Statistical Thermodynamics II
23743

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Aim

- In statistical thermodynamics II similar to statistical thermodynamics I, we deduce macroscopic properties of the system using microscopic properties of the constituent's of the system.
- In this course, we study equilibrium properties of dense systems as well as properties of non-equilibrium systems.
- Statistical Mechanics is about deducing macroscopic properties of a system from microscopic properties of the constituents of that same system (molecules).
- Equilibrium statistical mechanics aims at calculating equilibrium properties of the system, e.g., energy, entropy and free energy.
- Non-equilibrium statistical mechanics aims at calculating non-equilibrium (transport) properties of the system, e.g., chemical reaction rate, electrical conduction, heat conduction, absorption spectra and viscosity.

Note that

- At the end of this semester, at least in principle, you should be able to calculate both equilibrium and transport properties of any thermodynamic system.
- Raise your question and concern as it might be the question or concern of your classmates.
- Always remember that equations are the language of science but they never do suffice.
- Please engage in meta-cognition.

References

- Statistical Thermodynamics by Donald A. McQuarrie
- D.A. McQuarrie, Statistical Mechanics, University Science Books; 2000
- Statistical Thermodynamics, Theories and Applications by G. A. Parsafar (In Farsi)
- Terrell L. Hill, Statistical Mechanics: Principles and Selected Applications, Dover Publications; 1987
- Richard L. Liboff, Kinetic Theory: Classical, Quantum, and Relativistic Descriptions, Third edition, Springer, 2003.

Course structure

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Midterm exam	28 Ordibehesht 2 PM	Ch. 1 - 10 Thermo	35%
Final exam	6 Tir 9 am	Ch 11 - 15 Thermo, Ch. 13-14 Stat	45%
Class presentation	25 Khordad	10 Tir	20%

- Office hours: Due to specific situation resulting from Covid make appointment by email when you need to talk to me.

Topics

- Review of statistical thermodynamics I: the principle of a priori probabilities, various ensembles and expression of thermodynamic functions in terms of partition functions.
- Quantum statistics: Derivation of an equation of state for Fermi-Dirac ideal gas and for Bose-Einstein ideal gas, Blackbody radiation, density matrix, Classical limit for Q.
- Crystals: Einstein theory and Debye theory, Lattice dynamics, phonons, point defects.
- Real gases: Virial equation of state and quantum corrections to Virial coefficients.
- Radial distribution functions: classic monotonic liquids

Topics

- Perturbation theory: Thermodynamic properties of liquids.
- Debye-Huckel theory: Study of strong electrolyte solutions.
- Kinetic theory of gases: Molecular collisions, Boltzmann equation.
- Transport phenomena in dilute gases
- Brownian motion: Modeling by differential equations
- Time correlation functions: Linear response theory

Information

- In information theory, the entropy of a random variable is the average level of "information", "surprise", or "uncertainty" inherent in the variable's possible outcomes.
- Given a discrete random variable X, with possible outcomes $x_1, ..., x_n$, which occur with probability $\mathrm{P}(x_1), ..., \mathrm{P}(x_n)$, the entropy of X is formally defined as: $\mathrm{H}(X) = -\sum_{i=1}^{n} \mathrm{P}(x_i) \log \mathrm{P}(x_i)$
- An equivalent definition of entropy is the expected value of the self-information of a variable.
- The information content (also called the surprisal) of an event E is a function which decreases as the probability $p(E)$ of an event increases, defined by $I(E) = -\log_2(p(E))$ or equivalently $I(E) = \log_2(1/p(E))$
- Entropy measures the expected (i.e., average) amount of information conveyed by identifying the outcome of a random trial

Information

- The intuition behind quantifying information is the idea of measuring how much surprise there is in an event. Those events that are rare (low probability) are more surprising and therefore have more information than those events that are common (high probability).
- Shannon information, self-information, or simply the information, can be calculated for a discrete event x as follows: information(x) = -log(p(x))
- Calculating the information for a random variable is called information entropy, Shannon entropy, or simply entropy.
- The intuition for entropy is that it is the average number of bits required to represent or transmit an event drawn from the probability distribution for the random variable.

Information

- The information contained in a signal i, I_i depends on the probability of communicating that signal, p_i. $I_i(p_i)$ decreases as p_i increases.
- When independent signals i and j are communicated, $p_{ij} = p_i p_j$ and $I_{ij} = I_i + I_j$
- Thus $I_i = -k \ln p_i$.
- The microscopic state of a thermodynamic system can be considered as a signal.
- $-k \ln p_i$ is a piece of missing information in the system where $\mathrm{p_i}$ is the probability of the systems ith microstate.
- Average missing information $\bar{I} = \overline{-k \ln p_i} = -k \sum_i p_i \ln p_i$.
- Entropy of a system is equal to the average missing information $S = -k \sum_i p_i \ln p_i$

Quantum statistics

- All elementary particles with half-integral spin, e.g., electrons and protons, obey Fermi-Dirac statistics and are called fermions.
- Fermionic N-body wave-function changes sign upon the interchange of any two particles coordinate.
- Elementary particles with an integral spin obey Bose-Einstein statistics and are called bosons. Their N-body wave-function is unchanged upon the interchange of any two particles coordinate.
- For compound particles when the binding energy is greater than any other energy involved in the problem, an odd number of fermions give rise to a fermion, e.g., ^{3}He, while an even number of fermions give rise to a boson, e.g., ^{4}He.
- $\Xi(V, T, \lambda) = \Pi_k (1 \pm \lambda e^{-\beta \epsilon_k})^{\pm 1}$ where $\lambda = e^{\mu/kT}$
- $N = \sum_k \frac{\lambda e^{-\beta \epsilon_k}}{1 \pm \lambda e^{-\beta \epsilon_k}}$, upper sign $(+)$ corresponds to the FD statistics.

Quantum statistics

- $\bar{n}_k = \frac{\lambda e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}}$, lower sign (-) corresponds to the BE statistics.
- $\bar{E} = \sum_k \frac{\lambda \epsilon_k e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}}$
- $\bar{p}V = \pm kT \sum_k \ln(1 \pm \lambda e^{-\beta\epsilon_k})$
- Find an equation of state:
- One should solve λ in terms of N and $\beta\epsilon$'s, i.e., deriving λ as a function of N, V and T. To derive thermodynamic variables substituting such values of λ into the corresponding thermodynamic variables do the trick.
- In the limit of small λ FD and BE statistics both reduce to Boltzmann statistics where $\lambda = N/q$.
- Magnitude of λ is a measure of the systems quantum behavior.

Weakly degenerate ideal Fermi-Dirac gas

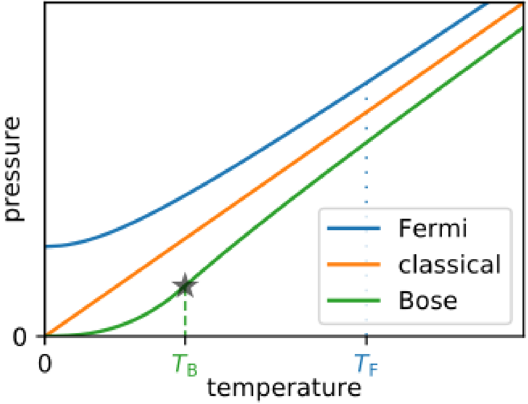
- An ideal Fermi gas is a state of matter which is an ensemble of many non-interacting fermions.
- examples are the behavior of charge carriers in a metal, nucleons in an atomic nucleus, neutrons in a neutron star, and electrons in a white dwarf.
- The total energy of the Fermi gas at absolute zero is larger than the sum of the single-particle ground states because the Pauli principle implies a sort of interaction or pressure that keeps fermions separated and moving.
- $N = \sum_{k=0}^{\infty} \frac{\lambda e^{-\beta\epsilon_k}}{1+\lambda e^{-\beta\epsilon_k}}$
- $pV = kT \sum_{k=0}^{\infty} \ln(1 + \lambda e^{-\beta\epsilon_k})$
- $\epsilon_{n_x,n_y,n_z} = \frac{h^2}{8mV^{2/3}}(n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, 3, \cdots$
- $\bar{n}_k = \frac{\lambda e^{-\beta\epsilon_k}}{1+\lambda e^{-\beta\epsilon_k}} \quad f(\epsilon) = \frac{1}{1+e^{\beta(\epsilon-\mu)}} = \frac{1}{1+e^{\beta\mu(\epsilon/\mu-1)}}$
- $N = \int_0^{\infty} \Omega(\epsilon) f(\epsilon) d\epsilon = (2s+1)2\pi(\frac{2m}{h^2})^{3/2} V \int_0^{\infty} \frac{\lambda\epsilon^{1/2}e^{-\beta\epsilon}}{1+\lambda e^{-\beta\epsilon}} d\epsilon$

Weakly degenerate ideal Fermi-Dirac gas

- $pV = kT\int_0^\infty \Omega(\epsilon)\ln(1+\lambda e^{-\beta\epsilon_k})d\epsilon =$ $(2s+1)2\pi kT(\frac{2m}{h^2})^{3/2}V\int_0^\infty \epsilon^{1/2}\ln(1+\lambda e^{-\beta\epsilon})d\epsilon$
- Expanding denominator (logarithm) in terms of λ and integration yields $\rho = \frac{1}{\Lambda^3}\sum_{l=1}^\infty \frac{(-1)^{l+1}\lambda^l}{l^{3/2}}$
- $\frac{p}{kT} = \frac{1}{\Lambda^3}\sum_{l=1}^\infty \frac{(-1)^{l+1}\lambda^l}{l^{5/2}}$
- Reversion of the first series to derive λ as a function of ρ and substituting the result in the second series, one derives the equation of state.
- Assume: $\lambda = a_0 + a_1\rho + a_2\rho^2 + \cdots$
- $\Lambda^3\rho = [(a_0 + a_1\rho + a_2\rho^2 + a_3\rho^3 + \cdots) - \frac{1}{2^{3/2}}(a_0 + a_1\rho + a_2\rho^2 + \cdots)^2 + \frac{1}{3^{3/2}}(a_0 + a_1\rho + a_2\rho^2 + \cdots)^3 + \cdots]$
- Derive $a_0 = 0 \quad a_1 = \Lambda^3 \quad a_2 - \frac{a_1^2}{2^{3/2}} = 0 \quad a_3 - \frac{a_1a_2}{2^{1/2}} + \frac{a_1^3}{3^{3/2}} = 0$
- $\lambda = \rho\Lambda^3 + \frac{1}{2^{3/2}}(\rho\Lambda^3)^2 + (\frac{1}{4} - \frac{1}{3^{3/2}})(\rho\Lambda^3)^3 + \cdots$

Weakly degenerate ideal Fermi-Dirac gas

- $\frac{p}{kT} = \rho + \frac{\Lambda^3}{2^{5/2}}\rho^2 + (\frac{1}{8} - \frac{2}{3^{5/2}})\Lambda^6\rho^3 + \cdots$
- Virial expansion: $\frac{p}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$
- Positive value of $B_2(T)$ increases pressure compared to its ideal gas value.



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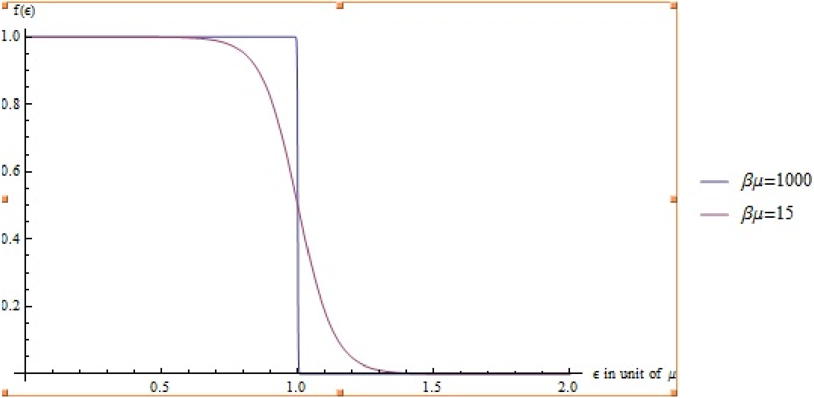
Weakly degenerate ideal Fermi-Dirac gas

- Quantum statistical effects decrease as the thermal De Broglie wavelength $\Lambda = (\frac{h^2}{2\pi mkT})^{1/2}$ decreases.
- $\frac{p}{\rho kT} = 1 + \frac{\Lambda^3\rho}{2^{5/2}} + (\frac{1}{8} - \frac{2}{3^{5/2}})(\Lambda^3\rho)^2 + \cdots$
- Thus $(\Lambda^3\rho)$ is a measure of quantum effects.
- $E = \sum_k \frac{\lambda\epsilon_k e^{-\beta\epsilon_k}}{1+\lambda e^{-\beta\epsilon_k}} = (2s+1)2\pi(\frac{2m}{h^2})^{3/2}V\int d\epsilon\frac{\lambda\epsilon^{3/2}e^{-\beta\epsilon}}{1+\lambda e^{-\beta\epsilon}} =$ $(2s+1)2\pi(\frac{2m}{h^2})^{3/2}V(kT)^{5/2}\int d(\beta\epsilon)\frac{(\beta\epsilon)^{3/2}\lambda e^{-\beta\epsilon}}{1+\lambda e^{-\beta\epsilon}} =$ $(2s+1)\frac{3}{2}VkT\frac{1}{\Lambda^3}\sum_{l=1}^{\infty}\frac{(-1)^{l+1}\lambda^l}{l^{5/2}} = (2s+1)\frac{3}{2}NkT(1+\frac{\Lambda^3}{2^{5/2}}\rho+\cdots)$

Strongly degenerate ideal Fermi-Dirac gas.

- $\bar{n}_k = \frac{\lambda e^{-\beta \epsilon_k}}{1+\lambda e^{-\beta \epsilon_k}} \quad f(\epsilon) = \frac{1}{1+e^{\beta(\epsilon-\mu)}} = \frac{1}{1+e^{\beta\mu(\epsilon/\mu-1)}}$
- Consider the limits $T \to 0$ ($\beta \to \infty$) and $T \to \infty$ ($\beta \to 0$).
- When $T \ll \mu_0/k$, $\quad f(\epsilon) = \begin{cases} 1 & \epsilon < \mu_0 \\ 0 & \epsilon > \mu_0 \end{cases}$, is an step function.
- 

Strongly degenerate ideal Fermi-Dirac gas.

- For electrons in an electron gas $\omega(\epsilon)d\epsilon = 4\pi(\frac{2m_e}{h^2})^{3/2}V\epsilon^{1/2}d\epsilon$.
- In the electron sea of a metal, Considering $T = 0,\ N = 4\pi(\frac{2m_e}{h^2})^{3/2}V\int_0^{\mu_0}\epsilon^{1/2}d\epsilon = \frac{8\pi}{3}(\frac{2m_e}{h^2})^{3/2}V(\mu_0)^{3/2}$
- Fermi energy of the electron sea in a metal: $\mu_0 = \frac{h^2}{2m_e}(\frac{3}{8\pi})^{2/3}(\frac{N}{V})^{2/3}$
- Use $V_{m,Na} = 23.7cm^3/mol$, to derive Sodium electrons Fermi energy and Fermi temperature, $T_F = \frac{\mu_0}{k}$.
- Zero point energy, $E_0 = 4\pi(\frac{2m}{h^2})^{3/2}V\int_0^{\mu_0}\epsilon^{3/2}d\epsilon = \frac{8\pi}{5}(\frac{2m}{h^2})^{3/2}V\mu_0^{5/2} = \frac{3}{5}N\mu_0$. Thus electrons do not contribute to the heat capacity of the metal.
- Zero point pressure, $p_0 = 4\pi kT(\frac{2m}{h^2})^{3/2}\int_0^{\mu_0}\epsilon^{1/2}\ln(1+e^{\beta(\mu-\epsilon)})d\epsilon$
- Degeneracy pressure: $p_0 = 4\pi(\frac{2m}{h^2})^{3/2}\int_0^{\mu_0}\epsilon^{1/2}(\mu_0-\epsilon)d\epsilon = 4\pi(\frac{2m}{h^2})^{3/2}[2/3-2/5]{\mu_0}^{5/2} = \frac{2}{5}N\mu_0/V$
- Given $\rho_{Na} = 0.971gr/cm^3$ and $M_{Na} = 22.99gr/mol$, find the zero point pressure for Sodium.

Strongly degenerate ideal Fermi-Dirac gas.

- Use $G = N\mu = E - TS + pV$ i.e., $S = \frac{E+pV-N\mu}{T}$ to derive zero point entropy, $S_0 = 0$.
- To find corrections to zero point thermodynamic quantities they can be written as $I = \int_0^\infty f(\epsilon)h(\epsilon)d\epsilon$. E.g.,

I	$h(\epsilon)$
N	$4\pi(\frac{2m}{h^2})^{3/2}V\epsilon^{1/2}$
E	$4\pi(\frac{2m}{h^2})^{3/2}V\epsilon^{3/2}$
p	$4\pi(\frac{2m}{h^2})^{3/2}V\epsilon^{1/2}\ln(1+\lambda e^{-\beta\epsilon})$

- $f(\epsilon)$ is a step function with rounded edges, therefore $f'(\epsilon)$ is zero except around $\epsilon = \mu_0$.
- Part by part integration: $I = -\int_0^\infty f'(\epsilon)H(\epsilon)d\epsilon$ where $H(\epsilon) = \int_0^\epsilon h(x)dx$ and $f'(\epsilon) = -\beta\frac{e^{\beta(\epsilon-\mu)}}{(1+e^{\beta(\epsilon-\mu)})^2}$.
- $H(\epsilon) = H(\mu) + (\epsilon-\mu)(\frac{dH}{d\epsilon})_{\epsilon=\mu} + \frac{1}{2}(\epsilon-\mu)^2(\frac{d^2H}{d\epsilon^2})_{\epsilon=\mu} + \cdots$
- $I = -\int_0^\infty f'(\epsilon)[H(\mu) + (\epsilon-\mu)(\frac{dH}{d\epsilon})_{\epsilon=\mu} + \frac{1}{2}(\epsilon-\mu)^2(\frac{d^2H}{d\epsilon^2})_{\epsilon=\mu} + \cdots]d\epsilon$

Strongly degenerate ideal Fermi-Dirac gas.

