangle = \frac{1}{\hbar^{3/2}} e^{i p \cdot r/\hbar}. \quad (DH11.46) \]

(3)

\[ \langle r_1|\langle r_2|p, p'\rangle = \frac{1}{\sqrt{2}} \langle r_1|p\rangle \langle r_2|p'\rangle \pm \langle r_1|p'\rangle \langle r_2|p\rangle. \quad (DH11.47) \]

(4) Using the results of (2) and (3), we get (the overall factor 1/2 comes from 1/N! in the definition of trace (DH11.39))

\[
Z = Tr e^{-\beta H} = \frac{1}{2} \int dr_1 dr_2 \langle r_1 \langle r_2 | e^{-\beta H} | r_1 \rangle | r_2 \rangle \\
= \frac{1}{2} \int dr_1 dr_2 \int dp dp' e^{-\beta (p^2 + p'^2)/2m} \left| \langle r_1 | r_2 \rangle | p, p' \rangle \right|^2 \\
= \frac{1}{2} \int dr_1 dr_2 \int dp dp' e^{-\beta (p^2 + p'^2)/2m} \frac{1}{2} \left| \langle r_1 | p \rangle \langle r_2 | p' \rangle \pm \langle r_1 | p' \rangle \langle r_2 | p \rangle \right|^2. \\

(DH11.48)

(DH11.49)

(DH11.50)

If we write the matrix elements explicitly,

\[
Z = \frac{1}{2\hbar^6} \int dr_1 dr_2 \int dp dp' e^{-\beta (p^2 + p'^2)/2m} \left[ 1 \pm Re \exp(i(p - p') \cdot (r_1 - r_2)/\hbar) \right].

(DH11.51)

(5) To obtain \(F\) we compute

\[
\frac{\int dp e^{-\beta (p^2/2m) + i p \cdot r/\hbar}}{\int dp e^{-\beta (p^2/2m)}} = e^{-mk_B T r^2/2\hbar^2}. \quad (DH11.52)\]

Hence,

\[ F = 1 \pm e^{-mk_B T (r_1 - r_2)^2/\hbar^2}. \quad (DH11.53) \]
If we introduce the effective potential $\phi$ by $F = e^{-\beta \phi}$, we get
\[
\beta \phi(r) = -\log[1 \pm e^{-mk_B T (r_1 - r_2)^2 / \hbar^2}].
\] (DH11.54)

The sketches of the potential are given in Fig. DH11.2.

As expected, the effective interaction is attractive for bosons, and repulsive for fermions.
Homework 12 due 9 am on April 23 (Tu), 2019.
Submit to compass2g

You may discuss with your friends AFTER you have made due efforts of your own to solve the problems. I trust you. I wish you to fully understand the solutions when you submit your homeworks (and get the full credit).

No solution without your justification will get any credit. You must know how to write proper reports. Writing only formulas is totally unacceptable; your solution must read as a proper English composition.

As to the use of TeX: It was announced that from week 10 use of TeX (of some version) would be strictly imposed. The purpose is that you learn how to write mathematics properly, so if proper math orthography would be met, anything, including extremely neat hand writing, will be accepted. You must use proper aligning of formulas, correct punctuations, and correct fonts, etc., even with handwriting. Errors in math orthography will be penalized (but at most 30\% of the total score). Except for punctuations most requirements will be automatically satisfied, if you use (La)TeX. With Words you will have to struggle to meet the requirement. Handwriting is strongly discouraged.

You may send me (yoono@illinois.edu) TeX questions like: how to write/program “…”?

1. [Cosmic background temperature]
At present, the cosmic background radiation is at 3 K. Suppose the universe expands adiabatically (but not necessarily quasistatically). What can you say about the temperature of the cosmic background radiation when the total volume of the universe was one half of the present volume?

2. [Electron-positron-photon equilibrium]
In Discussion 11.6 we discussed the electrons ‘e’ and the positrons ‘p’ in equilibrium
with the photon field (electromagnetic field) and determined their chemical potentials: \( \mu_e = \mu_p = 0 \).

1. Calculate the total energy \( E_p \) of electrons [You need not perform the integrals].
2. Find their \( T \) dependence.
3. Let \( E_{\text{hv}} \) be the total electromagnetic wave in this same volume. Which is larger, \( E_e \) or \( E_{\text{hv}} \)?

3. [Molecular vibration]

The vibrational spectrum of I\(_2\) is at (reciprocal wavelength) 213 cm\(^{-1}\).

1. What is the occupation number ratio of the ground and the first excited states at room temperature 300 K?
2. What is the contribution in % of vibration to the total \( C_V \)?