

Review Questions

(weeks of 20 and 27 July 2020)

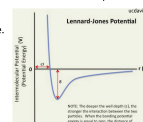
- The magnitude of the electric field due to an electric dipole, at a large distance from the dipole, depends on the distance as
- What are polar/non-polar molecules?
- The potential energy of interaction between a polar and non-polar molecule depends on the distance as
- Explain how a non-polar molecule can interact with an electric dipole?
- What is an induced electric dipole moment of a non-polar molecule?
- What does the electric polarizability quantify?
- What is the mechanism behind the London dispersion force? Is it **attractive** or repulsive?
- Name the contributions to the Van der Waals force.
- Sketch the approximate shape of the Lennard-Jones potential energy corresponding to intermolecular interaction.
- A spectrum of a diatomic molecule consists of electronic, vibrational and rotational energy levels. For these three groups of levels, the separation between the ground state and the first excited state is greatest for levels and smallest for levels.
- True or false?*
 - At the room temperature, transitions between electronic levels in a molecule can be induced by collisions with other molecules.
 - At the room temperature, transitions between rotational levels in a molecule can be induced by collisions with other molecules.
 - At the room temperature, transitions between vibrational levels in a molecule can be induced by collisions with other molecules.
- True** or false? Molecules without a permanent electric dipole moment cannot emit or absorb electromagnetic radiation as a result of transitions between rotational levels only.
- The selection rule for transitions between rotational levels of a molecule with a permanent electric dipole moment is
- Energies of photons emitted or absorbed by a diatomic molecule in a transition between rotational levels are typically in the part of the electromagnetic radiation spectrum.
- How, given the energy of a transition between rotational levels of a diatomic molecule, can we find the length of the bond?
- Why are the higher vibrational levels of a diatomic molecule not equally-spaced?
- Mark the correct answer. The force constant of the chemical bond in a HCl molecule is of the order of (a) 5 N/m, (b) 500 N/m, (c) 50 kN/m.



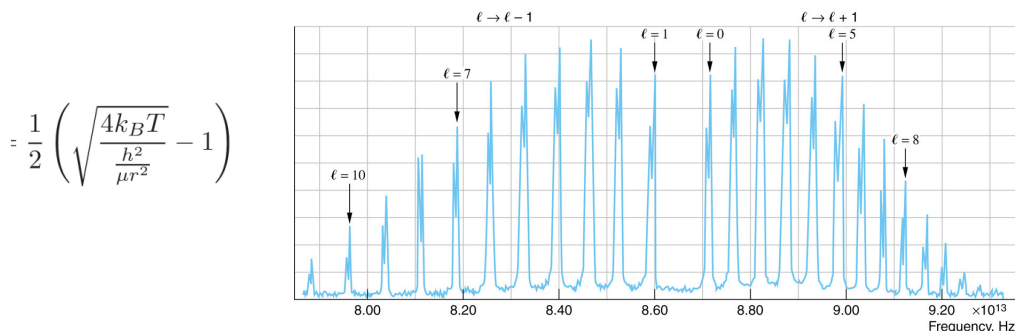
Components

- Repulsive component resulting from the Pauli exclusion principle that prevents the collapse of molecules.
- Attractive or repulsive electrostatic interactions between permanent charges or dipoles.
- Polarization term, i.e. attractive interaction between a dipole and an induced dipole.
- Attractive London dispersion force.

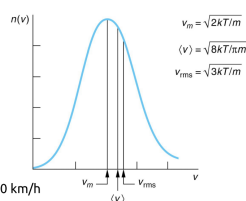
$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



18. **True** or false? The characteristic frequency of vibrations of a diatomic molecule with a permanent dielectric moment can be found directly from the absorption spectrum.
19. Why does the absorption spectrum of HCl have a double peak structure?
20. The figure below shows the absorption spectrum of a HCl molecule. How can we find the natural angular frequency of oscillations (i.e. the characteristic energy of vibrational energy levels)?



21. For a system of classical particles in equilibrium with a heat bath, the probability $f(E)dE$ of finding the in a microstate with energy $(E, E + dE)$ is given by the distribution



Z is the partition function.

$$f(E) = \frac{1}{Z} \exp\left(\frac{\dots\dots\dots}{\dots\dots\dots}\right)$$

Probability distribution (Boltzmann distribution) gives the probability of finding the "small" system in a microstate with energy ϵ_i

$$f_B(\epsilon_i) = \frac{1}{Z} \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

normalization factor (partition function) $Z = \sum_i e^{-\epsilon_i/k_B T}$ Boltzmann's constant $k_B = 1.38 \times 10^{-23} \text{ J/K}$

22. The distribution of molecular speeds in an ideal monoatomic classical gas is called the-..... (answer **Maxwell-Boltzmann**) distribution. The average speed of a particle of such a gas depends on the temperature as

23. Sketch the distribution of molecular speeds in an ideal monoatomic classical gas. This distribution is known as-..... distribution.