- $I = H(\mu)L_0 + (\frac{dH}{d\epsilon})_{\epsilon=\mu} L_1 + \frac{1}{2}(\frac{d^2H}{d\epsilon^2})_{\epsilon=\mu} L_2 + \cdots$ where $L_j = -\int_0^\infty (\epsilon-\mu)^j f'(\epsilon) d\epsilon$
- $L_0 = f(0) - f(\infty) = 1$
- $x = \beta(\epsilon-\mu) \quad L_j = \frac{1}{\beta^j} \int_{-\infty}^{\infty} \frac{x^j e^x}{(1+e^x)^2} dx \quad j = 0, 1, 2, \cdots$
- Considering the parity of the integrand $L_j = 0$ for odd values of j.
- $\int_{-\infty}^{\infty} \frac{x^2 e^x}{(1+e^x)^2} dx = \frac{\pi^2}{3}$. Thus $L_2 = \pi^2 (kT)^2/3$
- $I = H(\mu) + \frac{\pi^2}{6}(kT)^2 H''(\mu) + \cdots$
- $N = \int_0^\infty \frac{1}{1+e^{\beta(\epsilon-\mu)}} 4\pi (\frac{2m}{h^2})^{3/2} V \epsilon^{1/2} d\epsilon = -\int_0^\infty f'(\epsilon) H(\epsilon) d\epsilon =$ $4\pi(\frac{2m}{h^2})^{3/2} V\beta \int_0^\infty \frac{e^{\beta(\epsilon-\mu)}}{(1-e^{\beta(\epsilon-\mu)})^2} 2/3\epsilon^{3/2} d\epsilon =$ $\frac{8\pi}{3}(\frac{2m}{h^2})^{3/2} V\mu^{3/2}[1 + \frac{\pi^2}{8}(\beta\mu)^{-2} + \cdots]$
- $\mu_0 = \mu[1 + \frac{\pi^2}{8}(\beta\mu)^{-2} + \cdots]^{2/3} = \mu[1 + \frac{\pi^2}{12}(\beta\mu)^{-2} + \cdots]$
- $\frac{\mu}{\mu_0} = 1 - \frac{\pi^2}{12}(\beta\mu)^{-2} + \cdots$

Strongly degenerate ideal Fermi-Dirac gas

- Defining $\eta = (\beta\mu)^{-1}$ and substituting the value of μ on the right hand side $\mu = \mu_0[1 - \frac{\pi^2}{12}(\eta)^2 + \cdots]$
- Thus μ changes very slowly with temperature.
- Similarly $E = \frac{8\pi}{5}(\frac{2m}{h^2})^{3/2} V \mu^{5/2}[1 + \frac{5\pi^2}{8}(\beta\mu)^{-2} + \cdots] = E_0(\frac{\mu}{\mu_0})^{5/2}[1 + \frac{5\pi^2}{8}(\beta\mu)^{-2} + \cdots]$
- $E = E_0[1 + \frac{5\pi^2}{12}\eta^2 + \cdots]$
- $C_V = \frac{\pi^2 NkT}{2(\mu_0/k)} = \frac{\pi^2}{2} Nk(\frac{T}{T_F})$
- FD statistics is applied to electrons in metals, white dwarf stars and nuclear gases.

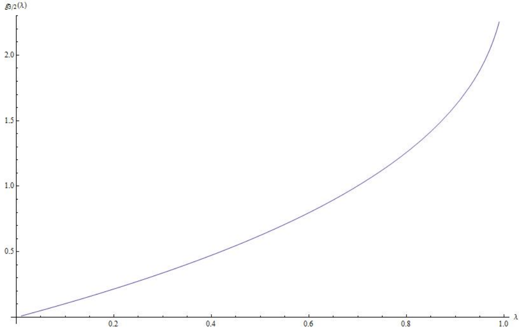
Ideal Bose-Einstein gas

- $N = \sum_k \frac{\lambda e^{-\beta \epsilon_k}}{1-\lambda e^{-\beta \epsilon_k}} \rightarrow \bar{n}_k = \frac{\lambda e^{-\beta \epsilon_k}}{1-\lambda e^{-\beta \epsilon_k}}$
- $pV = -kT \sum_k \ln(1 - \lambda e^{-\beta \epsilon_k})$
- For n_k to be positive and finite, $0 \leq \lambda = e^{\beta \mu} < e^{\beta \epsilon_0}$
- $N = \frac{\lambda e^{-\beta \epsilon_0}}{1-\lambda e^{-\beta \epsilon_0}} + \sum_{k \neq 0} \frac{\lambda e^{-\beta \epsilon_k}}{1-\lambda e^{-\beta \epsilon_k}} =$ $\frac{\lambda e^{-\beta \epsilon_0}}{1-\lambda e^{-\beta \epsilon_0}} + 2\pi (\frac{2m}{h^2})^{3/2} V \int_{\epsilon > \epsilon_0}^{\infty} \frac{\lambda \epsilon^{1/2} e^{-\beta \epsilon} d\epsilon}{1-\lambda e^{-\beta \epsilon}}$
- While in two dimensions $N = \frac{\lambda e^{-\beta \epsilon_0}}{1-\lambda e^{-\beta \epsilon_0}} + \frac{2\pi m}{h^2} A \int_{\epsilon > \epsilon_0}^{\infty} \frac{\lambda e^{-\beta \epsilon} d\epsilon}{1-\lambda e^{-\beta \epsilon}}$
- Setting $\epsilon_0 = 0 \quad \rho = \frac{N}{V} = 2\pi (\frac{2m}{h^2})^{3/2} \int_{\epsilon > 0}^{\infty} \frac{\lambda \epsilon^{1/2} e^{-\beta \epsilon}}{1-\lambda e^{-\beta \epsilon}} d\epsilon + \frac{\lambda}{V(1-\lambda)}$. In two dimension $\rho = \frac{N}{A} = \frac{2\pi m}{h^2} \int_{\epsilon > 0}^{\infty} \frac{\lambda e^{-\beta \epsilon}}{1-\lambda e^{-\beta \epsilon}} d\epsilon + \frac{\lambda}{A(1-\lambda)}$.
- $\frac{p}{kT} = -2\pi (\frac{2m}{h^2})^{3/2} \int_{\epsilon > 0}^{\infty} \epsilon^{1/2} \ln(1 - \lambda e^{-\beta \epsilon}) d\epsilon - \frac{1}{V} \ln(1 - \lambda)$ where $0 \leq \lambda < 1$.
- For dilute systems $\lambda \ll 1$ thus the $\frac{1}{V}$ term is negligible in the thermodynamic limit.

Weakly degenerate ideal Bose-Einstein gas

- In two dimensions $\frac{p}{kT} = -\frac{2\pi m}{h^2}\int_{\epsilon>0}^{\infty} \ln(1-\lambda e^{-\beta\epsilon})d\epsilon - \frac{1}{A}\ln(1-\lambda)$
- Evaluating integrals as power series in λ,
  $\rho = 2\pi(\frac{2m}{h^2})^{3/2}\int_{\epsilon>0}^{\infty} \lambda\epsilon^{1/2}e^{-\beta\epsilon}\sum_{l=0}^{\infty}(\lambda e^{-\beta\epsilon})^l d\epsilon =$
  $2\pi(\frac{2m}{h^2})^{3/2}\sum_{l=0}^{\infty}\lambda^{l+1}\int_{\epsilon>0}^{\infty}\epsilon^{1/2}e^{-\beta(l+1)\epsilon}d\epsilon =$
  $2\pi(\frac{2m}{h^2})^{3/2}\sum_{l=0}^{\infty}\lambda^{l+1}(\frac{1}{\beta(l+1)})^{3/2}2\int_0^{\infty}x^2e^{-x^2}dx =$
  $2\pi(\frac{2m}{h^2})^{3/2}\sum_{l=0}^{\infty}\lambda^{l+1}(\frac{1}{\beta(l+1)})^{3/2}2\frac{\sqrt{\pi}}{4} = \frac{1}{\Lambda^3}g_{3/2}(\lambda).$
  $x^2 = \beta(l+1)\epsilon \rightarrow d\epsilon = \frac{2xdx}{\beta(l+1)}$
- $g_n(\lambda) = \sum_{l=1}^{\infty}\frac{\lambda^l}{l^n}$
- In 2-D, $\rho = \frac{2\pi m}{h^2}\int_0^{\infty}\lambda e^{-\beta\epsilon}\sum_{l=0}^{\infty}(\lambda e^{-\beta\epsilon})^l d\epsilon =$
  $\frac{2\pi m}{h^2}\sum_{l=0}^{\infty}\lambda^{l+1}\int_0^{\infty}e^{-\beta(l+1)\epsilon}d\epsilon = \frac{2\pi m}{h^2}\sum_{l=0}^{\infty}\lambda^{l+1}\frac{1}{\beta(l+1)} =$
  $\frac{1}{\Lambda^2}\sum_{l=0}^{\infty}\frac{\lambda^{l+1}}{(l+1)} = \frac{-\ln(1-\lambda)}{\Lambda^2}$
- $\frac{p}{kT} = 2\pi(\frac{2m}{h^2})^{3/2}\int_0^{\infty}\epsilon^{1/2}\sum_{l=0}^{\infty}\frac{(\lambda e^{-\beta\epsilon})^{l+1}}{(l+1)}d\epsilon =$
  $2\pi(\frac{2m}{h^2})^{3/2}\sum_{l=0}^{\infty}\frac{(\lambda)^{l+1}}{(l+1)}\int_0^{\infty}\epsilon^{1/2}e^{-\beta(l+1)\epsilon}d\epsilon =$
  $2\pi(\frac{2m}{h^2})^{3/2}\sum_{l=0}^{\infty}\frac{(\lambda)^{l+1}}{(l+1)}(\frac{1}{\beta(l+1)})^{3/2}2\int_0^{\infty}x^2e^{-x^2}dx = \frac{1}{\Lambda^3}g_{5/2}(\lambda)$

Weakly degenerate ideal Bose-Einstein gas

- Writing λ in terms of ρ and substituting into the $\frac{p}{kT}$ expression yields the equation of state $\frac{p}{\rho kT} = 1 - \frac{\Lambda^3}{2^{5/2}}\rho + \cdots$
- A negative second virial coefficient implying an effective attraction among ideal bosons.
- 

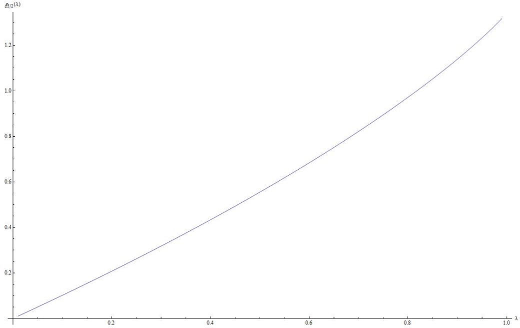
Strongly degenerate ideal Bose-Einstein gas

- $E = \frac{3}{2}VkT\frac{1}{\Lambda^3}g_{5/2}(\lambda) = \frac{3}{2}NkT(1 - \frac{\Lambda^3}{2^{5/2}}\rho + \cdots)$
- Average number of particles in the ground state $\bar{n}_0 = \frac{\lambda}{1-\lambda}$.
- Thus for bosons $0 \leq \lambda < 1$ while for fermions $0 \leq \lambda < \infty$.
- $\rho = \frac{1}{\Lambda^3}g_{3/2}(\lambda) + \frac{\lambda}{V(1-\lambda)}$
- In 2-D: $N = A\frac{-\ln(1-\lambda)}{\Lambda^2} + \frac{\lambda}{(1-\lambda)}$
- $\frac{p}{kT} = \frac{1}{\Lambda^3}g_{5/2}(\lambda) - \frac{1}{V}\ln(1-\lambda)$
- $g_{3/2}(1) = \sum_{l=1}^{\infty}\frac{1}{l^{3/2}} = \zeta(3/2) = 2.612$ but its first derivative diverges.
- Riemann zeta function, $\zeta(n) = \sum_{l=1}^{\infty}\frac{1}{l^n}$
- $\rho\Lambda^3 = g_{3/2}(\lambda) + \frac{\Lambda^3}{V}\frac{\lambda}{(1-\lambda)}$ cannot be solved analytically for λ and should be solved graphically.
- $\frac{\Lambda^3}{V}\frac{\lambda}{(1-\lambda)}$ is negligible compared to $g_{3/2}(\lambda)$ except when $\lambda = 1 - O(1/V) = 1 - a/V$.

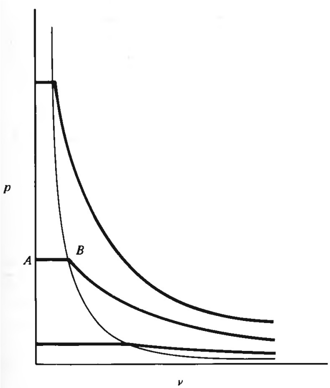
Strongly degenerate ideal Bose-Einstein gas

- $\lambda = \begin{cases} 1 - \frac{a}{V} & \rho\Lambda^3 > g_{3/2}(1) \\ \text{root of } g_{3/2}(\lambda) = \rho\Lambda^3 & \rho\Lambda^3 < g_{3/2}(1) \end{cases}$
- $a = \frac{\Lambda^3}{\rho\Lambda^3 - g_{3/2}(1)}$
- $\bar{n}_0 = \frac{\lambda}{1-\lambda} = \frac{V}{a} = \frac{V}{\Lambda^3}(\rho\Lambda^3 - g_{3/2}(1))$ when $\rho\Lambda^3 > 2.612$
- $\frac{\bar{n}_0}{N} = \frac{V(\rho\Lambda^3 - g_{3/2}(1))}{\Lambda^3\rho V} = 1 - \frac{g_{3/2}(1)}{\rho\Lambda^3}$
- Define T_0 via, $\rho\Lambda_0^3 = \rho(\frac{h^2}{2\pi mkT_0})^{3/2} = g_{3/2}(1)$
- $\frac{\bar{n}_0}{N} = \begin{cases} 1 - (\frac{T}{T_0})^{3/2} & T < T_0 \\ 0 & T > T_0. \end{cases}$
- Condensation of the molecules into their ground state around $T = T_0$ is called **Bose-Einstein condensation.**
- Define ρ_0 at constant T such that $\rho_0\Lambda^3 = g_{3/2}(1)$.
- $\frac{\bar{n}_0}{N} = \begin{cases} 1 - \frac{\rho_0}{\rho} & \rho > \rho_0, \\ 0 & \rho < \rho_0. \end{cases}$

Strongly degenerate ideal Bose-Einstein gas

- $\frac{p}{kT} = \frac{1}{\Lambda^3} g_{5/2}(\lambda) - \frac{1}{V} \ln(1-\lambda)$
- In the thermodynamic limit $\frac{p}{kT} = \frac{1}{\Lambda^3} g_{5/2}(\lambda) = \begin{cases} \frac{1}{\Lambda^3} g_{5/2}(\lambda) & \rho < \rho_0, \\ \frac{1}{\Lambda^3} g_{5/2}(1) & \rho > \rho_0. \end{cases}$
- $g_n(\lambda) = \sum_{l=1}^{\infty} \frac{\lambda^l}{l^n}$
- $g_{5/2}(1) = \zeta(\frac{5}{2}) = 1.342$
- 

Strongly degenerate ideal Bose-Einstein gas

- 

- Vapor pressure: $p_0(T) = \frac{kT}{\Lambda^3} g_{5/2}(1) = \frac{(2\pi m)^{3/2}(kT)^{5/2}}{h^3} g_{5/2}(1)$
- $\frac{dp_0}{dT} = \frac{5(2\pi m)^{3/2} k^{5/2} T^{3/2}}{2h^3} g_{5/2}(1) = \frac{5k}{2\Lambda^3} g_{5/2}(1)$
- Compare to Clapeyron
$$\frac{dp}{dT} = \frac{\Delta H_{cond}}{T\Delta V_{cond}} = \frac{\Delta H_{cond}}{TV_{m,nc}} = \frac{\Delta H_{cond}\rho_{nc}}{TN_A} = \frac{\Delta H_{cond}\rho_0}{TN_A} = \frac{\Delta H_{cond} g_{3/2}(1)}{\Lambda^3 TN_A}$$
- $\Delta H_{cond} = \frac{5}{2} kT \frac{g_{5/2}(1)}{g_{3/2}(1)}$

Strongly degenerate ideal Bose-Einstein gas

- $E = \sum_k \frac{\lambda \epsilon_k e^{-\beta\epsilon_k}}{1-\lambda e^{-\beta\epsilon_k}} = (2s+1)2\pi(\frac{2m}{h^2})^{3/2} V \int d\epsilon \frac{\lambda \epsilon^{3/2} e^{-\beta\epsilon}}{1-\lambda e^{-\beta\epsilon}} = \frac{3}{2}\frac{kTV}{\Lambda^3} g_{5/2}(\lambda)$
- $\frac{E}{N} = \begin{cases} \frac{3}{2}\frac{kTV_m}{\Lambda^3} g_{5/2}(\lambda) & T > T_0, \\ \frac{3}{2}\frac{kTV_m}{\Lambda^3} g_{5/2}(1) & T < T_0. \end{cases}$
- $\frac{C_v}{Nk} = \begin{cases} \frac{15}{4}\frac{V_m}{\Lambda^3} g_{5/2}(\lambda) - \frac{9}{4}\frac{g_{3/2}(\lambda)}{g_{1/2}(\lambda)} & T > T_0, \\ \frac{15}{4}\frac{V_m}{\Lambda^3} g_{5/2}(1) & T < T_0. \end{cases}$
- Condensation due to the effective interaction through the symmetry requirement of the N-body wavefunction of the system.
- ^{4}He has a spin of zero and exhibits a lambda transition.

An ideal gas of photons: Black body radiation

- $E(x,t) = \sin[\frac{2\pi}{\lambda}(x - ct)] = \sin(kx - \omega t)$ is a traveling wave.
- Describes a photon with energy $\epsilon = h\nu = \hbar\omega = \hbar ck$ and momentum$=\frac{h}{\lambda} = \hbar k$
- $\phi(x,t) = \sin(kx - \omega t) + \sin(kx + \omega t) = \sin(kx)\cos(\omega t) - \cos kx \sin \omega t + \sin(kx)\cos(\omega t) + \cos kx \sin(\omega t) = 2\sin kx \cos \omega t$
- Boundary condition $\rightarrow k = \frac{n\pi}{L} \quad n \in \mathcal{N}$
- Harmonic wave traveling in the positive x-direction: $E(x,t) = e^{i(kx - \omega t)}$
- Stationary wave: $E(x,t) = e^{i(kx-\omega t)} + e^{i(kx+\omega t)} = 2e^{ikx}\cos\omega t$
- In 3-D, $\vec{E}(r,t) = 2\vec{\sigma}e^{i(\vec{k}\cdot\vec{r} - \omega t)}$ is a traveling wave in direction $\vec{k}$.
- Polarization vector $\vec{\sigma}$ is perpendicular to the wave vector $\vec{k}$.
- For nodes to vanish at the boundaries of a cube $\vec{k} = \frac{\pi}{L}\vec{n}$, $\epsilon = \hbar c|\vec{k}| = \hbar ck$ and momentum $= \hbar|\vec{k}| = \hbar k$.
- $k^2 = \frac{\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2)$

An ideal gas of photons: Black body radiation

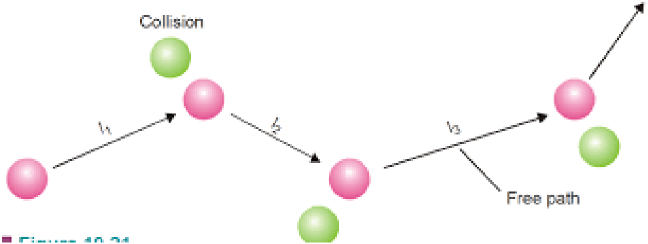
- Number of wavevectors with wavenumber $\leq k$: $\Phi(k) = \frac{\pi}{6}(\frac{Lk}{\pi})^3 = \frac{Vk^3}{6\pi^2}$.
- Number of wavevectors with wavenumber between k and $k + dk$: $\omega(k)dk = \frac{d\Phi}{dk}dk = \frac{Vk^2}{2\pi^2}dk$.
- There are two polarizations corresponding to each wavevector, thus $\omega(\epsilon)d\epsilon = \frac{V\epsilon^2 d\epsilon}{\pi^2 c^3 \hbar^3}$.
- $E(\{n_k\}) = \sum_k \epsilon_k n_k = \sum_k \hbar c k n_k$.
- $Q(V, T) = \sum_{\{n_k\}} e^{-\beta E(\{n_k\})} = \sum_{\{n_k\}} e^{-\beta \sum_k \epsilon_k n_k}$.
- $Q(V, T) = \sum_{\{n_k\}} \Pi_k (e^{-\beta\epsilon_k})^{n_k} = \Pi_k \sum_{n_k} (e^{-\beta\epsilon_k})^{n_k} = \Pi_k \frac{1}{1-e^{-\beta\epsilon_k}}$.
- $\ln Q(V, T) = -\sum_k \ln(1 - e^{-\beta\epsilon_k}) = -\frac{V}{\pi^2 c^3 \hbar^3} \int_0^\infty \epsilon^2 \ln(1 - e^{-\beta\epsilon}) d\epsilon = \frac{V}{\pi^2 c^3 \hbar^3} \int_0^\infty \epsilon^2 \sum_{n=1}^\infty e^{-n\beta\epsilon} d\epsilon = \frac{V}{\pi^2 c^3 \hbar^3} \frac{2}{\beta^3} \sum_{n=1}^\infty \frac{1}{n^4} = \frac{2V}{\pi^2 (c\hbar\beta)^3} \zeta(4)$ where $\zeta(4) = \pi^4/90$.
- $E = kT^2 (\frac{\partial \ln Q}{\partial T})_v = \frac{\pi^2 V (kT)^4}{15(\hbar c)^3}$.

An ideal gas of photons: Black body radiation

- Number of gas molecules striking a surface per unit area per unit time $= \rho \bar{v}/4$
- Energy incident per unit area per unit time on the wall $= cE(T)/4V$
- Stefan-Boltzmann law: Energy radiated per unit time, $R = \frac{cE}{4V} = \frac{\pi^2 (kT)^4}{60\hbar^3 c^2} = \sigma T^4$
- $p = kT(\frac{\partial \ln Q}{\partial V})_T = \frac{2(kT)^4}{\pi^2(\hbar c)^3}\zeta(4) = \frac{\pi^2(kT)^4}{45(\hbar c)^3}$
- $S = k \ln Q + kT(\frac{\partial \ln Q}{\partial T})_V = \frac{4\pi^2 V k (kT)^3}{45(\hbar c)^3}$
- $\bar{N}\mu = E - TS + pV = 0$ thus $\mu = 0$ for an ideal gas of photons.
- When the number of particles is not conserved $mA \leftrightarrow nA$, in equilibrium $\Delta G = mG - nG = (m-n)G = 0$. Thus $\lambda = 1$.
- $\ln Q = -\sum_\omega \ln(1 - e^{-\beta\hbar\omega})$ thus $E = \sum_\omega \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega$
- Noting $\frac{E}{V} = \int_0^\infty \rho(\omega, T) d\omega$ derive the black-body distribution law $\rho(\omega, T) d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega$

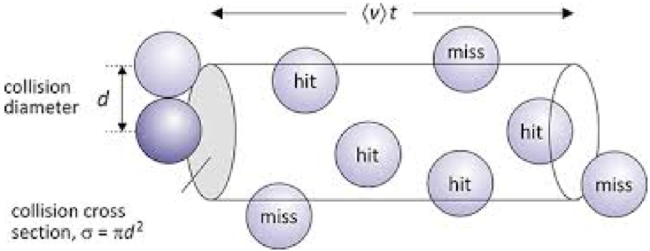
Kinetic theory of gases.

- Concentration of molecules: $n \equiv \frac{N}{V}$, characteristic distance between the molecules: $r_0 = n^{-1/3}$.
- Average number of collisions per unit time = volume of collision cylinder× molecules/unit volume $= \pi \rho^2 \bar{c} n$.



- Mean free path of a molecule? $\lambda = \frac{\bar{c}}{\pi \rho^2 \bar{c} n} = \frac{1}{\pi \rho^2 n}$. Assuming $\rho = \sigma \approx 3 \times 10^{-8}$ cm, $\lambda \approx 10^{-5}$ cm explains poor diffusion and thermal conduction in gases.

Kinetic theory

- 

- Velocity and speed distribution functions: $dN = NG(v_x, v_y, v_z)dv_x dv_y dv_z$.
- Normalization condition: $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} G(v_x, v_y, v_z)dv_x dv_y dv_z = 1$
- G only depends on speed $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$
- Differential volume in spherical coordinate $d^3v = dv \times vd\theta \times v\sin\theta d\phi$

Kinetic theory

- $dN_{v,\theta,\phi} = NG(v)v^2 dv d\Omega$, where $d\Omega \equiv \sin\theta d\theta d\phi$.
- Number of molecules within a spherical shell $dN_v = NG(v)4\pi v^2 dv = Nf(v)dv$
- Normalization: $\int_0^\infty f(v)dv = 1$. Also for a differential volume element, $dN_{v,\theta,\phi} = Nf(v)dv\frac{d\Omega}{4\pi}$.
- Molecular flux: $\Phi = \frac{dN}{dSdt}$
- $dN_{\theta,\phi}$ coming from direction Θ, ϕ within solid angle $d\Omega$ around dS.
- $dN_{\theta,\phi}$ molecules withing the slant cylinder with base dS and height $v\cos\theta dt$. $dN_v = ndSv\cos\theta dt$
- $dN_{v,\theta,\phi} = dN_v f(v)dv\frac{d\Omega}{4\pi} = ndSv\cos\theta dt f(v)dv\frac{\sin\theta d\theta d\phi}{4\pi}$
- $\Phi = \int \frac{dN_{v,\theta,\phi}}{dSdt} = n\int_0^\infty f(v)vdv\frac{1}{4\pi}\int_0^{\pi/2} d\theta \sin\theta\cos\theta \int_0^{2\pi} d\phi = \frac{n\bar{v}}{4}$

Kinetic theory

- $P = \frac{dp}{dSdt} = \int 2mv\cos\theta \frac{dN_{v,\theta,\phi}}{dSdt} =$
  $2nm\int_0^\infty f(v)v^2dv \frac{1}{4\pi}\int_0^{\pi/2} d\theta \sin\theta\cos^2\theta \int_0^{2\pi} d\phi = \frac{1}{3}nm\overline{v^2}$
- $PV = 1/3Nm\overline{v^2} = NkT \rightarrow 1/3m\overline{v^2} = kT$
- Equipartition theorem
- Heat capacity
- $G(v) = G(\sqrt{v_x^2 + v_y^2 + v_z^2}) = g(v_x)g(v_y)g(v_z)$
- $dN_{v_x} = N[\int\int_{-\infty}^{\infty} dv_y dv_z G(v)]dv_x = Ng(v_x)dv_x$
- $\ln G(v) = \ln g(v_x) + \ln g(v_y) + \ln g(v_z) \rightarrow \frac{G'(v)}{G}\frac{\partial v}{\partial v_x} = \frac{G'(v)}{G}\frac{v_x}{v} = \frac{g'(v_x)}{g(v_x)}$
- $\frac{1}{v}\frac{G'(v)}{G} = \frac{1}{v_x}\frac{g'(v_x)}{g(v_x)} = \frac{1}{v_y}\frac{g'(v_y)}{g(v_y)} = \frac{1}{v_z}\frac{g'(v_z)}{g(v_z)}$
- $\frac{1}{v}\frac{G'(v)}{G} = -2k, \qquad \frac{1}{v_x}\frac{g'(v_x)}{g(v_x)} = -2k$
- $G(v) = Ae^{-kv^2} \qquad g(v_x) = A^{1/3}e^{-kv_x^2}$

Kinetic theory

- $f(v) = 4\pi v^2 A e^{-kv^2} \qquad \int_0^\infty f(v)dv = 1 = \pi^{3/2} A k^{-3/2}$
- $\frac{3kT}{m} = \overline{v^2} = \int_0^\infty f(v) v^2 dv = \frac{3\pi^{3/2}}{2} A k^{-5/2}$
- $k = \frac{m}{2kT} \qquad A = (\frac{k}{\pi})^{3/2} = (\frac{m}{2\pi kT})^{3/2}$
- Maxwell-Boltzmann distribution: $f(v) = (\frac{m}{2\pi kT})^{3/2} 4\pi v^2 e^{-mv^2/2kT}$
- $g(v_x) = (\frac{m}{2\pi kT})^{1/2} e^{-\epsilon_x/kT}$
- $v_{rms}, \quad \bar{v}, \quad v_{mp}$
- Effusion, $\Phi \Delta S$
- $\Phi = \int dv \Phi_v$, where $\Phi_v = \frac{nv}{4} f(v)$
- $v_{ef,mp},$
- Diffusion is the movement of a substance from a region of high concentration to a region of low concentration without bulk motion.

Molecular diffusion

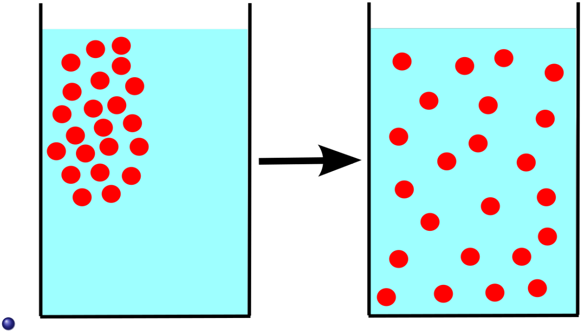


Figure: Molecular diffusion taken from `https://en.wikipedia.org`

- Fick's first law: the diffusion flux is proportional to the negative of the concentration gradient: $\mathbf{J} = -D\,\nabla n\ ,\quad J_i = -D\frac{\partial n}{\partial x_i}$.
- Transfer of a physical quantity N through a small area ΔS with normal ν per time Δt, $\quad \Delta N = (\mathbf{J}, \nu)\,\Delta S\,\Delta t$.

Molecular diffusion

- Dimensional analysis: $D(\frac{cm^2}{s}) \propto \lambda \bar{c}(\frac{cm^2}{s})$
- The rate at which molecules cross a unit area in one direction is $n\bar{c}/4$.
- Average vertical distance of the crossing molecules from the surface $= \frac{\int dv d\theta d\phi \lambda \cos\theta dN_{v,\theta,\phi}}{\int dv d\theta d\phi dN_{v,\theta,\phi}} = \lambda \frac{\int dv d\theta d\phi \cos\theta n dS v \cos\theta dt f(v) dv \frac{\sin\theta d\theta d\phi}{4\pi}}{\int dv d\theta d\phi n dS v \cos\theta dt f(v) dv \frac{\sin\theta d\theta d\phi}{4\pi}} =$ $\lambda \frac{\int dv d\theta d\phi v \cos^2\theta dt f(v) dv \sin\theta d\theta d\phi}{\int dv d\theta d\phi v \cos\theta dt f(v) dv \sin\theta d\theta d\phi} = \frac{2}{3}\lambda$
- Number of molecules crossing from above $\frac{\bar{c}}{4}[n_i(0) + \frac{2}{3}\lambda \frac{\Delta n_i}{\Delta d}]$. Number of molecules crossing from below $\frac{\bar{c}}{4}[n_i(0) - \frac{2}{3}\lambda \frac{\Delta n_i}{\Delta d}]$.
- Net flux $= -\frac{1}{3}\lambda \bar{c} \frac{\Delta n_i}{\Delta d} = -D \frac{\Delta n_i}{\Delta d}$. Thus $D = \frac{1}{3}\lambda \bar{c}$.

Viscosity coefficient

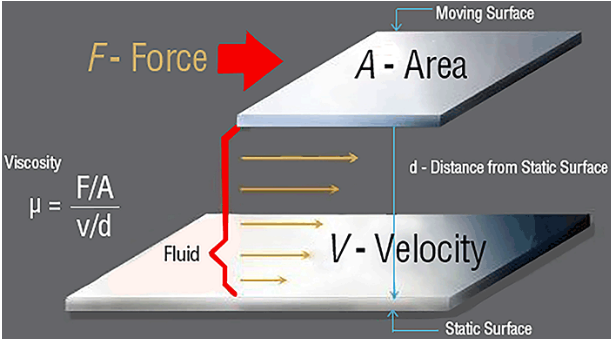
- 

Figure: Schematic for measuring viscosity courtesy of Hydraulic Institute `http://pumps.org`

Viscosity coefficient

- Dimensional analysis for viscosity coefficient: force/area $= -\eta \frac{\Delta u}{\Delta d}$. Thus η (gr/s cm). Achieved by writing $\eta \propto nm\bar{c}\lambda$
- Molecular origin of viscosity is transport of momentum among fluid layers.
- Average values of transported momentum two third mean free path above and below the reference plane is, respectively, $m(u + \frac{2}{3}\lambda\frac{\Delta u}{\Delta d})$ and $m(u - \frac{2}{3}\lambda\frac{\Delta u}{\Delta d})$.
- Multiplying by $n\bar{c}/4$ one finds momentum transport in each direction.
- momentum transport rate per unit area $= -\frac{1}{3}nm\bar{c}\lambda\frac{\Delta u}{\Delta d}$
- $\eta = \frac{1}{3}nm\bar{c}\lambda$

Conductivity

- To determine thermal conductivity we consider a reference plane perpendicular to the temperature gradient. At this plane average molecular energy is $u = c_v T$.
- Average energies $\frac{2}{3}\lambda$ above and below the the reference plane is respectively $u^+ = c_v(T + \frac{2}{3}\lambda\frac{\Delta T}{\Delta d})$ and $u^- = c_v(T - \frac{2}{3}\lambda\frac{\Delta T}{\Delta d})$
- rate of energy transport per unit area $=$ $\frac{n\bar{c}}{4}u^- - \frac{n\bar{c}}{4}u^+ = -\frac{1}{3}n\bar{c}c_v\lambda\frac{\Delta T}{\Delta d} = -\kappa\frac{\Delta T}{\Delta d}$
- $\kappa = \frac{1}{3}n\bar{c}c_v\lambda$

Density matrix

- A density matrix is a matrix that describes the statistical state of a system in quantum mechanics. The density matrix is especially helpful for dealing with mixed states, which consist of a statistical ensemble of several different quantum systems.
- State vectors, also called kets, describe only pure states, whereas a density matrix can describe both pure and mixed states.
- Describing a quantum state by its density matrix is a fully general alternative formalism to describing a quantum state by its ket or by its statistical ensemble of kets.
- It is often most convenient to use density matrices for calculations involving mixed states, and to use kets for calculations involving only pure states.
- The density matrix is the quantum-mechanical analogue to a phase-space probability measure (probability distribution of position and momentum).

Density matrix

- Mixed states arise in situations where the experimenter does not know which particular states are being manipulated.
- Examples include a system in thermal equilibrium at a temperature above absolute zero, or a system with an uncertain or randomly varying preparation history.
- Also, if a quantum system has two or more subsystems that are entangled, then each subsystem must be treated as a mixed state even if the complete system is in a pure state. The density matrix is also a crucial tool in quantum decoherence theory.
- The density matrix is a representation of a linear operator called the density operator. The density matrix is obtained from the density operator by choice of basis in the underlying space.
- Both matrix and operator are self-adjoint (or Hermitian), positive semi-definite, of trace one, and may be infinite-dimensional.

Partition function in terms of Density matrix

- $\hat{H}\psi_j = E_j\psi_j$ thus $\hat{H}^n\psi_j = E_j^n\psi_j$
- $e^{-\beta\hat{H}}\psi_j = (\sum_{n=0}^{\infty}\frac{(-\beta)^n}{n!}\hat{H}^n)\psi_j = \sum_{n=0}^{\infty}\frac{(-\beta)^n}{n!}\hat{H}^n\psi_j = \sum_{n=0}^{\infty}\frac{(-\beta)^n}{n!}E_j^n\psi_j = e^{-\beta E_j}\psi_j$
- $\psi_j^* e^{-\beta\hat{H}}\psi_j = \psi_j^* e^{-\beta E_j}\psi_j$ thus $e^{-\beta E_j} = \int \psi_j^* e^{-\beta\hat{H}}\psi_j d\tau$.
- $Q = \sum_j e^{-\beta E_j} = \sum_j \int \psi_j^* e^{-\beta\hat{H}}\psi_j d\tau = \sum_j (e^{-\beta\hat{H}})_{jj} = Tr(e^{-\beta\hat{H}})$
- If $\phi_j = \sum_n a_{jn}\psi_n$ then $a_{jn} = \int \psi_n^*\phi_j d\tau$
- $\sum_n a_{jn}^* a_{jn} = 1$
- Also $\psi_s = \sum_t b_{st}\phi_t$ where $b_{st} = \int \phi_t^*\psi_s d\tau = a_{ts}^*$ and $\sum_n b_{jn}^* b_{jn} = 1$.
- $\int \phi_j^* e^{-\beta\hat{H}}\phi_j d\tau = \sum_{m,n} a_{jm}^* a_{jn} e^{-\beta E_n}\int \psi_m^*\psi_n d\tau = \sum_{m,n} a_{jm}^* a_{jn} e^{-\beta E_n}\delta_{mn} = \sum_n a_{jn}^* a_{jn} e^{-\beta E_n}$
- Thus $\sum_j \int \phi_j^* e^{-\beta H}\phi_j d\tau = \sum_n e^{-\beta E_n} = Q$, i.e., trace is independent of the basis.

Average value in terms of Density matrix

- $\bar{M} = \frac{\sum_j M_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$
- $\sum_j M_j e^{-\beta E_j} = \sum_j e^{-\beta E_j} \int \psi_j^* \hat{M} \psi_j d\tau = \sum_j \int \psi_j^* \hat{M} e^{-\beta E_j} \psi_j d\tau = \sum_j \int \psi_j^* \hat{M} e^{-\beta \hat{H}} \psi_j d\tau = \sum_j (\hat{M} e^{-\beta \hat{H}})_{jj} = Tr(\hat{M} e^{-\beta \hat{H}})$
- $\bar{M} = \frac{Tr(\hat{M} e^{-\beta \hat{H}})}{Tr(e^{-\beta \hat{H}})}$
- Define, $\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Tr(e^{-\beta \hat{H}})}$ conclude $\bar{M} = Tr(\hat{M}\hat{\rho})$
- Corresponds to $\bar{M} = \frac{\int \cdots \int dpdqM(p,q)e^{-\beta H(p,q)}}{\int \cdots \int dpdqe^{-\beta H(p,q)}}$

Another representation for delta

- Assume $\{u_k(x)\}$ to constitute a complete basis.
- $\psi(x) = \sum_k a_k u_k(x)$ where $a_k = \int \psi(x) u_k^*(x) dx$
- $\psi(x) = \sum_k \int \psi(x') u_k^*(x') dx' u_k(x) = \int dx' \psi(x') (\sum_k u_k^*(x') u_k(x))$
- $\sum_k u_k^*(x') u_k(x) = \delta(x - x')$
- E.g.,
  $u_k(x) = e^{-ikx}, \quad \delta(x - x') = \frac{1}{2\pi} \int dk e^{-ik(x-x')} = \frac{1}{2\pi\hbar} \int dp e^{-\frac{i}{\hbar} p(x-x')}$

The classical limit of canonical partition function

- $Q = \sum_j \int \phi_j^* e^{-\beta \hat{H}} \phi_j dr$
- Should turn this expression into an integration over phase space.
- Consider eigenfunctions of the momentum operator, -$i\hbar\nabla$:
  $u(p_1 \cdots, r_N) = e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k}$
- $-i\hbar\nabla_i u = p_i u$
- Neglecting the symmetry requirement of the wave-function
  $\phi_j(r_1, \cdots, r_N) = \int \cdots \int A_j(p_1, \cdots, p_N) e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} dp_1 \cdots dp_N$
- $A_j(p_1, \cdots, p_N) = \frac{1}{(2\pi\hbar)^{3N}} \int \cdots \int \phi_j(r_1, \cdots, r_N) e^{-\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} dr_1 \cdots dr_N$

$$
\begin{aligned}
Q &= \sum_j \int \cdots \int \phi_j^*(r_1, \cdots, r_N) A_j(p_1, \cdots, p_N) e^{-\beta \hat{H}} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} dp_1 \cdots dr_N \\
&= \frac{1}{h^{3N}} \int \cdots \int [\sum_j \phi_j^*(r_1, \cdots, r_N) \phi_j(r_1', \cdots, r_N')] e^{-\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k'} \\
&\qquad \times e^{-\beta \hat{H}} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} dp_1 \cdots dr_N dr_1' \cdots dr_N'
\end{aligned}
$$