Mark the most probable speed, and (approximately): the average speed, and the root-mean square speed. How do they depend on temperature?

24. The average energy per particle in an ideal gas of (classical) monoatomic molecules is

25. State the equipartition principle (equipartition theorem).

26. How can you use the equipartition principle to argue that matter needs to have a discrete structure?

(Answer – idea: If it was continuous, there would be an infinite number of particles in a finite volume, each contributing $(3k_B T/2)$ to the average energy (assume monoatomic particles), implying that the average energy of a finite volume of matter is infinite.)

27. What is the heat capacity of a system at constant volume (average energy).

GASES

heat capacity at constant volume $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ (internal) energy per mole

volume kept constant

How $E = \underbrace{\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2}_{\text{translational DoF}} + \underbrace{\frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2}_{\text{rotational DoF}} + \underbrace{\frac{p^2}{2\mu} + \frac{1}{2}\mu\omega^2 s^2}_{\text{vibrational DoF}}$

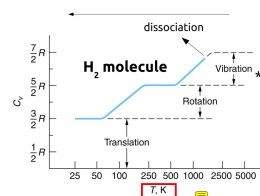
$\Rightarrow \frac{\partial}{\partial T} \left(\frac{7}{2} RT \right) = \frac{7}{2} R$

28. According to the equipartition principle, what is the heat capacity (at constant volume) of (a) monoatomic gas, (b) diatomic gas.

Does the equipartition principle predict its temperature dependence?

29. The contribution to the heat capacity of a diatomic gas at low temperatures is due to degrees of freedom.

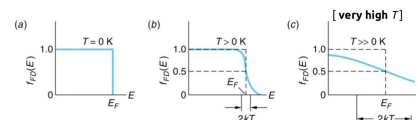
30. Sketch the temperature dependence of the specific heat of H_2 . On the temperature scale mark where particular degrees of freedom are activated.



31. A system of bosons is described by the-..... distribution function.

32. A system of fermions is described by the-..... distribution function.

33. State the general criterion that we use to decide whether a system of identical particles should be treated as a system of classical particles (i.e. distinguishable) or a system of quantum particles (i.e. indistinguishable).
34. Identical particles are distinguishable if the temperature is and particle concentration is
35. What is a (free) electron gas? What system can it model?
36. Why do we introduce periodic boundary conditions?
37. The concentration of electrons (the number of electrons per unit volume) in two metallic samples is n_1 and n_2 , with $n_1 < n_2$. What is the relation between the Fermi energies of these two metals?
38. What is the density of states?
39. The density of states in the 3D free electron gas depends on energy as (answer $\sim \sqrt{E}$; give the answer up to a multiplicative constant).
40. The same question for the 2D/1D case.
41. What is the Fermi energy?
42. The Fermi temperature for most of metals is of the order of 10^4 K.
43. Sketch the Fermi-Dirac distribution at $T = 0$ K and $T = T_F/100$.
44. (Choose the correct answer) At $T = T_F/100$ The fraction of electrons excited above the Fermi level is large/small.
45. Explain why there is no significant difference in the specific heat due to electrons in insulators and metals at high temperatures.
46. At low temperatures, the specific heat of metals has contributions due to both the crystal lattice and the itinerant electrons, depending on the temperature as The main contribution at low temperatures is due to
47. At high temperatures, the contribution to the specific heat of metals is mainly due to



Recall that $T_F \sim 10^4$ K. For the room temperature $T \sim 300$ K and $T/T_F \sim 1/100$.

Hence only a small fraction ($\sim 1\%$) of electrons can be excited above the Fermi level. Therefore their contribution to the specific heat (per mole) is only a small fraction of $(3/2) R$. That explains that there is no significant difference between the heat capacity of metals and insulators at high temperatures, which is $3 R$ (the law of Dulong-Petit) and is due to the atoms of the crystal lattice.

At low temperatures,

$$C_V = AT^3 + \gamma T$$

\nearrow lattice vibrations (phonons)
 \nwarrow electrons

i.e. the contribution due to electrons dominates.