The classical limit of partition function

- $Q = \frac{1}{h^{3N}} \int \cdots \int e^{-\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} e^{-\beta \hat{H}} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} dp_1 \cdots dr_N$
- Define $e^{-\beta \hat{H}} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} = e^{-\beta H} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} w(p_1, \cdots, r_N, \beta) = F(p_1, \cdots, r_N, \beta)$
- $Q = \frac{1}{h^{3N}} \int \cdots \int e^{-\beta H} w(p_1, \cdots, r_N, \beta) dp_1 \cdots dr_N$
- Noting that $\hat{H} = U + \hat{K} = U - \sum_l \frac{\hbar^2}{2m_l} \nabla_l^2$
- $e^{-\beta \hat{H}} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} = (1 - \beta \hat{H} + \frac{\beta^2}{2} \hat{H}^2 - \frac{\beta^3}{3!} \hat{H}^3 + \cdots) e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} = e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} - \beta(U - \sum_l \frac{\hbar^2}{2m_l} \nabla_l^2) e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} + \frac{\beta^2}{2}[(U - \sum_l \frac{\hbar^2}{2m_l} \nabla_l^2)(U - \sum_n \frac{\hbar^2}{2m_n} \nabla_n^2)] e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} - \frac{\beta^3}{3!}[] e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} + \cdots = e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} - \beta(U + \sum_l \frac{p_l^2}{2m_l}) e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} + \frac{\beta^2}{2}(U - \sum_l \frac{\hbar^2}{2m_l} \nabla_l^2)[(U + \sum_l \frac{p_l^2}{2m_l}) e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k}] - \frac{\beta^3}{3!}[] e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} + \cdots = e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} - \beta(H) e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} + \frac{\beta^2}{2}[H^2 - \sum_l \frac{\hbar^2}{2m_l} \nabla_l^2 U - \sum_l \frac{i\hbar}{2m_l} \nabla_l U \cdot p_l) e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k}] - \frac{\beta^3}{3!}[] e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} + \cdots = (1 - \beta H + \frac{\beta^2 H^2}{2!} - \frac{\beta^3 H^3}{3!} + \cdots) e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} (1 + \hbar W') = e^{-\beta H} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} (1 + \hbar W')$

The classical limit of partition function

- $\frac{\partial F}{\partial \beta} = \frac{\partial}{\partial \beta} e^{-\beta \hat{H}} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} = \frac{\partial}{\partial \beta}(1 - \beta \hat{H} + \frac{\beta^2}{2}\hat{H}^2 - \cdots) e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} = -\hat{H}F$
- Bloch differential equation with the boundary condition $F(\beta = 0) = e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k}$
- $w(p_1, \cdots, r_N, \beta) = \sum_{l=0}^{\infty} \hbar^l w_l(p_1, \cdots, r_N, \beta)$
- $F(p_1, \cdots, r_N, \beta) = e^{-\beta H} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} w(p_1, \cdots, r_N, \beta) = e^{-\beta H} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} \sum_{l=0}^{\infty} \hbar^l w_l(p_1, \cdots, r_N, \beta)$
- $\frac{\partial F}{\partial \beta} = -\hat{H}F$, thus $\frac{\partial}{\partial \beta}[e^{-\beta H} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} \sum_{l=0}^{\infty} \hbar^l w_l(p_1, \cdots, r_N, \beta)] = -\hat{H}[e^{-\beta H} e^{\frac{i}{\hbar}\sum_{k=1}^{N} p_k \cdot r_k} \sum_{l=0}^{\infty} \hbar^l w_l(p_1, \cdots, r_N, \beta)]$
-

Crystals

- Normal coordinates allows us to treat a crystal as a system of independent particles.
- Consider a one dimensional lattice with the potential $U(\xi_1, \xi_2, \cdots, \xi_N)$.
- $U(\xi_1, \xi_2, \cdots, \xi_N) = U(0, 0, \cdots, 0) + \sum_{j=1}^{N} (\frac{\partial U}{\partial \xi_j})_0 \xi_j + \frac{1}{2} \sum_{i,j} (\frac{\partial^2 U}{\partial \xi_i \partial \xi_j})_0 \xi_i \xi_j + \cdots = U(0; \rho) + \frac{1}{2} \sum_{i,j} k_{ij} \xi_i \xi_j + \cdots$
- Define mass weighted Cartesian coordinates as $q_1 = \sqrt{m_1} x_1,\ q_2 = \sqrt{m_1} y_1,\ q_3 = \sqrt{m_1} z_1,\ \cdots$
- Define mass weighted Hessian $K_{MW} = (\frac{\partial^2 U}{\partial q_i \partial q_j})$.
- Diagonalizing this matrix the 3 smallest eigenvalues correspond to translation, while 2 or 3 next lowest frequencies correspond to rotation.
- Remaining eigenvalues correspond to the force constants of the molecule (crystal).

Crystals

- Normal coordinate analysis (diagonalizing the Hessian) results in 3N-6 (3N-5) uncoupled force constant, k_j and corresponding frequencies $\nu_j = \frac{1}{2\pi}(\frac{k_j}{\mu_j})^{1/2}$.
- Normal modes are concerted harmonic motion of all the atoms.
- $Q(\rho, T) = e^{-U(0;\rho)/kT}\prod_{j=1}^{3N-6} q_{vib,j} = \prod_{j=1}^{3N-6}(\frac{e^{-h\nu_j/2kT}}{1-e^{-h\nu_j/kT}})e^{-U(0;\rho)/kT}$
- $-\ln Q = \frac{U(0;\rho)}{kT} + \sum_j[\ln(1-e^{-h\nu_j/kT}) + \frac{h\nu_j}{2kT}] = \frac{U(0;\rho)}{kT} + \int_0^\infty[\ln(1-e^{-h\nu/kT}) + \frac{h\nu}{2kT}]g(\nu)d\nu$
- $\int_0^\infty g(\nu)d\nu = 3N$
- $E = U(0;\rho) + \int_0^\infty[\frac{h\nu e^{-h\nu/kT}}{1-e^{-h\nu/kT}} + \frac{h\nu}{2}]g(\nu)d\nu$
- $C_v = k\int_0^\infty(h\nu/kT)^2\frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2}g(\nu)d\nu$
- Equipartition of energy predicts a value of 3R for crystal heat capacity, known as Dulong and Petit law.
- T^3 law, $\lim_{T\to 0} C_v \propto T^3$.
- Einstein assumed that $g(\nu) = 3N\delta(\nu - \nu_E)$
- $C_v = 3Nk(\frac{h\nu_E}{kT})^2\frac{e^{-h\nu_E/kT}}{(1-e^{-h\nu_E/kT})^2} = 3Nk(\frac{\Theta_E}{T})^2\frac{e^{-\Theta_E/T}}{(1-e^{-\Theta_E/T})^2}$

Crystals

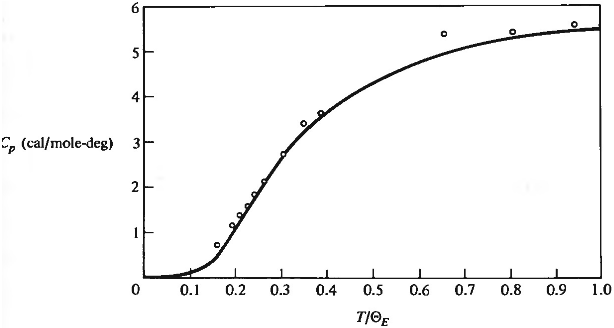
- 

  Figure 11–4. **Comparison of the experimental heat capacity of diamond with the prediction based on the Einstein theory with $\Theta_E = 1320$°K. (From C. Kittel.** ***Solid State Physics*****, 3rd** ***ed.***
- $\lim_{T \to 0} C_v = 3Nk(\frac{\Theta_E}{T})^2 e^{-\Theta_E/T}$
- A law of corresponding states for heat capacity.

Crystals: Debye theory

- Debye introduced a model for the specific heat of a material that extended Einsteins approach by formulating the lattice dynamics in terms of sound waves
- Debye theory assumes the crystal as a continuous vibrating medium.
- Standing wave described by the imaginary part of $u(\vec{r}, t) = 2\vec{A}e^{i\vec{k}\cdot\vec{r}} \cos \omega t$.
- For a cube of length L, the boundary condition in terms of the wavevector (phase variation for a plane wave per unit length) would be $\vec{k} = \frac{\pi}{L}\vec{n}$
- The magnitude of the wavevector is the wavenumber, $k^2 = (\frac{\pi}{L})^2(n_x^2 + n_y^2 + n_z^2)$
- $\Phi(k) = \frac{\pi}{6}(\frac{Lk}{\pi})^3 = \frac{Vk^3}{6\pi^2}$
- $\omega(k)dk = \frac{d\Phi}{dk}dk = \frac{Vk^2dk}{2\pi^2}$

Crystals: Debye theory

- Using $k = \frac{2\pi}{\lambda} = \frac{2\pi\nu}{v}$, $g(\nu)d\nu = \frac{4\pi V\nu^2}{v^3}d\nu$
- Since two traverse and one longitudinal wave correspond to each wavevector, $g(\nu)d\nu = (\frac{2}{v_t^3} + \frac{1}{v_l^3})4\pi V\nu^2 d\nu$
- Average velocity, $\frac{3}{v_0^3} \equiv \frac{2}{v_t^3} + \frac{1}{v_l^3}$ thus $g(\nu)d\nu = \frac{12\pi V}{v_0^3}\nu^2 d\nu$
- Since there are 3N vibrational modes, we introduce a cut off frequency called Debye frequency ν_D, $\int_0^{\nu_D} g(\nu)d\nu = 3N = \int_0^{\nu_D} \frac{12\pi V}{v_0^3}\nu^2 d\nu = \frac{4\pi V}{v_0^3}{\nu_D}^3$ thus $\nu_D = (\frac{3N}{4\pi V})^{1/3}v_0$
- $g(\nu)d\nu = \begin{cases} \frac{9N}{\nu_D^3}\nu^2 d\nu & 0 \leq \nu \leq \nu_D \\ 0 & \nu > \nu_D \end{cases}$

Crystals: Debye theory

- $C_v = k\int_0^{\infty}(h\nu/kT)^2 \frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2} g(\nu)d\nu =$ $k\int_0^{\nu_D}(h\nu/kT)^2 \frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})^2}\frac{9N}{\nu_D^3}\nu^2 d\nu,$ $C_V = 9Nk(\frac{T}{\Theta_D})^3\int_0^{\Theta_D/T}\frac{x^4e^x}{(e^x-1)^2}dx$ where $x = h\nu/kT$
- Debye function, $D(y) = 3y^3\int_0^{1/y}\frac{x^4e^x}{(e^x-1)^2}dx$, so $C_V = 3NkD(T/\Theta_D)$
- $\lim_{T\to\infty}\int_0^{\theta_D/T}\frac{x^4e^x}{(e^x-1)^2}dx = \int_0^{\theta_D/T}x^2dx = \frac{1}{3}(\frac{\Theta_D}{T})^3$ thus $C_V \to 3Nk$
- $\lim_{T\to 0}\int_0^{\theta_D/T}\frac{x^4e^x}{(e^x-1)^2}dx = \int_0^{\infty}\frac{x^4e^x}{(e^x-1)^2}dx = 4\pi^4/15$ Thus $C_V \to \frac{12\pi^4}{5}Nk(T/\Theta_D)^3$
- A law of corresponding states for heat capacity.

Crystals: Debye theory

- Elemental Debye temperature taken from Wikipedia:

Aluminium	428 K	Beryllium	1440 K
Cadmium	209 K	Caesium	38 K
Carbon	2230 K	Chromium	630 K
Copper	343 K	Germanium	374 K
Gold	170 K	Iron	470 K
Lead	105 K	Manganese	410 K
Nickel	450 K	Platinum	240 K
Rubidium	56 K	Sapphire	1047 K
Selenium	90 K	Silicon	645 K
Silver	215 K	Tantalum	240 K
Tin (white)	200 K	Titanium	420 K
Tungsten	400 K	Zinc	327 K

Crystals: Debye theory

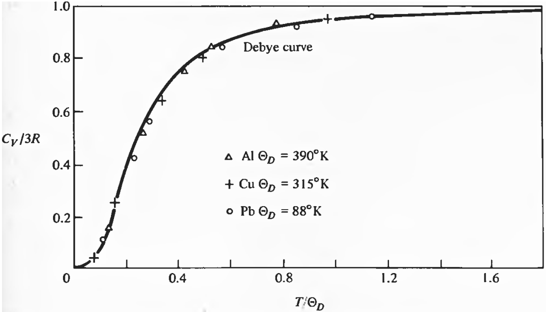
- 

Figure 11–7. **An illustration of the law of corresponding states predicted by the Debye theory.** (From F. Mandl, *Statistical Physics*. New York: Wiley, 1971).

Crystals: Lattice dynamics

- The subject of lattice dynamics is the study of the vibrations of the atoms in a crystal.
- The propagation of sound waves in crystals are a practical example of the role of lattice dynamics, as also is the interaction of materials with light.
- Lattice dynamics also gives us properties such as thermodynamics, superconductivity, phase transitions, thermal conductivity, and thermal expansion.
- atomic motions are frequently found to be adequately described as harmonic traveling waves. Each wave can be fully characterized in terms of its wavelength, λ, angular frequency, ω, amplitude and direction of travel.
- ω is a function of both k and the forces between atoms, and the amplitude of any wave is a function of $\vec{k}$ and temperature.
- In 1912 Born and von Karman created the model for lattice dynamics that introduced all the key components that are the foundation of the modern theory of lattice dynamics

Crystals: Lattice dynamics

- it was shown that atomic vibrations had a significant effect on the intensity of Bragg reflections in x-ray crystallography, which had quickly become the established technique for deducing the atomic structure of materials.
- early 1960s saw the development and refinement of the use of neutron scattering to measure vibrational frequencies, and in particular the development of the triple-axis spectrometer as the primary piece of instrumentation
- the development of the computer and programming languages, which on one hand made routine lattice dynamics calculations feasible, and on the other hand enabled experiments to be automated.
- Inelastic neutron scattering enabled the measurements of the frequencies of lattice waves for any chosen wave vector, $\omega(k)$.
- In the harmonic approximation Hamiltonian for a 1-D lattice consisting of a single type of oscillator, $H = \sum_{j=1}^{N} \frac{m}{2}\dot{\xi}_j^2 + \sum_{j=2}^{N} \frac{f}{2}(\xi_j - \xi_{j-1})^2$ where ξ is deviation from equilibrium position.

Crystals: Lattice dynamics

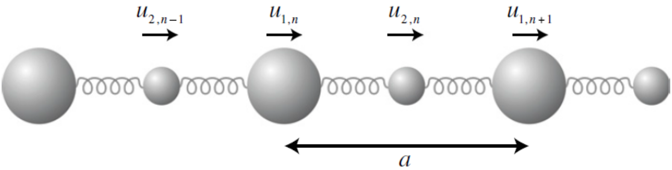
- harmonic approximation is effectively the only model for lattice dynamics that has an exact solution. it gives us many features that survive addition of higher-order terms. These include the link between vibrational frequencies, wave vector and interatomic forces and thermodynamic properties of materials.
- the harmonic model is easily adapted to incorporate quantum mechanics.
- not explained by the harmonic model include properties such as thermal expansion and thermal conductivity, and behavior such as phase transitions.
- $m\ddot{\xi}_j = f(\xi_{j+1} + \xi_{j-1} - 2\xi_j)$
- Assuming $\xi_j(t) = e^{i\omega t} y_j$, where y is the amplitude of lattice vibrations, gives difference equation $-m\omega^2 y_j = f(y_{j+1} + y_{j-1} - 2y_j)$
- Assuming $y_j = A^j$ and $A = e^{i\phi}$ results in $-m\omega^2 = f(e^{i\phi} + e^{-i\phi} - 2) = f(2\cos\phi - 2)$ or $\omega^2 = \frac{4f}{m}\sin^2(\phi/2)$
- $\omega = \omega_{max}|\sin(\phi/2)|$
- $\xi_j(t) = e^{i(\omega t + j\phi)}$ which repeats after $\delta j = 2\pi/\phi$

Crystals: 1-D Lattice dynamics

- $\lambda = a\delta j = 2\pi a/\phi$ thus $\phi = 2\pi a/\lambda \equiv ka$
- $\xi_j(t) = e^{i(\omega t + jka)}$
- Dispersion curve is frequency vs. wavevector $\omega = \omega_{max}|\sin(ka/2)|$ in the limit of very long wavelength $\omega = \omega_{max} ka/2$, i.e., $\frac{\omega}{k} = \lambda\nu = \omega_{max} a/2 =$ constant velocity.
- In general, phase velocity, $\lambda\nu = \frac{\omega}{k} = \frac{\omega_{max}}{k}|\sin(ka/2)| = c(k)$, this is the cause of light dispersion by a prism.
- Non-repetitive angular frequency is derived from $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$ since there is no difference between k and $k + 2\pi n/a$.
- Periodic boundary condition $\xi_j(t) = \xi_{j+N}(t) \rightarrow e^{iNka} = 1 \rightarrow k = 2\pi j/Na \rightarrow j = \pm 1, \pm 2, \cdots, \pm N/2$
- $E = \sum_{j=-N/2}^{N/2} \frac{\hbar\omega_j}{e^{\beta\hbar\omega_j}-1} = \int_{j=-N/2}^{N/2} \frac{\hbar\omega_j}{e^{\beta\hbar\omega_j}-1} dj = \frac{Na}{\pi} \int_0^{\pi/a} \frac{\hbar\omega(k)dk}{e^{\beta\hbar\omega(k)}-1}$
- $dk = \frac{d}{d\omega}[\frac{2}{a}\sin^{-1}(\frac{\omega}{\omega_{max}})]d\omega = \frac{2d\omega}{a(\omega_{max}^2-\omega^2)^{1/2}}$
- Thus $E = \frac{2N}{\pi} \int_0^{\omega_{max}} \frac{\hbar\omega d\omega}{[e^{\beta\hbar\omega}-1][\omega_{max}^2-\omega^2]^{1/2}}$
- Comparing with $E = \int_0^{\infty} [\frac{h\nu e^{-h\nu/kT}}{1-e^{-h\nu/kT}} + \frac{h\nu}{2}]g(\nu)d\nu$

Crystals: 1-D Lattice dynamics

- $g(\nu) = \frac{2N}{\pi} \frac{1}{(\nu_{max}^2 - \nu^2)^{1/2}}$
- $d\nu/dk$ is group velocity of the wave and represents the rate of energy transmission of the wave.
- For a continuum group velocity and phase velocity are equal and constant.
- 1 D lattice with alternating masses m_1 and m_2.



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- $H = \sum_{j=1}^{N} [\frac{m_1}{2} \dot{\xi}_{2j}^2 + \frac{m_2}{2} \dot{\xi}_{2j-1}^2] + \frac{f}{2} \sum_{j=1}^{N} [(\xi_{2j} - \xi_{2j-1})^2 + (\xi_{2j+1} - \xi_{2j})^2]$
- Defining $\omega_0^2 = \frac{f}{\mu}$, one derives $\omega^2 = \omega_0^2 [1 \pm (1 - \frac{4 m_1 m_2 \sin^2 \phi}{(m_1 + m_2)^2})^{1/2}]$
- High frequency branch is called the optical branch while low frequency branch is called acoustical branch.
- Lattice vibrations of a salt produce a vibrating dipole moment which in turn produces an infrared absorption band.

Crystals: Phonons

- $E(\{n_j\}) = \sum_{j=1}^{3N} h\nu_j(n_j + \frac{1}{2}) = \sum_{j=1}^{3N} h\nu_j n_j + \sum_{j=1}^{3N} \frac{h\nu_j}{2} = \sum_{j=1}^{3N} h\nu_j n_j + E_0$
- Interpret as the sum of independent particle energies.
- Occupation numbers $\{n_j\}$ completely specify the state of the system.
- Treat vibrations of the lattice, quasi-particles known as phonons, as an ideal Bose-Einstein gas.
- Phonons are quanta of lattice vibrations as photons are quanta of electromagnetic vibrations.
- $\bar{n}_j = \frac{\lambda e^{-\beta\epsilon_j}}{1-\lambda e^{-\beta\epsilon_j}} = \frac{1}{\lambda^{-1}e^{\beta\epsilon_j}-1}$
- When the number of particles is not conserved $mA \leftrightarrow nA$, in equilibrium $\Delta G = m\mu - n\mu = (m-n)\mu = 0$. Thus $\lambda = 1$.
- $\bar{n}_j = \frac{\lambda e^{-\beta\epsilon_j}}{1-\lambda e^{-\beta\epsilon_j}} = \frac{1}{\lambda^{-1}e^{\beta\epsilon_j}-1} = \frac{1}{e^{\beta\epsilon_j}-1}$
- $\bar{E} = E_0 + \sum_{j=1}^{3N} h\nu_j \bar{n}_j = E_0 + \sum_{j=1}^{3N} \frac{h\nu_j}{e^{\beta\epsilon_j}-1} = E_0 + \int_0^\infty \frac{h\nu}{e^{\beta h\nu}-1} g(\nu) d\nu$
- $C_V =$

Crystals: Point defects

- Conductivity, color, mechanical and elastic properties of crystals and diffusion in crystals depend on crystal defects.
- A missing atom or ion is called a Schottky defect.
- ϵ_s is the energy required to bring an atom from interior to the surface.
- $A = E - TS = n\epsilon_s - kT \ln \frac{N!}{n!(N-n)!}$
- $(\frac{\partial A}{\partial n})_T = 0 \rightarrow n \approx Ne^{-\epsilon_s/kT}$
- Frenkel defect is displacement of an atom from a lattice to an interstitial position, call energy cost ϵ_I.
- If N is the number of lattice sites and N' the number of interstitial sites $A(n) = n\epsilon_I - kT \ln[\frac{N!}{n!(N-n)!} \frac{N'!}{n!(N'-n)!}]$
- $(\frac{\partial A}{\partial n})_T = 0 \rightarrow n \approx (NN')^{1/2} e^{-\epsilon_I/2kT}$
- Schottky most common in Alkali halides, while Frenkel in silver halides.
- Schottky defects lower the density.

Crystals: Point defects

- Defects change conductivity.
- Probability per unit time that an atom pass over a barrier is $p \approx \nu e^{-\epsilon/kT}$
- Two parallel planes of impurity atoms separated by lattice constant a. C impurity atoms on one plane and c+a(dc/dx) on other
- pa(dc/dx) crossing between these planes. where c=na
- $j = -pa^2(\frac{\partial n}{\partial x})$
- Fick's law $j = -D(\frac{\partial n}{\partial x})$, thus $D = pa^2 \approx \nu a^2 e^{-\epsilon/kT}$
- Color center
- F-Center

Liquids: A hole theory, theory of significant structures

- In 1930's Eyring considered a liquid as a solid with many vacant sites.
- Partition function is assumed a product of a gas like and a solid like partition functions.
- V is liquid volume while V_s is solid volume.
- $N(V - V_s)/V$ is number of gas like molecules while NV_s/V is the number of solid like molecules.
- $Q_g = [(\frac{2\pi mkT}{h^2})^{3/2} V_g]^{N_g}/N_g! =$ $[(\frac{2\pi mkT}{h^2})^{3/2}(V - V_s)]^{N(V-V_s)/V}[\frac{N(V-V_s)}{V}!]^{-1}$
- I.e., molecules beside holes behave as gas while molecules surrounded by other molecules behave as solid.
- Positional degeneracy causes $1 + n_h e^{-\epsilon/kT}$ positions to be available to each solid like molecule.

Liquids: A hole theory, theory of significant structures

- Use Einstein approximation for the solid like atoms $Q_s = e^{-U(0,\rho)/kT}[\frac{e^{-\Theta_E/2T}}{(1-e^{-\Theta_E/T})}]^{3N_s}$
- $U(0,\rho) = N_s\phi_0/2$
- $Q_s = [\frac{e^{-\phi(0)/2kT}e^{-3\Theta_E/2T}}{(1-e^{-\Theta_E/T})^3}]^{N_s} = [\frac{e^{E_s/kT}}{(1-e^{-\Theta_E/T})^3}]^{N_s}$
- $Q_{sl} = [\frac{e^{E_s/kT}}{(1-e^{-\Theta_E/T})^3}(1 + n_h e^{-\epsilon/kT})]^{NV_s/V}$
- $Q = [\frac{e^{E_s/kT}}{(1-e^{-\Theta_E/T})^3}(1 + n_h e^{-\epsilon/kT})]^{NV_s/V}[(\frac{2\pi mkT}{h^2})^{3/2}(V - V_s)]^{N(V-V_s)/V}[\frac{N(V-V_s)}{V}!]^{-1}$

Liquids: A cell theory, Lennard-Jones Devonshire theory

- Lennard-Jones Devonshire (LJD) cell theory is a lattice approximation to the liquid state.
- Historically LJD was the prototype microscopic model to predict the location of the liquid-vapor critical point of a simple fluid and, as such, is widely employed as an introduction to mean field theory in a number of standard texts and papers.
- particles are considered to be localized in singly occupied cells, centered on the sites of a fully occupied lattice (of some prescribed symmetry), within which they move independently.
- Consider liquid as a set of molecules each moving in its own cage.

Liquids: A cell theory, Lennard Jones-Devonshire theory

- $V_f = \int_\Delta e^{-[\phi(r)-\phi(0)]/kT} dr$
- $q = (\frac{2\pi mkT}{h^2})^{3/2} V_f$
- $Q = e^{-N\phi(0)/2kT}[(\frac{2\pi mkT}{h^2})^{3/2} V_f]^N$ similar to Einstein partition function $Q = e^{-N\phi(0)/2kT}[(q_{vib})^3]^N$
- Assuming $\phi(r) - \phi(0) = \frac{f}{2} r^2, \quad V_f = \int_0^\infty 4\pi r^2 e^{-fr^2/2kT} dr = (\frac{2\pi kT}{f})^{3/2}$
- $q = (\frac{2\pi mkT}{h^2})^{3/2} (\frac{2\pi kT}{f})^{3/2} = (\frac{kT}{h\nu})^3$ where $\nu = \frac{1}{2\pi}\sqrt{f/m}$
- For an ideal gas $S = Nk + Nk \ln[(\frac{2\pi mkT}{h^2})^{3/2} \frac{Ve^{3/2}}{N}]$. If each atom where confined to a volume $V/N, \quad Q = (\frac{2\pi mkT}{h^2})^{3N/2} (\frac{V}{N})^N$ and $S = Nk \ln[(\frac{2\pi mkT}{h^2})^{3/2} \frac{Ve^{3/2}}{N}]$.
- Communal entropy of a gas is Nk.
- Partition function is multiplied by e^N to introduce communal entropy.

Liquids: A cell theory, Lennard-Jones Devonshire theory

- $Q = e^{-N\phi(0)/2kT}[(\frac{2\pi mkT}{h^2})^{3/2} V_f e]^N$
- Assume all C nearest neighbors to spread uniformly around the center of the cage in a distance a determined by number density, e.g., for an FCC lattice C=12 and $a^3 = \sqrt{2}\frac{V}{N}$
-

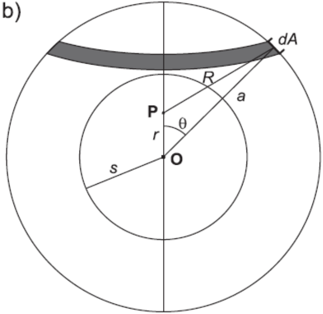


Figure: Taken from arXiv:cond-mat/0111240v1

Liquids: A cell theory, Lennard-Jones Devonshire theory

- $C\frac{2\pi a^2 \sin\theta d\theta}{4\pi a^2} = \frac{C}{2}\sin\theta d\theta$
- $u(R)\frac{C}{2}\sin\theta d\theta$ where $R^2 = r^2 + a^2 - 2ar\cos\theta$
- $\phi(r) = \frac{C}{2}\int_0^\pi u(R)\sin\theta d\theta$
- Lennard-Jones potential $u(R) = \epsilon(\frac{r^*}{R})^{12} - 2\epsilon(\frac{r^*}{R})^6$ where ϵ is the potential well depth and r^* is the equilibrium distance of molecules.
- $\phi(r) = \frac{C}{2}\int_0^\pi[\epsilon(\frac{r^*}{\sqrt{r^2+a^2-2ar\cos\theta}})^{12} - 2\epsilon(\frac{r^*}{\sqrt{r^2+a^2-2ar\cos\theta}})^6]\sin\theta d\theta =$ $C\epsilon[\frac{r^{*12}}{2}\int_0^\pi \frac{\sin\theta d\theta}{(r^2+a^2-2ar\cos\theta)^6} - r^{*6}\int_0^\pi \frac{\sin\theta d\theta}{(r^2+a^2-2ar\cos\theta)^3}]$
- Assuming $x = r^2 + a^2 - 2ar\cos\theta$ and $dx = 2ar\sin\theta d\theta$, $\phi(r) = C\epsilon\frac{1}{2ar}[\frac{r^{*12}}{2}\int_{(r-a)^2}^{(r+a)^2}\frac{dx}{x^6} - r^{*6}\int_{(r-a)^2}^{(r+a)^2}\frac{dx}{x^3}] = \frac{C\epsilon}{2ar}r^{*6}[\frac{1}{2}x^{-2}|_{(r-a)^2}^{(r+a)^2} -$ $\frac{r^{*6}}{10}x^{-5}|_{(r-a)^2}^{(r+a)^2}] = \frac{C\epsilon}{4ar}r^{*6}[\frac{1}{(r+a)^4} - \frac{1}{(r-a)^4} - \frac{r^{*6}}{5}(\frac{1}{(r+a)^{10}} - \frac{1}{(r-a)^{10}})]$
- $\phi(0) = 0$
- $a' = a/r^*$ and $r' = r/r^*$
- $\phi(r') = \frac{C\epsilon}{4a'r'}[\frac{1}{(r'+a')^4} - \frac{1}{(r'-a')^4} - \frac{1}{5}(\frac{1}{(r'+a')^{10}} - \frac{1}{(r'-a')^{10}})]$

Liquids: A cell theory, Lennard-Jones Devonshire theory

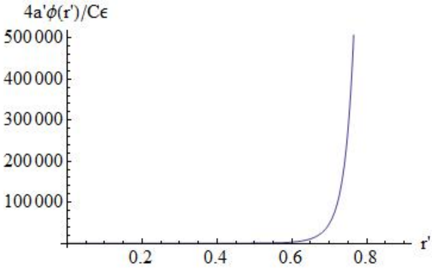


Figure: Cage potential deduced from a 12-6 potential

- $V_f = \int_0^\infty e^{-[\phi(r)-\phi(0)]/kT} dr = r^* \int_0^\infty e^{-[\frac{C\epsilon}{4a'r'}[\frac{1}{(r'+a')^4} - \frac{1}{(r'-a')^4} - \frac{1}{5}(\frac{1}{(r'+a')^{10}} - \frac{1}{(r'-a')^{10}})]]/kT} dr'$

A molecule in an Electric field

- $\delta w = N\sum_j \pi_j d\epsilon_j = N\sum_j \pi_j(\frac{\partial \epsilon_j}{\partial V})dV = -N\sum_j \pi_j p_j dV = -\bar{p}dV$
- $\mu_{jz} = -(\frac{\partial \epsilon_j}{\partial E_z})_V$ and $\delta w_j = -\mu_{jz} dE_z$
- The electric dipole moment is a measure of the separation of positive and negative electrical charges within a system $\bar{\mu}_z = \sum_j \pi_j \mu_{jz}$
- $\delta w = \sum_j \pi_j(\frac{\partial \epsilon_j}{\partial E_z})_V dE_z = -\bar{\mu}_z dE_z$
- $\delta w = -N\bar{\mu}_z dE_z = -\bar{M}_z dE_z$
- An object with an electric dipole moment is subject to a torque τ when placed in an external electric field. The torque tends to align the dipole with the field. $\vec{\tau} = \vec{\mu} \times \vec{E}$
- $u_d = -\vec{\mu} \cdot \vec{E}$ and $\vec{\mu}_{ind} = \alpha \vec{E}$,
- $u_p = -\int_0^E \mu_{ind} dE' = -\frac{\alpha}{2}E^2$
- $u(\vec{E}) = -\vec{\mu} \cdot \vec{E} - \frac{\alpha}{2}E^2$

A molecule in an Electric field

- For a molecule in an external electric field use perturbation theory. $(\hat{H} - \hat{\mu} \cdot \vec{E})\psi = \epsilon\psi \rightarrow (\hat{H} - \hat{\mu} \cdot \vec{E})\psi_k = \epsilon_k \psi_k$.
- $\psi_k^{(0)}$ and $\epsilon_k^{(0)}$ are respectively wave-functions and energy levels of molecule in the absence of external electric field.
- Without loss of generality assume electric field to be in the z direction $\psi_k = \psi_k^{(0)} + \psi_k^{(1)} E_z + \psi_k^{(2)} E_z^2 + \cdots$.
- $\epsilon_k = \epsilon_k^{(0)} + \epsilon_k^{(1)} E_z + \epsilon_k^{(2)} E_z^2 + \cdots$
- $(\hat{H} - \mu_z E_z)(\psi_k^{(0)} + \psi_k^{(1)} E_z + \psi_k^{(2)} E_z^2 + \cdots) =$ $(\epsilon_k^{(0)} + \epsilon_k^{(1)} E_z + \epsilon_k^{(2)} E_z^2 + \cdots)(\psi_k^{(0)} + \psi_k^{(1)} E_z + \psi_k^{(2)} E_z^2 + \cdots)$
- $\hat{H}\psi_k^{(1)} E_z - \mu_z\ E_z \psi_k^{(0)} = \epsilon_k^{(0)} \psi_k^{(1)} E_z + \epsilon_k^{(1)} E_z \psi_k^{(0)}$
- $\int d\tau \psi_k^{(0)*} \hat{H} \psi_k^{(1)} - \int d\tau \psi_k^{(0)*} \mu_z \psi_k^{(0)} =$ $\int d\tau \psi_k^{(0)*} \epsilon_k^{(0)} \psi_k^{(1)} + \int d\tau \psi_k^{(0)*} \epsilon_k^{(1)} \psi_k^{(0)}$

A molecule in an Electric field

- $-\int d\tau \psi_k^{(0)*} \mu_z \psi_k^{(0)} = \int d\tau \psi_k^{(0)*} \epsilon_k^{(1)} \psi_k^{(0)} \rightarrow \epsilon_k^{(1)} = -\int d\tau \psi_k^{(0)*} \hat{\mu}_z \psi_k^{(0)} = - < k|\hat{\mu}_z|k >$
- $\int d\tau \psi_j^{(0)*} \hat{H} \psi_k^{(1)} - \int d\tau \psi_j^{(0)*} \hat{\mu}_z \psi_k^{(0)} = \int d\tau \psi_j^{(0)*} \epsilon_k^{(0)} \psi_k^{(1)} + \int d\tau \psi_j^{(0)*} \epsilon_k^{(1)} \psi_k^{(0)}$
- $\epsilon_j^0 \int d\tau \psi_j^{(0)*} \psi_k^{(1)} - \int d\tau \psi_j^{(0)*} \hat{\mu}_z \psi_k^{(0)} = \epsilon_k^{(0)} \int d\tau \psi_j^{(0)*} \psi_k^{(1)} \rightarrow (\epsilon_j^{(0)} - \epsilon_k^{(0)}) \int d\tau \psi_j^{(0)*} \psi_k^{(1)} =< j|\hat{\mu}_z|k >.$
- i.e., $\psi_k^{(1)} = \sum_{j \neq k} c_{kj} \psi_j^{(0)}$, where $c_{kj} = \frac{<j|\hat{\mu}_z|k>}{(\epsilon_j^{(0)} - \epsilon_k^{(0)})}$
- $\hat{H} \psi_k^{(2)} E_z^2 - \hat{\mu}_z E_z^2 \psi_k^{(1)} = \epsilon_k^{(0)} \psi_k^{(2)} E_z^2 + \epsilon_k^{(1)} \psi_k^{(1)} E_z^2 + \epsilon_k^{(2)} E_z^2 \psi_k^{(0)}$
- $\int d\tau \psi_k^{(0)*} \hat{H} \psi_k^{(2)} - \int d\tau \psi_k^{(0)*} \hat{\mu}_z \psi_k^{(1)} = \int d\tau \psi_k^{(0)*} \epsilon_k^{(0)} \psi_k^{(2)} + \int d\tau \psi_k^{(0)*} \epsilon_k^{(1)} \psi_k^{(1)} + \int d\tau \psi_k^{(0)*} \epsilon_k^{(2)} \psi_k^{(0)}$

A molecule in an Electric field

- $-\int d\tau \psi_k^{(0)*} \hat{\mu}_z \psi_k^{(1)} = \epsilon_k^{(1)} \int d\tau \psi_k^{(0)*} \psi_k^{(1)} + \epsilon_k^{(2)}$
- $\epsilon_k^{(2)} = -\int d\tau \psi_k^{(0)*} \hat{\mu}_z \psi_k^{(1)} - \epsilon_k^{(1)} \int d\tau \psi_k^{(0)*} \psi_k^{(1)}$
- $\epsilon_k^{(2)} = -\sum_{j \neq k} [c_{kj} \int d\tau \psi_k^{(0)*} \hat{\mu}_z \psi_j^{(0)} - c_{kj} < k|\hat{\mu}_z|k > \int d\tau \psi_k^{(0)*} \psi_j^{(0)}]$
- $\epsilon_k^{(2)} = -\sum_{j \neq k} [\frac{<j|\hat{\mu}_z|k>}{(\epsilon_j^{(0)} - \epsilon_k^{(0)})} \int d\tau \psi_k^{(0)*} \hat{\mu}_z \psi_j^{(0)} - \frac{<j|\hat{\mu}_z|k>}{(\epsilon_j^{(0)} - \epsilon_k^{(0)})} < k|\hat{\mu}_z|k > \delta_{kj}]$
- $\epsilon_k^{(2)} = -\sum_{j \neq k} \frac{<k|\hat{\mu}_z|j><j|\hat{\mu}_z|k>}{(\epsilon_j^{(0)} - \epsilon_k^{(0)})}$
- Assume the molecule in its ground electronic state, ψ. Define $\vec{\mu} =< \psi|\hat{\mu}|\psi >$ and $\alpha = 2 \sum_{j \in \text{excited electronic states}} \frac{|<\psi|\hat{\mu}_z|j>|^2}{\epsilon_j^{(0)}}$.

Ideal gas in an electric field

- $Q(N, V, T, E^*) = \frac{q(V,T,E^*)^N}{N!}$
- E^* is the local electric field around each molecule.
- For a linear molecule

$$q(V, T, E^*) = q_{vib}\frac{1}{h^5}\int\cdots\int e^{-\frac{p_x^2+p_y^2+p_z^2}{2MkT}} e^{-\frac{p_\theta^2}{2IkT}-\frac{p_\phi^2}{2I\sin^2\theta kT}}$$

$$\times\ e^{\frac{\mu E^*\cos\theta}{kT}} e^{\frac{\alpha E^{*2}}{2kT}} dp_x dp_y dp_z dx dy dz dp_\theta dp_\phi d\theta d\phi$$

$$= e^{\alpha E^{*2}/2kT}\frac{V}{\Lambda^3}(\frac{4\pi^2 IkT}{h^2})\Pi_j\frac{e^{-\Theta_{\nu,j}/2T}}{1-e^{-\Theta_{\nu,j}/T}}2\frac{\sinh(\mu E^*/kT)}{(\mu E^*/kT)}$$

- $\bar{M} = N\bar{\mu}$ and $dU = TdS - \bar{p}dV - \bar{M}\cdot dE^*$ thus
  $dA = -SdT - \bar{p}dV - \bar{M}\cdot dE^*$

Ideal gas in an electric field

- Average moment of the system, $\bar{M} = -(\frac{\partial A}{\partial E^*})_{N,V,T} = kT(\frac{\partial \ln Q}{\partial E^*})_{N,V,T} = kT\nabla_{E^*} \ln Q$
- $\bar{p} = -(\frac{\partial A}{\partial V}) = -kT(\frac{\partial \ln Q}{\partial V}) \qquad pV = NkT$
- $\frac{(\frac{\sinh x}{x})'}{(\frac{\sinh x}{x})} = \coth x - \frac{1}{x}$
- $\bar{M} = N\bar{\mu} = N(\alpha E^* + \mu\mathcal{L}(\mu E^*/kT))$ where Langevin function $\mathcal{L}(y) = \coth(y) - \frac{1}{y}$
- $\overline{\mu_E} = \mu\overline{\cos\theta} = \mu\frac{\int_0^\pi e^{\mu E^* \cos\theta/kT}\cos\theta\sin\theta d\theta}{\int_0^\pi e^{\mu E^* \cos\theta/kT}\sin\theta d\theta} = \mu\mathcal{L}(\mu E^*/kT)$
- $\overline{\vec{\mu}} \to 0 \iff \vec{E}^* \to 0$
- $1D = 3.336 \times 10^{-30} Cm$

Matter in an electric field

- $\mathcal{L}(y) = \frac{y}{3} - \frac{y^3}{45} + \cdots$ thus $\overline{\vec{M}} = N(\alpha + \frac{\mu^2}{3kT})\vec{E}^*$
- A parallel plate capacitor with charge densities $+\sigma$ and $-\sigma$.
- Gauss's law: $\int_S \vec{E} \cdot d\vec{\sigma} = \frac{q}{\epsilon_0}$.
- $E_0 = \frac{\sigma}{\epsilon_0}$.
- Capacitance $C_0 = \frac{Q}{V} = \frac{\sigma A}{E_0 d} = \frac{\epsilon_0 A}{d}$
- After introducing a dielectric material $C = \epsilon_r C_0$, $E = E_0/\epsilon_r$.
- Polarization density or electric polarization is the vector field that expresses the density of permanent or induced electric dipole moments in a dielectric material.
- When a dielectric is placed in an external electric field, its molecules gain electric dipole moment and the dielectric is said to be polarized.
- The electric dipole moment induced per unit volume of the dielectric material is called the electric polarization of the dielectric, $\vec{P}$.

Matter in an electric field

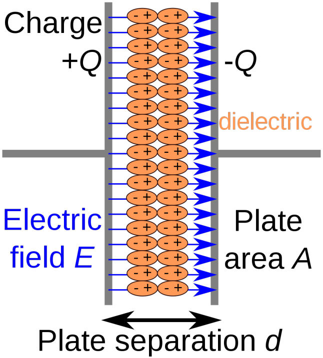
- 

Figure: Taken from `en.wikipedia.org/wiki/Dielectric`

- Electric displacement field $D = \epsilon_0 E + P = \epsilon E$
- The displacement field satisfies Gauss's law in a dielectric: $\nabla \cdot \mathbf{D} = \rho - \rho_{\mathrm{b}} = \rho_{\mathrm{f}}$

Matter in an electric field

- The flux lines of D must begin and end on the free charges. In contrast ρ_b is the density of all those charges that are part of a dipole, each of which is neutral.
- In a linear, homogeneous, isotropic dielectric with instantaneous response to changes in the electric field, P depends linearly on the electric field, $\mathbf{P} = \varepsilon_0 \chi \mathbf{E}$, where the constant of proportionality χ is called the electric susceptibility of the material.
- Thus $\mathbf{D} = \varepsilon_0 (1 + \chi) \mathbf{E} = \varepsilon \mathbf{E}$ where $\epsilon = \epsilon_0 \epsilon_r$ is the permittivity, and $\epsilon_r = 1 + \chi$ the relative permittivity of the material.
- $P_z = \frac{\bar{M}_z}{V} = \epsilon_0 (\epsilon_r - 1) E_z$
- The net charge appearing as a result of polarization is called bound charge
- Polarization only gives rise to surface bound charge density.
- $\sigma_b = \hat{\mathbf{n}}_\mathrm{out} \cdot \mathbf{P}$

Matter in an electric field

- $\overline{\vec{M}} = N(\alpha + \frac{\mu^2}{3kT})\vec{E}^*$
- For an ideal gas $E^* = \frac{D}{\epsilon_0} = \epsilon_r E$
- Thus $\frac{\epsilon_r - 1}{\epsilon_r} = \frac{\rho}{\epsilon_0}(\alpha + \frac{\mu^2}{3kT})$
- $\epsilon_r - 1 \approx \frac{\rho}{\epsilon_0}(\alpha + \frac{\mu^2}{3kT})$
- $\frac{E}{NkT} = \frac{E(0)}{NkT} - \frac{1}{kT}(\frac{\alpha}{2} + \frac{\mu^2}{3kT})E^{*2}$
- According to classical electrostatics $P = \epsilon_0(\epsilon_r - 1)E$
- $P = \frac{N\bar{\mu}}{V} = \rho(\alpha + \frac{\mu^2}{3kT})E^*$
- Local field problem: determination of the relation between E^* and E.
- Semi-molecular theory: nearby molecules are considered as molecules while the rest of the dielectric is treated as a continuum.
- $E^* = E_0 + E_1 + E_2 + E_3$
- $E_0 = \frac{\sigma}{\epsilon_0}, \quad E_1 = \frac{-\sigma'}{\epsilon_0}$, and $E_0 + E_1 = \frac{\sigma - \sigma'}{\epsilon_0} = D - \frac{P}{\epsilon_0} = E$.

Matter in an electric field

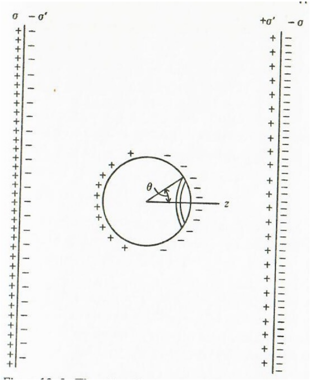
- 

Figure: From Statistical Thermodynamics by D.A. McQuarrie

- Charge density at the spherical surface: $P\cos\theta$ and area of the spherical ring is $2\pi a^2 \sin\theta d\theta$
- $dq = (P\cos\theta)(2\pi a^2 \sin\theta d\theta)$

Matter in an electric field

- $dE_2 = \frac{1}{4\pi\epsilon_0}\frac{dq}{a^2}\cos\theta = \frac{P}{2\epsilon_0}\cos^2\theta\sin\theta d\theta$ and $E_2 = \frac{P}{2\epsilon_0}\int_0^\pi \cos^2\theta\sin\theta d\theta = \frac{P}{3\epsilon_0}$
- The field due to molecules inside the sphere E_3 is zero for simple cubic, body centered cubic and face centered cubic crystals. Also $E_3 = 0$ for an ideal gas.Thus it is hoped that $E_3 = 0$ for a dense gas or liquid.
- $E^* = E + \frac{P}{3\epsilon_0}$ is called the Lorentz-Lorenz field.
- $E^* = E + \frac{(\epsilon_r - 1)}{3}E = \frac{\epsilon_r + 2}{3}E$
- Clausius-Mossotti equation: $\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{\rho}{3\epsilon_0}(\alpha + \frac{\mu^2}{3kT})$
- $\lim_{\rho \to 0}\epsilon_r = 1$ and $\lim_{\epsilon_r \to 1} E^* = E$
- Clausius-Mossotti equation is not applicable to polar liquids.

Magnetic dipole moment

- Magnetic moment is a quantity that represents the magnetic strength and orientation of a magnet.
- Loops of electric current (such as electromagnets), permanent magnets, elementary particles (such as electrons), various molecules, and many astronomical objects poses magnetic dipole moment.
- The magnetic dipole moment of an object is readily defined in terms of the torque that object experiences in a given magnetic field. $\boldsymbol{\tau} = \mathbf{m} \times \mathbf{B}$
- The direction of the magnetic moment points from the south to north pole of the magnet (inside the magnet).
- $\mathbf{m} = -\hat{\mathbf{x}}\frac{\partial U_{\mathrm{int}}}{\partial B_x} - \hat{\mathbf{y}}\frac{\partial U_{\mathrm{int}}}{\partial B_y} - \hat{\mathbf{z}}\frac{\partial U_{\mathrm{int}}}{\partial B_z}$.
- A magnetic moment in an externally produced magnetic field has a potential energy $U = -\mathbf{m} \cdot \mathbf{B}$.
- $\mathbf{m} = I\boldsymbol{S}$, $\mathbf{m} = NI\mathbf{S}$.
- $\mathbf{m} = \frac{1}{2}\iiint_V \mathbf{r} \times \mathbf{j}\,\mathrm{d}V,$

Atom in a magnetic field

- Since the particles creating the current (by rotating around the loop) have charge and mass, both the magnetic moment and the angular momentum increase with the rate of rotation. The ratio of the two is called the gyromagnetic ratio or γ so that: $\mathbf{m} = \gamma \mathbf{L}$
- Magnetic dipole moment for a molecule in the j state: $\mu_j = -\nabla_{B^*}\epsilon_j$
- $\delta w_j = -\mu_j \cdot dB^*$
- $\bar{\mu} = \sum_j \pi_j \mu_j$ and $\delta w = -\sum_j \pi_j \nabla_{B^*}\epsilon_j \cdot dB^* = -\bar{\mu} \cdot dB^*$
- $\delta w = -N\bar{\mu} \cdot dB^* = -M \cdot dB^*$
- Electric current due to circular motion of a charge $i = qv/2\pi r$
- Dipole moment due to this charge motion
  $m = iS = (qv/2\pi r)(\pi r^2) = qvr/2$.
- More generally, $m = \frac{q}{2}(r \times v) = \frac{q}{2m} l$
- For a magnetic field in the z direction,
  $U = -m \cdot B^* = -\frac{e}{2}(x\dot{y} - y\dot{x})B^*_z$

Atom in a magnetic field

- $L(\dot{x},\dot{y},\dot{z},x,y,z)=\frac{m}{2}(\dot{x}^2+\dot{y}^2+\dot{z}^2)-U(x,y,z)-\frac{e}{2}(x\dot{y}-y\dot{x})B_z^*$
- $p_x=\frac{\partial L}{\partial \dot{x}}=m\dot{x}+\frac{eyB_z^*}{2} \quad p_y=\frac{\partial L}{\partial \dot{y}}=m\dot{y}-\frac{exB_z^*}{2}$
- $H=\sum_j p_j\dot{q}_j-L=$ $\frac{1}{2m}(p_x^2+p_y^2+p_z^2)+U(x,y,z)+\frac{eyB_z^*}{2m}(xp_y-yp_x)+\frac{e^2(x^2+y^2)B_z^{*2}}{8m}$
- Perturbation Hamiltonian for a one electron atom or molecule, $H'=\frac{eyB_z^*}{2m}(xp_y-yp_x)+\frac{e^2(x^2+y^2)B_z^{*2}}{8m}$
- $\epsilon(B^*)=\epsilon_0-\mu\cdot B^*+\frac{\alpha}{2}B^{*2}$
- $\mu_z=-\int\psi_0^*\frac{eyB_z^*}{2m}(xp_y-yp_x)\psi_0 d\tau$
- For paramagnetic material which are of most interest to us $\mu_z\neq 0$.
- $\mu=-\frac{e}{2m}\int\psi_0^*\hat{l}\psi_0 d\tau$
- For a one electron atom without spin $\mu^2=\frac{e^2\hbar^2}{4m^2}l(l+1)=\beta_0^2 l(l+1)$ and $\mu_z=-\beta_0 m_j$
- Bohr magneton $\beta_0=\frac{e\hbar}{2m}$
- Generally $\mu^2=g^2\beta_0^2J(J+1)$ and $\mu_z=-g\beta_0 M_J$

Noninteracting paramagnetic atoms

- Lande g factor to within the Russel-Saunders approximation is $g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$
- For a monatomic gas: $q(V,T,B^*) = (\frac{2\pi mkT}{h^2})^{3/2} V q_{elec}(T,B^*)$
- $\epsilon_{M_J} = g\beta_0 B_z^* M_j \qquad -J \leq M_J \leq J$
- $q_{elec}(T,B^*) = \sum_{M_J=-J}^{J} e^{g\beta_0 B_z^* M_j/kT} = \frac{\sinh[(2J+1)y/2]}{\sinh(y/2)}$ where $y = g\beta_0 B_z^*/kT$
- $dA = -SdT - pdV - M \cdot dB^*$
- For non-interacting magnetic moments $M = N\bar{\mu} = kT\nabla_B \ln Q = NkT\nabla_B \ln q_{elec}$
- $\frac{\bar{\mu}_z}{g\beta_0} = \frac{\bar{\mu}}{g\beta_0} = \frac{2J+1}{2}\coth\frac{(2J+1)y}{2} - \frac{1}{2}\coth\frac{y}{2}$ which is called the Brillouin function.
- Expanding the Brillouin function $\bar{\mu} = \frac{g^2\beta_0^2 J(J+1)}{3kT} B = \frac{\mu^2}{3kT} B$

Noninteracting paramagnetic atoms

- Magnetic susceptibility, $\chi = \frac{M_z}{B_z}$ can be measured from the force exerted in a non-uniform magnetic field.
- $\chi = \frac{N\mu^2}{3kT} = \frac{Ng^2\beta_0^2 J(J+1)}{3kT}$
- Proportionality of the paramagnetic contribution to χ with $1/T$ is known as Curie's law.
- Lattice of N equivalent noninteracting magnetic dipoles: $Q(N, T, B_z) = [q_{int}(T) q_{elec}(T, B_z)]^N$
- Noninteracting dipoles pointing in one of two possible directions, $\epsilon = \beta_0 m B_z \quad m = \pm 1$
- $E(N_+, N_-) = \beta_0 (N_+ - N_-) B_z = \beta_0 (2N_+ - N) B_z$
- $Q(N, T, B_z) = q_{int}^N \sum_{N_+=0}^{N} \frac{N!}{N_+!(N-N_+)!} e^{-\beta_0 (2N_+ - N) B_z / kT} = [q_{int}(e^{\beta_0 B_z/kT} + e^{-\beta_0 B_z/kT})]^N$

Polymers

- High molecular-weight molecules made of repeated addition of a fundamental unit (monomer)
- Random flight
- Consider a 1-D random walk with p=1/2.
- After N steps position can range from -N to +N
- W(m,N) = ?
- (N+m)/2 steps in the positive direction and (N-m)/2 in the negative direction.
- N and m must have the same parity.
- $W(m,N) = \frac{N!}{[(N+m)/2]![(N-m)/2]!}(\frac{1}{2})^N$
- $\bar{m} = 0$
- $\ln W \approx N \ln N - N - (\frac{N+m}{2}) \ln(\frac{N+m}{2}) + (\frac{N+m}{2}) - (\frac{N-m}{2}) \ln(\frac{N-m}{2}) + (\frac{N-m}{2}) - N \ln 2 = N \ln N - (\frac{N+m}{2}) \ln(\frac{N+m}{2}) - (\frac{N-m}{2}) \ln(\frac{N-m}{2}) - N \ln 2 = N \ln N - \frac{N}{2}(1+\frac{m}{N}) \ln[\frac{N}{2}(1+\frac{m}{N})] - \frac{N}{2}(1-\frac{m}{N}) \ln[\frac{N}{2}(1-\frac{m}{N})] - N \ln 2 = -\frac{N}{2} \ln(1+\frac{m}{N}) - \frac{m}{2} \ln(1+\frac{m}{N}) - \frac{N}{2} \ln(1-\frac{m}{N}) + \frac{m}{2} \ln(1-\frac{m}{N})$

Polymers

- $\ln W(m,N) \approx -\frac{m^2}{2N}$ or $W(m,N) \approx e^{-\frac{m^2}{2N}}$
- Define $\zeta = mh$ then $W(\zeta) \propto e^{-\zeta^2/2Nh^2}$ the probability the system is a distance ζ from the origin after N displacements of length h.
- $W(\zeta) = \frac{1}{(2\pi Nh^2)^{1/2}} e^{-\zeta^2/2Nh^2}$
- With steps of different sizes $W(\zeta) = \frac{1}{(2\pi N\sigma^2)^{1/2}} e^{-\zeta^2/2N\sigma^2}$ where $\sigma^2 = \bar{h}^2$
- For the z component of a random flight $\zeta = z$ and $h = l\cos\theta$
- $\sigma^2 = \overline{l^2 \cos^2\theta} = l^2/3$
- z-component of a random flight $W(z)dz = (\frac{3}{2\pi Nl^2})^{1/2} e^{-3z^2/2Nl^2} dz$
- Probability of a flight of length r is given by $W(x,y,z)dxdydz = W(x)W(y)W(z)dxdydz = (\frac{3}{2\pi Nl^2})^{3/2} e^{-3r^2/2Nl^2} dxdydz$
- End to end distribution in a freely jointed polymer chain $W(r) = (\frac{3}{2\pi Nl^2})^{3/2} e^{-3r^2/2Nl^2} dr$

Polymers

- $\bar{r} = (\frac{8nl^2}{3\pi})^{1/2}$
- $\bar{r^2} = \int_0^\infty W(r)4\pi r^4 dr = Nl^2$
- Root mean squared length, $(\bar{r^2})^{1/2} = N^{1/2}l$
- $W(r)4\pi r^2 dr = 4\pi(\frac{3}{2\pi \bar{r^2}})^{3/2} e^{-3r^2/2\bar{r^2}} r^2 dr$
- $\vec{l_j}$ is the vector depicting j's bond, the chain vector is $\vec{r} = \sum_{j=1}^N \vec{l_j}$
- $\bar{r^2} = \overline{(\sum_{i=1}^N \vec{l_i}) \cdot (\sum_{j=1}^N \vec{l_j})} = \sum_{i,j=1}^N \overline{\vec{l_i} \cdot \vec{l_j}}$
- If θ is the angle between two successive bonds $\overline{\vec{l_i} \cdot \vec{l_{i+1}}} = l_i l_{i+1} \overline{\cos\theta} = 0$
- Only nonzero terms in $\bar{r^2}$ are those which has $i = j$.
- $\bar{r^2} = \sum_{i=1}^N l_i^2 = Nl_{av}^2$
- For carbon chains $l = 1.54\AA$ and $\theta = 180^\circ - 109^\circ 29' = 70^\circ 32'$
- $\bar{r^2} = \sum_{i=1}^N \overline{l_i^2} + 2\sum_{i=1}^{N-1} \overline{\vec{l_i} \cdot \vec{l_{i+1}}} + 2\sum_{i=1}^{N-2} \overline{\vec{l_i} \cdot \vec{l_{i+2}}} + \cdots +$ $2\sum_{i=1}^{2} \overline{\vec{l_i} \cdot \vec{l_{i+N-2}}} + 2\overline{\vec{l_1} \cdot \vec{l_N}} =$ $Nl^2 + 2(N-1)\overline{\vec{l_1} \cdot \vec{l_2}} + 2(N-2)\overline{\vec{l_1} \cdot \vec{l_3}} + \cdots + 2(N-(N-2))\overline{\vec{l_1} \cdot \vec{l_{N-1}}} + 2\overline{\vec{l_1} \cdot \vec{l_N}}$

Polymers

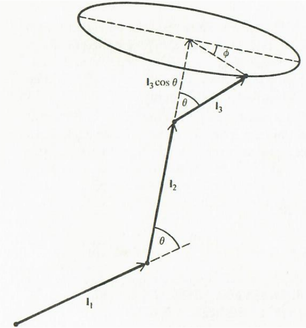
- 

Figure: From Statistical Thermodynamics by D.A. McQuarrie

- $\vec{l}_1 \cdot \vec{l}_2 = l^2\cos\theta$, $\vec{l}_1 \cdot \vec{l}_3 = l^2\cos^2\theta$ and $\vec{l}_1 \cdot \vec{l}_{n+1} = l^2\cos^n\theta$
- $\overline{r^2} = l^2[N + 2(N-1)\cos\theta + 2(N-2)\cos^2\theta + 2(N-3)\cos^3\theta + \cdots + 2\cos^{(N-1)}\theta]$
- $\overline{r^2} \approx l^2 N(1 + 2\cos\theta + 2\cos^2\theta + 2\cos^3\theta + \cdots) = l^2 N\frac{1+\cos\theta}{1-\cos\theta}$

Polymers

- For polyethylene $\cos\theta = 1/3$ and $\bar{r^2} = 2Nl^2$
- Taking into account the dihedral rotation potential $\bar{r^2} = l^2 N (\frac{1+\cos\theta}{1-\cos\theta})(\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}})$
- $\overline{\cos\phi} = \frac{\int_0^{2\pi} \cos\phi e^{-u(\phi)/kT} d\phi}{\int_0^{2\pi} e^{-u(\phi)/kT} d\phi}$
- $\bar{r^2} = \beta^2 N$
- Flexible chains restricted by rotation may be treated as freely jointed chains with a bond length β instead of l.
- For a carbon-carbon chain with free dihedral rotations $\beta/l = \sqrt{2}$
- $\bar{r^2}$ can be deduced from dipole moment measurement.
- $\vec{\mu} = \sum_j \vec{\mu}_j$
- $\overline{\mu^2} = N\mu_1^2$, where μ_1 is the effective dipole moment of the repeating unit.

Polymers

- Radius of gyration or gyradius of a body about an axis of rotation is the radial distance of a point from the axis of rotation at which, if whole mass of the body is assumed to be concentrated, its moment of inertia about the given axis would be the same as with its actual distribution of mass.
- The radius of gyration is the root mean square distance of the object's parts from either its center of mass or a given axis, depending on the relevant application.
- R_G is the perpendicular distance from point mass to the axis of rotation.
- $R_G^2 = \frac{\sum_{j=1}^{N} m_j d_j^2}{\sum_{j=1}^{N} m_j}$
- For equal masses $R_G^2 = \frac{1}{N} \sum_{j=1}^{N} d_j^2$

Polymers

- Radius of gyration can be determined experimentally with static light scattering as well as with small angle neutron and x-ray scattering.
- Center of mass coordinate $\vec{d}_j = \vec{r}_j - \vec{\alpha}$ where Center of mass $\vec{\alpha} = \frac{1}{N}\sum_{j=1}^{N} \vec{r}_j$
- $R_G^2 = \frac{1}{N}\sum_{j=1}^{N} \vec{d}_j \cdot d_j = \frac{1}{N}\sum_{j=1}^{N} (\vec{r}_j - \vec{\alpha}) \cdot (\vec{r}_j - \vec{\alpha}) = \frac{1}{N}[\sum_{j=1}^{N} r_j^2 - 2\vec{\alpha} \cdot \sum_{j=1}^{N} \vec{r}_j + N\alpha^2]$
- $R_G^2 = \frac{1}{N}\sum_{j=1}^{N} r_j^2 - \frac{1}{N^2}\sum_{i,j=1}^{N} \vec{r}_i \cdot \vec{r}_j$
- $r_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos\theta_{ij} = r_i^2 + r_j^2 - 2\vec{r}_i \cdot \vec{r}_j$
- $R_G^2 = \frac{1}{N}\sum_{j=1}^{N} r_j^2 - \frac{1}{2N^2}\sum_{i,j=1}^{N} (r_i^2 + r_j^2 - r_{ij}^2) = \frac{1}{2N^2}\sum_{i,j=1}^{N} r_{ij}^2$ for a fixed configuration.
- For a flexible chain $R_G^2 = \frac{1}{2N^2}\sum_{i,j=1}^{N} \overline{r_{ij}^2}$
- $\overline{r_{ij}^2} = \beta^2 |j - i|$

Polymers

- $R_G^2 = \frac{\beta^2}{2N^2} \sum_{i,j=1}^{N} |j-i|$
- $\sum_{j=1}^{N} |j-i| = \sum_{j=1}^{i}(i-j) + \sum_{j=i+1}^{N}(j-i) = i^2 - i(i+1)/2 + N(N+1)/2 - i(i+1)/2 - i(N-i) = i^2 - i(N+1) + N(N+1)/2$
- $\sum_{i=1}^{n} i^2 = n(n+1)(2n+1)/6$
- $R_G^2 = \frac{\beta^2}{2N^2}[\frac{N(N+1)(2N+1)}{6} - \frac{N(N+1)^2}{2} + \frac{N^2(N+1)}{2}] \approx \frac{\beta^2 N}{6} = \frac{\bar{r}^2}{6}$
- For a uniform sphere $R_G^2 = \frac{\int_{sphere} r^2 dm}{\int_{sphere} dm} = \frac{1}{M} \int_0^R dr \int_0^\pi d\theta \int_0^{2\pi} d\phi r^\rho r^2 \sin\theta = \frac{4\pi\rho R^5}{5M} = \frac{3}{5}R^2$
- Uniform cylinder of radius R and length L, $R_G^2 = \frac{R^2}{2} + \frac{L^2}{12}$

Light scattering by Polymers

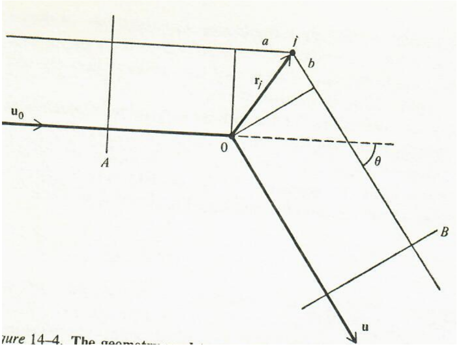


Figure: From Statistical Thermodynamics by D.A. McQuarrie

- N single scatterers connected by bonds or links freely jointed.
- Each single scatterer scatters spherically.
- Incident radiation in direction $\vec{u}_0$ and scattered radiation in direction $\vec{u}$.
- $P(\theta) = \frac{\text{scattered intensity from a collection of scatterers}}{\text{initial intensity}} = \frac{\text{scattered intensity thorough an angle } \theta}{\text{scattered intensity through an angle } \theta \to 0} = \frac{I(\theta)}{I(0)}$

Light scattering by Polymers

- $a = \vec{r}_j \cdot \hat{u}_0$ and $b = -\vec{r}_j \cdot \hat{u}$. Thus extra distance $a + b = \vec{r}_j \cdot (\hat{u}_0 - \hat{u})$
- $|\hat{u}_0 - \hat{u}| = [u_0^2 + u^2 - 2\hat{u}_0 \cdot \hat{u}]^{1/2} = [2 - 2\cos\theta]^{1/2} = 2\sin(\theta/2)$
- $\hat{u}_0 - \hat{u} = 2\hat{n}\sin(\theta/2)$. Thus $a + b = \vec{r}_j \cdot 2\hat{n}\sin(\theta/2)$
- $\phi_j = (a+b)/\lambda = \vec{r}_j \cdot \hat{n}\frac{2}{\lambda}\sin(\theta/2)$
- Electric field at B due to scattering by j $\epsilon_j = A\cos[2\pi(\nu t - \phi_j)]$
- $\epsilon = \sum_{j=1}^{N} A\cos[2\pi(\nu t - \phi_j)]$
- Intensity is derived by averaging ϵ^2 over one period.
- $I(\theta) = \frac{\int_0^{1/\nu} dt \epsilon^2}{\int_0^{1/\nu} dt} = \nu A^2 \int_0^{1/\nu} dt (\sum_{j=1}^{N} \cos\alpha_j)^2$
- $(\sum_{j=1}^{N} \cos\alpha_j)^2 = \sum_{i,j=1}^{N} \cos\alpha_i \cos\alpha_j =$
  $\sum_{i,j=1}^{N} [\cos(\alpha_i - \alpha_j) + \cos(\alpha_i + \alpha_j)]/2$
- $I(\theta) = \frac{\nu}{2} A^2 \int_0^{1/\nu} dt \sum_{i,j=1}^{N} \{\cos[2\pi(\phi_i - \phi_j)] + \cos[2\pi(2\nu t - (\phi_i + \phi_j))]\} = \frac{A^2}{2} \sum_{i,j=1}^{N} \cos[2\pi(\phi_i - \phi_j)]$

Light scattering by Polymers

- $\lim_{\theta\to 0}\phi_i = 0$ in this limit $I(\theta) \to A^2N^2/2$
- $P(\theta) = \frac{1}{N^2}\sum_{i,j=1}^{N}\cos[2\pi(\phi_i - \phi_j)] = \frac{1}{N^2}\sum_{i,j=1}^{N}\cos[s\hat{n}\cdot(\vec{r}_i - \vec{r}_j)]$ where $s = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$
- Take the z axis along $\vec{r}_i - \vec{r}_j$, denote the angle between $\hat{n}$ and the z axis by α and the other spherical coordinate angle by β.
- $\overline{\cos[s\hat{n}\cdot(\vec{r}_{ij})]} = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}\cos(sr_{ij}\cos\alpha)\sin\alpha d\alpha d\beta = \frac{\sin sr_{ij}}{sr_{ij}}$
- $P(\theta) = \frac{1}{N^2}\sum_{i,j=1}^{N}\frac{\sin sr_{ij}}{sr_{ij}}$
- For small angles $P(\theta) = \frac{1}{N^2}\sum_{i,j=1}^{N}(1 - \frac{s^2r_{ij}^2}{3!} + \frac{s^4r_{ij}^4}{5!} + \cdots) = 1 - \frac{s^2}{3!N^2}\sum_{i,j=1}^{N} r_{ij}^2 + \cdots$
- $P(\theta) = 1 - \frac{s^2}{3!N^2}\sum_{i,j=1}^{N}\overline{r_{ij}^2} + \cdots = 1 - \frac{s^2R_G^2}{3} + \cdots = 1 - \frac{16\pi^2R_G^2}{3\lambda^2}\sin^2\frac{\theta}{2} + \cdots$
- $\frac{1}{P(\theta)} = 1 + \frac{16\pi^2R_G^2}{3\lambda^2}\sin^2\frac{\theta}{2} + \cdots$
- Thus small angle scattering can measure radius of gyration directly

Light scattering by Polymers

- $P(\theta)$ for larger values of θ depends on the molecular structure.
- $P(\theta) = \frac{1}{N^2} \sum_{i,j=1}^{N} \frac{\sin sr_{ij}}{sr_{ij}}$
- N+1 scattering elements in a straight line.
- $P(\theta) = \frac{1}{(N+1)^2} \sum_{k=0}^{N} 2(N+1-k) \frac{\sin skl}{skl} - \frac{1}{(N+1)}$

Imperfect gases

- $Q = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\beta[\sum_{i=1}^{N}(p_{xi}^2+p_{yi}^2+p_{zi}^2)/2m+U(x_1,y_1,\cdots,z_N)]} dp_1 \cdots dp_N dr_1 \cdots dr_N$
- $Q = \frac{1}{N!}(\frac{2\pi mkT}{h^2})^{3N/2} Z_N$ where $Z_N = \int \cdots \int e^{-\beta[U(x_1,y_1,\cdots,z_N)]} dr_1 \cdots dr_N$
- Virial equation of state proposed by Thiesen and developed by Kamerlingh-Onnes, $\frac{p}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$
- $\Xi(V,T,\mu) = \sum_{N=0}^{\infty} Q(N,V,T)\lambda^N = 1 + \sum_{N=1}^{\infty} Q_N(V,T)\lambda^N$
- $pV = kT \ln \Xi$
- $N = kT(\frac{\partial \ln \Xi}{\partial \mu})_{T,V} = \lambda(\frac{\partial \ln \Xi}{\partial \lambda})_{T,V}$
- $\lim_{\lambda \to 0} N = \lim_{\lambda \to 0} \lambda(\frac{\partial \ln \Xi}{\partial \lambda})_{T,V} = \lambda Q_1$
- $\lim_{\lambda \to 0} \rho = \lambda Q_1/V$, Define activity $z = \lambda Q_1/V$
- $\Xi(V,T,\mu) = 1 + \sum_{N=1}^{\infty}(\frac{Q_N V^N}{Q_1^N})z^N = 1 + \sum_{N=1}^{\infty}(\frac{Z_N(V,T)}{N!})z^N$ where $Z_N(V,T) = N!(\frac{V}{Q_1})^N Q_N$.

Imperfect gases

- $p = kT \sum_{j=1}^{\infty} b_j z^j$
- $\Xi = e^{pV/kT} = e^{V\sum_{j=1}^{\infty} b_j z^j} =$
  $1 + V\sum_{j=1}^{\infty} b_j z^j + (V\sum_{j=1}^{\infty} b_j z^j)^2/2 + \cdots = 1 + \sum_{N=1}^{\infty}(\frac{Z_N(V,T)}{N!})z^N$
- $b_1 = (1!V)^{-1}Z_1 = 1, \quad b_2 = (2!V)^{-1}(Z_2 - Z_1^2), \quad b_3 = (3!V)^{-1}(Z_3 - 3Z_2Z_1 + 2Z_1^3), \quad b_4 = (4!V)^{-1}(Z_4 - 4Z_3Z_1 - 3Z_2^2 + 12Z_2Z_1^2 - 6Z_1^4)\cdots$
- N-body problem is reduced to a series of few body problems.
- $\rho = \frac{N}{V} = \frac{\lambda}{V}(\frac{\partial \ln \Xi}{\partial \lambda})_{T,V} = \frac{z}{V}(\frac{\partial \ln \Xi}{\partial z})_{T,V} = \frac{z}{kT}(\frac{\partial p}{\partial z})_{T,V} = \sum_{j=1}^{\infty} jb_j z^j$
- Assume $z = a_1\rho + a_2\rho^2 + a_3\rho^3 + \cdots$ thus
  $\rho = a_1(\sum_{j=1}^{\infty} jb_j z^j) + a_2(\sum_{j=1}^{\infty} jb_j z^j)^2 + a_3(\sum_{j=1}^{\infty} jb_j z^j)^3 + \cdots$
- $a_1 = 1, \quad a_2 = -2b_2, \quad a_3 = -3b_3 + 8b_2^2, \quad \cdots$
- $\frac{p}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$ where
  $B_2(T) = -b_2 = -(2!V)^{-1}(Z_2 - Z_1^2), \quad B_3(T) = 4b_2^2 - 2b_3 = -\frac{1}{3V^2}[V(Z_3 - 3Z_2Z_1 + 2Z_1^3) - 3(Z_2 - Z_1^2)^2]$

Virial coefficients

- $Q_N = \frac{Z_N}{N!\Lambda^{3N}} = \frac{1}{N!}(\frac{Q_1}{V})^N Z_N$
- $Z_1 = \int dr_1 = V$
- $Z_2 = \int\int e^{-U_2/kT} dr_1 dr_2$
- $Z_3 = \int\int\int e^{-U_3/kT} dr_1 dr_2 dr_3$
- $B_2(T) = -\frac{1}{2V}\int\int [e^{-u(r_{12})/kT} - 1] dr_1 dr_2 = -\frac{1}{2V}\int dr_1 \int [e^{-u(r_{12})/kT} - 1] dr_{12} = -2\pi \int_0^\infty f(r) r^2 dr$
- Mayer f-function is defined as $f_{ij} = f(r_{ij}) = f(r) = e^{-u(r_{12})/kT} - 1$
- $U_3(r_1, r_2, r_3) = u(r_{12}) + u(r_{13}) + u(r_{23}) + \Delta(r_{12}, r_{13}, r_{23}) = u_{12} + u_{13} + u_{23} + \Delta_3 \approx u(r_{12}) + u(r_{13}) + u(r_{23})$
- $Z_3 = \int\int\int (1+f_{12})(1+f_{13})(1+f_{23}) dr_1 dr_2 dr_3 = \int\int\int (f_{12}f_{13}f_{23} + f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12} + f_{13} + f_{23} + 1) dr_1 dr_2 dr_3$
- $Z_1 Z_2 = V \int\int (1+f_{12}) dr_1 dr_2 = \int\int\int (1+f_{12}) dr_1 dr_2 dr_3 = \int\int\int (1+f_{13}) dr_1 dr_2 dr_3 = \int\int\int (1+f_{23}) dr_1 dr_2 dr_3$
- $Z_3 - 3Z_1 Z_2 = \int\int\int (f_{12}f_{13}f_{23} + f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} - 2) dr_1 dr_2 dr_3$

Virial coefficients

- $6Vb_3 = \int\int\int(f_{12}f_{13}f_{23} + f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23})dr_1dr_2dr_3$
- $B_3(T) = -\frac{1}{3V}(6Vb_3 - 12Vb_2^2)$
- $b_2 = \frac{1}{2}\int f_{12}dr_{12}$
- $4b_2^2 = [\int f_{12}dr_{12}]^2 = [\int f_{12}dr_{12}][\int f_{13}dr_{13}]$
- $4Vb_2^2 = \int dr_1 \int f_{12}dr_{12} \int f_{13}dr_{13} = \int\int\int f_{12}f_{13}dr_1dr_2dr_3$
- $B_3(T) = -\frac{1}{3V}\int\int\int f_{12}f_{13}f_{23}dr_1dr_2dr_3$
- In general $B_{j+1} = \frac{-j}{j+1}\beta_j$
- $\beta_j = \frac{1}{j!V}\int\cdots\int S'_{1,2,\cdots,j+1}dr_1dr_2\cdots dr_{j+1}$
- $S'_{1,2,\cdots,j+1}$ is the sum of all products of f-functions that connect molecules 1,2, ..., j+1 such that the removal of any point together with all lines associated with it result in a connected graph.
- Perturbation result $u(r) \to -C_6r^{-6}$
- Well known analytic expression with adjustable parameters $u(r) = \frac{n\epsilon}{n-6}(\frac{n}{6})^{6/(n-6)}[(\frac{\sigma}{r})^n - (\frac{\sigma}{r})^6]$ where $u(\sigma) = 0$ and ϵ is the depth of the well.
- n is usually between 9 and 15 but 12 is the most popular value.

Virial coefficients

- Hard sphere potential $u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}$
- $B_2(T) = -\frac{1}{2}\int_0^\infty [e^{-u(r)/kT} - 1]4\pi r^2 dr = -\frac{1}{2}\int_0^\sigma -4\pi r^2 dr = \frac{2\pi\sigma^3}{3}$
- Square well potential: $u(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma < r < \lambda\sigma \\ 0 & r > \sigma \end{cases}$
- λ is usually between 1.5 and 2.
- $B_2(T) = -\frac{1}{2}[\int_0^\sigma -4\pi r^2 dr + \int_\sigma^{\lambda\sigma} (e^{\epsilon/kT} - 1)4\pi r^2 dr + \int_{\lambda\sigma}^\infty 0 dr] = \frac{2\pi\sigma^3}{3} - 2\pi(e^{\beta\epsilon} - 1)\frac{\lambda^3\sigma^3 - \sigma^3}{3} = b_0[1 - (\lambda^3 - 1)(e^{\beta\epsilon} - 1)]$ where $b_0 = 2\pi\sigma^3/3$
- Square well potential fits the experimental data very well.
- For LJ potential $B_2(T) = -\frac{1}{2}\int_0^\infty [\exp\{-\frac{4\epsilon}{kT}[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]\} - 1]4\pi r^2 dr$
- $B_2^*(T^*) = -3\int_0^\infty [\exp\{-\frac{4}{T^*}(x^{-12} - x^{-6})\} - 1]x^2 dx$
- $B_2^*(T^*)$ is a well tabulated function.

Virial coefficients

- To deduce LJ parameters, use trial and error to solve $\frac{B_2(T_2)}{B_2(T_1)}|_{experm} = \frac{B_2^*(kT_2/\epsilon)}{B_2^*(kT_1/\epsilon)}$ for ϵ.
- Solve $\frac{B_2(T_1)}{B_2^*(T_1^*)} = \frac{2\pi\sigma^3}{3}$ for σ
- Other potentials are used as well, e.g., $u(r) = \frac{A}{r^n} - \frac{C_6}{r^6} - \frac{C_8}{r^8}$
- $\frac{u(r)}{\epsilon} = \frac{6+2\gamma}{n-6}(\frac{d\sigma}{r})^n - \frac{n-\gamma(n-8)}{n-6}(\frac{d\sigma}{r})^6 - \gamma(\frac{d\sigma}{r})^8$
- $B_3(T) = -\frac{1}{3V}\int\int\int f_{12}f_{13}f_{23}dr_1dr_2dr_3 = -\frac{1}{3}\int\int f_{12}f_{13}f_{23}dr_{12}dr_{13}$
- $B_3^*(T^*) = -\frac{3}{4\pi^2}\int\int f_{12}f_{13}f_{23}dr_{12}^*dr_{13}^*$
- $B_3 = -\frac{1}{3}\int\int f(|\rho_2|)f(|\rho_3|)f(|\rho_3 - \rho_2|)d\rho_2 d\rho_3$
- $\gamma(t) = \gamma(|\vec{t}|) = (2\pi)^{-3/2}\int f(|\vec{\rho}|)e^{-i\vec{t}\cdot\vec{\rho}}d\vec{\rho} =$ $(2\pi)^{-3/2}\int\int\int f(|\vec{\rho}|)e^{-i\rho t\cos\theta}\rho^2 d\rho\sin\theta d\theta d\phi =$ $(2\pi)^{-1/2}\int f(\rho)\rho^2 d\rho\frac{e^{-i\rho t\cos\theta}}{-i\rho t}|_0^\pi = \sqrt{2/\pi}\int_0^\infty f(\rho)\frac{\sin(\rho t)}{t}\rho d\rho$

Virial coefficients

- $f(\rho) = (2\pi)^{-3/2} \int \gamma(t) e^{i\vec{t}\cdot\vec{\rho}} d\vec{t} =$
  $(2\pi)^{-3/2} \int \gamma(t) e^{it\rho\cos\theta} t^2 dt \sin\theta d\theta d\phi =$
  $(2\pi)^{-1/2} \int \gamma(t) t^2 dt \frac{e^{i\rho t\cos\theta}}{i\rho t}|_0^\pi = \sqrt{2/\pi} \int_0^\infty \gamma(t) \frac{\sin(\rho t)}{\rho} tdt$
- For hard spheres, $f(\rho) = \begin{cases} -1 & 0 < \rho < 1 \\ 0 & \rho > 1 \end{cases}$
- $\gamma(t) = \sigma^3 (\frac{2}{\pi})^{1/2} [\frac{\cos(\sigma t)}{(\sigma t)^2} - \frac{\sin(\sigma t)}{(\sigma t)^3}] = -\sigma^3 \frac{J_{3/2}(\sigma t)}{(\sigma t)^{3/2}}$
- $f(|\rho_3 - \rho_2|) = (2\pi)^{-3/2} \int \gamma(t) e^{i\vec{t}\cdot\vec{\rho}_3 - i\vec{t}\cdot\vec{\rho}_2} d\vec{t}$
- $B_3 = -\frac{(2\pi)^{-3/2}}{3} \int\int\int \gamma(t) f(\rho_2) f(\rho_3) e^{i\vec{t}\cdot\vec{\rho}_3 - i\vec{t}\cdot\vec{\rho}_2} d\vec{\rho}_2 d\vec{\rho}_3 d\vec{t} =$
  $-\frac{(2\pi)^{-3/2}}{3} \int \gamma(t)^3 d\vec{t} = -\frac{(2\pi)^{-3/2}}{3} \sigma^9 \int 4\pi t^2 \frac{[J_{3/2}(\sigma t)]^3}{(\sigma t)^{9/2}} dt$
- $U = \sum_{i,j} u(r_{ij}) = \sum_{i,j} \epsilon \phi(\frac{r_{ij}}{\sigma})$

Virial coefficients

- $Z_N = \int \cdots \int e^{-U/kT} d\vec{r}_1 \cdots d\vec{r}_N =$
  $\sigma^{3N} \int \cdots \int e^{-\epsilon/kT \sum_{i,j} \phi(\frac{r_{ij}}{\sigma})} d(\frac{\vec{r}_1}{\sigma}) \cdots d(\frac{\vec{r}_N}{\sigma}) = \sigma^{3N} f(T^*, \frac{V}{\sigma^3}, N)$
- $\frac{A}{NkT} = -\frac{1}{N} \ln Q = -\frac{1}{N} \ln \frac{Z_N}{N! \Lambda^{3N}} = -\frac{1}{N} \ln \frac{Z_N}{N!} + 3 \ln \Lambda$
- $\frac{1}{N} \ln \frac{Z_N}{N!}$ is a function of v and T only
- $\ln \frac{Z_N}{N!} = \frac{\sigma^{3N}}{N!} f(T^*, \frac{V}{\sigma^3}, N) = \sigma^{3N} [g(T^*, \frac{v}{\sigma^3})]^N$
- $Q(N, V, T) = [\frac{\sigma^3 g(T^*, \frac{v}{\sigma^3})}{\Lambda^3}]^N$
- $p = kT(\frac{\partial \ln Q}{\partial V})_{N,T} = \frac{kT}{N\sigma^3}(\frac{\partial \ln Q}{\partial (v/\sigma^3)})_{N,T} = \frac{kT}{\sigma^3}(\frac{\partial \ln g}{\partial (v/\sigma^3)})_{T^*}$
- $\frac{Pv}{kT} = \frac{v}{\sigma^3}(\frac{\partial \ln g}{\partial (v/\sigma^3)})_{T^*}$

Distribution functions in liquids

- Radius of convergence of the virial equation might have to do with the onset of liquid state.
- Truncated power series of a function is an unsatisfactory method of approximating it.
- Instead one might use the Pade approximants, consider $f(x) = a_0 + a_1 x + \cdots + a_n x^n + O(x^{n+1})$
- Its N, M Pade approximant is $f(x) \approx \frac{c_0 + c_1 x + \cdots + c_{N-1} x^{N-1}}{1 + d_1 x + \cdots + d_{M-1} x^{M-1}}$
- E.g., Ree and Hoover used 6 hard-sphere virial coefficients to construct $(\frac{p}{\rho kT} - 1) = b_0 \rho \frac{1 + 0.063507 b_0 \rho + 0.017329 b_0^2 \rho^2}{1 - 0.561493 b_0 \rho + 0.239465 b_0^2 \rho^2}$
- $P^{(N)}(r_1, \cdots, r_N) dr_1 \cdots dr_N = \frac{e^{-\beta U_N}}{Z_N} dr_1 \cdots dr_N$
- $P^{(n)}(r_1, \cdots, r_n) = \frac{\int \cdots \int e^{-\beta U_N} dr_{n+1} \cdots dr_N}{Z_N}$
- $\rho^{(n)}(r_1, \cdots, r_n) = \frac{N!}{(N-n)!} P^{(n)}(r_1, \cdots, r_n)$

Distribution functions in liquids

- $\frac{1}{V}\int \rho^{(1)}(r_1)dr_1 = \rho^{(1)} = \frac{N}{V} = \rho$
- Correlation function $g^{(n)}(r_1, \cdots, r_n)$ is defined by $\rho^{(n)}(r_1, \cdots, r_n) = \rho^n g^{(n)}(r_1, \cdots, r_n)$
- $g^{(n)}(r_1, \cdots, r_n) = \frac{V^n N!}{N^n(N-n)!}\frac{\int\cdots\int e^{-\beta U_N} dr_{n+1}\cdots dr_N}{Z_N} = V^n(1 + O(N^{-1}))\frac{\int\cdots\int e^{-\beta U_N} dr_{n+1}\cdots dr_N}{Z_N}$
- Radial distribution function $g^{(2)}(\vec{r}_1, \vec{r}_2) = g^{(2)}(r_{12}) = g(r)$ is important since it can be measured experimentally.
- $\int_0^\infty \rho g(r) 4\pi r^2 dr = N - 1 \approx N$
- If $U_N(r_1, \cdots, r_N) = \sum_{i<j} u(r_{ij})$ all thermodynamic functions can be written in terms of $g(r)$.
- $P(\theta) \propto \int_0^\infty 4\pi r^2 g(r)\frac{\sin(sr)}{(sr)}dr = \int_0^\infty 4\pi r^2 (g(r) - 1)\frac{\sin(sr)}{(sr)}dr + \int_0^\infty 4\pi r^2 \frac{\sin(sr)}{(sr)}dr$ where $s = \frac{4\pi}{\lambda}\sin(\theta/2)$

Distribution functions in liquids

- $P(\theta) \propto \int_0^\infty 4\pi r^2 (g(r)-1)\frac{\sin(sr)}{(sr)} dr = \int (g(r)-1) e^{i\vec{s}\cdot\vec{r}} d\vec{r}$
- Fourier transform of $h(r) = (g(r)-1)$ is proportional to scattering through θ
- Structure factor $\hat{h}(\vec{s}) = \rho \int h(r) e^{i\vec{s}\cdot\vec{r}} d\vec{r}$
- For a fluid $E = \frac{3}{2}NkT + kT^2(\frac{\partial \ln Z_N}{\partial T})_{N,V} = \frac{3}{2}NkT + \bar{U}$, where $\bar{U} = \frac{\int \cdots \int U e^{-\beta U} dr_1 \cdots dr_N}{Z_N}$
- $\bar{U} = \frac{N(N-1)}{2Z_N} \int \cdots \int u(r_{12}) e^{-\beta U} dr_1 \cdots dr_N = \frac{N(N-1)}{2} \int \int u(r_{12}) [\frac{\int \cdots \int e^{-\beta U} dr_3 \cdots dr_N}{Z_N}] = \frac{1}{2} \int \int u(r_{12}) \rho^{(2)}(r_1, r_2) dr_1 dr_2 = \frac{N^2}{2V} \int_0^\infty u(r) g(r) 4\pi r^2 dr$
- $\frac{E}{NkT} = \frac{3}{2} + \frac{\rho}{2kT} \int_0^\infty u(r) g(r, \rho, T) 4\pi r^2 dr$
- $p = kT(\frac{\partial \ln Q}{\partial V})_{N,T} = kT(\frac{\partial \ln Z_N}{\partial V})_{N,T}$, where assuming a cubic volume $Z_N = \int_0^{V^{1/3}} \cdots \int_0^{V^{1/3}} e^{-\beta U} dx_1 dy_1 \cdots dy_N dz_N$

Distribution functions in liquids

- $Z_N = V^N \int_0^1 \cdots \int_0^1 e^{-\beta U} dx_1' dy_1' \cdots dy_N' dz_N'$ where $x_k = V^{1/3} x_k'$
- $(\frac{\partial Z_N}{\partial V})_{N,T} = N V^{N-1} \int_0^1 \cdots \int_0^1 e^{-\beta U} dx_1' dy_1' \cdots dy_N' dz_N' - \frac{V^N}{kT} \int_0^1 \cdots \int_0^1 e^{-\beta U} (\frac{\partial U}{\partial V})_{N,T} dx_1' dy_1' \cdots dy_N' dz_N'$
- $(\frac{\partial U}{\partial V})_{N,T} = \sum_{1 \le i < j \le N} \frac{du(r_{ij})}{dr_{ij}} \frac{dr_{ij}}{dV} = \frac{du(r_{ij})}{dr_{ij}} \frac{r_{ij}}{3V}$
- $(\frac{\partial \ln Z_N}{\partial V})_{N,T} = \frac{N}{V} - \frac{1}{6VkT} \int_V \int_V r_{12} \frac{du(r_{12})}{dr_{12}} \rho^{(2)}(r_1, r_2) dr_1 dr_2$
- The pressure equation: $\frac{p}{kT} = \rho - \frac{\rho^2}{6kT} \int_0^\infty r u'(r) g(r) 4\pi r^2 dr$ is an equation of state for fluid.
- $g(r, \rho, T) = g_0(r, T) + \rho g_1(r, T) + \rho^2 g_2(r, T) + \cdots$
- $\frac{p}{kT} = \rho - \frac{\rho^2}{6kT} \sum_{j=0}^\infty \rho^j \int_0^\infty r u'(r) g_j(r) 4\pi r^2 dr$
- $B_{j+2}(T) = -\frac{1}{6kT} \int_0^\infty r u'(r) g_j(r) 4\pi r^2 dr$
- $B_2(T) = -\frac{1}{2} \int_0^\infty (e^{-\beta u(r)} - 1) 4\pi r^2 dr = -\frac{1}{6kT} \int_0^\infty r \frac{du(r)}{dr} e^{-\beta u(r)} 4\pi r^2 dr$ thus $g_0(r, T) = e^{-\beta u(r)}$.

Distribution functions in liquids

- Gibbs-Helmholtz equation $(\frac{\partial(A/T)}{\partial(1/T)})_{N,V} = E$ can be used to derive Helmholtz free energy and thus chemical potential.
- $d(A/T) = [\frac{3}{2} + \frac{\rho}{2kT} \int_0^\infty u(r)g(r, \rho, T)4\pi r^2 dr]NkTd(1/T)$
- Introducing coupling parameter ζ,
  $U(r_1, \cdots, r_N, \zeta) = \sum_{j=2}^{N} \zeta u(r_{1j}) + \sum_{2\le i<j\le N} u(r_{ij})$
- $\mu = (\frac{\partial A}{\partial N})_{V,T} = A(N, V, T) - A(N-1, V, T)$
- $-\frac{A}{kT} = \ln Q_N = \ln Z_N - \ln N! - 3N \ln \Lambda$
- $-\frac{\mu}{kT} = \ln \frac{Z_N}{Z_{N-1}} - \ln N - \ln \Lambda^3$
- $\ln \frac{Z_N}{Z_{N-1}} = \ln \frac{Z_N(\zeta=1)}{Z_N(\zeta=0)} + \ln V = \ln V + \int_0^1 (\frac{\partial \ln Z_N}{\partial \zeta}) d\zeta$
- $(\frac{\partial Z_N}{\partial \zeta}) = -\beta \int \cdots \int e^{-\beta U_N(\zeta)} [\sum_{j=2}^{N} u(r_{1j})] d\vec{r}_1 \cdots d\vec{r}_N$
- $(\frac{\partial \ln Z_N}{\partial \zeta}) = -\frac{1}{NkT} \int_V \int_V u(r_{12}) \rho^{(2)}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 =$
  $-\frac{\rho}{kT} \int_0^\infty u(r) g(r;\zeta) 4\pi r^2 dr$

Distribution functions in liquids: Kirkwood equation

- $\frac{\mu}{kT} = \ln \rho\Lambda^3 + \frac{\rho}{kT}\int_0^1\int_0^\infty u(r)g(r;\zeta)4\pi r^2 dr d\zeta$
- $\rho^{(n)}(1,2,\cdots,n;\zeta) = \frac{N!}{(N-n)!}\frac{\int\cdots\int e^{-\beta U(\zeta)} d\vec{r}_{n+1}\cdots d\vec{r}_N}{Z_N(\zeta)}$
- $kT\frac{\partial\rho^{(n)}}{\partial\zeta} = \frac{\rho^{(n)}}{Z_N(\zeta)}\sum_{j=2}^N \int\cdots\int e^{-\beta U(\zeta)} u(r_{1j}) d\vec{r}_1\cdots d\vec{r}_N -$
  $\frac{N!}{(N-n)!}\frac{1}{Z_N(\zeta)}\sum_{j=2}^N\int\cdots\int e^{-\beta U(\zeta)}u(r_{1j})d\vec{r}_{n+1}\cdots d\vec{r}_N$
- $\frac{Z_N(\zeta)}{N(N-1)}\sum_{j=2}^N\int_V\int_V u(r_{1j})\rho^{(2)}(\vec{r}_1,\vec{r}_j)d\vec{r}_1 d\vec{r}_j$
- Fot j=2, ..., n,
  $\sum_{j=2}^N u(r_{1j})\frac{N!}{(N-n)!}\frac{\int\cdots\int e^{-\beta U(\zeta)} d\vec{r}_{n+1}\cdots d\vec{r}_N}{Z_N(\zeta)} = \rho^{(n)}(1,2,\cdots,n)\sum_{j=2}^n u(r_{1j})$
- Fot j=n+1, ..., N,
  $\int_V u(r_{1j})(\int\cdots\int e^{-\beta U(\zeta)} d\vec{r}_{n+1}\cdots d\vec{r}_{j-1}d\vec{r}_{j+1}\cdots d\vec{r}_N)d\vec{r}_j =$
  $\frac{Z_N(\zeta)(N-n-1)!}{N!}\int_V u(r_{1j})\rho^{(n+1)}(1,2,\cdots,n,j,\zeta)d\vec{r}_j$
- $kT\frac{\partial\rho^{(n)}}{\partial\zeta} = -\sum_{j=2}^n u(r_{1j}) + \frac{1}{N}\int_V\int_V u(r_{12})\rho^{(2)}(\vec{r}_1,\vec{r}_2,\zeta)d\vec{r}_1 d\vec{r}_2 -$
  $\int_V u(r_{1,n+1})\frac{\rho^{(n+1)}(1,2,\cdots,n,n+1,\zeta)}{\rho^{(n)}(1,2,\cdots,n,\zeta)}dr_{n+1}$

Class presentations

Ms. Dehnary	Polymers	14 Tir 9 am
Ms. Sharifi	Imperfect gases	15 Tir 9 am
Ms. Mohammady	Distribution functions in liquids	16 Tir 9 am
Mr. Mohammady	Time correlation functions	17 Tir 9 am

Table of physico-chemical constants

Quantity	Symbol	Value (SI units)
atomic mass constant	$m_u = 1\ u$	$1.6605389 \times 10^{-27}$ kg
Avogadro's number	N_A, L	6.0221417×10^{23}
Boltzmann constant	$k = R/N_A$	$1.3806505 \times 10^{-23} JK^{-1}$
Faraday constant	$F = N_A e$	96485.338 Cmol^{-1}
gas constant	R	8.314472 JK^{-1}mol^{-1}, 0.08205 L atm mol^{-1}K^{-1}, 8.20573 m^3 atm mol^{-1}K^{-1}
molar Planck constant	$N_A h$	3.99031×10^{-10} J s mol^{-1}
electric constant (vacuum permittivity)	$\varepsilon_0 = 1/(\mu_0 c^2)$	$8.854187817 \times 10^{-12}$ Fm^{-1}

Table of physico-chemical constants

Quantity	Symbol	Value (SI units)
magnetic constant (vacuum permeability)	μ_0	$12.56637061 \times 10^{-7}$ NA^{-2}
Newtonian constant of gravitation	G	6.67408×10^{-11} m^{3}kg^{-1}s^{-2}
Planck constant	h	$6.626070040 \times 10^{-34}$ Js
reduced Planck constant	$\hbar$	$1.054571800 \times 10^{-34}$ Js
speed of light in vacuum	c	299792458 m/s
electronic charge	e	1.60219×10^{-19}C
electron mass	m_e	9.10956×10^{-31}Kg