# Basics: statistical physics and quantum mechanics

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## I. MANY-BODY PHYSICS IN CONDENSED MATTER, GENERAL REMARKS

Condensed matter physics is quite vast. Therefore, I start with some general (and thus rather trivial) remarks, in order to clarify what will be adressed in this course, and what will be dropped under the carpet.

In some sense, condensed matter physics could be summarized writing down the QED Lagrangian

$$\mathcal{L} = i \sum_n \bar{\psi}_n \left( \not{\partial} - m_n \right) \psi_n - \frac{1}{4} F_{\mu\nu}^2 \tag{1}$$

where $\psi_n$ are fermionic fields describing electrons and protons of mass $m_n$ and charge $e_n$, respectively, and $F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu$ the electronmagnetic field tensor of the photons, and $D_\mu \psi_n = (\partial_\mu + i e_n A_\mu)\psi_n$ is the minimal coupling between fermions and photons. Altough we believe that all "usual" condensed matter phenomena are described within the frame of this simple expression for the Lagrangian, explicit solutions/predictions for situations containing more than a few particles remain extremely challenging. In general, this is also not really necessary, since some simplyfications due to various energy scales occuring in the problem can be introduced:

- Typical energies are low compared to the rest masses of electrons and protons such that they can be treated non relativisticaly. The Dirac equation then reduces to the usual non-relativistic Schrödinger equation for electrons and protons. (However: spin-orbit....)
- In the Coulomb gauge, we can split off the static Coulomb interaction between the fermions and the Hamiltonian can be written as

$$H = \sum_i \frac{\left(\mathbf{p}_i - e_i \mathbf{A}\right)^2}{2m_i} + \sum_{i<j} \frac{e_i e_j}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{2}$$

  where $\mathbf{A}$ describes the external photonic field (dropped in the following).
- Within the Born-Oppenheimer approximation, one separates the dynamics of electrons and protons (ions), due to their large mass ration $m_p/m_e \approx 1024$. Integrating out the electronic degrees of freedom, one arrives at an effective Hamiltonian for the protons/ions (atoms) of the form

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + V_{BO}(\mathbf{R}) \tag{3}$$

  where $m$ is the atoms mass and $V(\mathbf{R})$ is the Born-Oppenheimer potential, which in general depends on the positions of all atoms $\mathbf{R} \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots)$.
- The electronic ground state energies $V_{BO}(\mathbf{R})$ for given proton/ion (atom) positions $\mathbf{R}$ can be addressed by electronic structure calculations.
- Frequently the Born-Oppenheimer energy surface is replaced by a simple pair interaction

$$V_{BO}(\mathbf{R}) \approx \sum_{i<j} v(|\mathbf{r}_i - \mathbf{r}_j|) \tag{4}$$

  with a phenomenological potential $v(r)$.

Solving condensed matter problems deductively by starting from the QED Lagrangian might be a dream of every theoretician which could turn over to a nightmare.... and a more phenomenological approach is the usual starting point of condensed matter theory based on an effective Hamiltonian. Frequently the effective Hamiltonian used for explicit calculations is reduced further to a minimal form expected to capture the observed phenomena. However, one

should not forget that it is in principle possible to go backwards, and check how much the different approximations underlying the effective Hamiltonian approach affect the results. Looking at the details, there are still many open problems, technical, methodological, and fundamental ones.

The *quantum many-body problem* in condensed matter systems consists of solving the resulting Schrödinger equation

$$i\hbar\partial_t \Psi(\mathbf{R},t) = H\Psi(\mathbf{R},t) \quad (5)$$

$$H = K + V \quad (6)$$

where $K$ is the kinetic energy and $V$ the interaction potential in the limit of a large number of particles given the initial conditions of the many-body wave function $\Psi(\mathbf{R}, t=0)$ (+ boundary conditions) or at/close to thermal equilibrium.

For some systems, $v(r)$ is rather well known, which makes them of some more "fundamenental" interest, since we can aim for quantitative comparions with experiments:

- liquid (fluid) and solid hydrogen, where $v(r)$ is just the bare Coulomb interaction
- smearing out the protonic charge to a unifrom background, the electron gas model (relevant for simple alcaline metals)
- rare gases fluids and solids are rather well described by a Lennard-Jones 6-12 interaction.
- liquid and solid helium: phenomenological pair interaction very well known (beyond Lennard-Jones)
- dilute ultracold atom/molecular gases: metastable, effective interaction very well known from scattering properties

In the cours, after a short reminder of classical/quantum statistical mechanics, I will start with two related phenomena, Bose-Einstein condensation and superfluidity, where quantum effects occur at a macroscopic scale.

All over the course, we will consider systems containing a large number of particles, $N \gg 1$, in a mesoscopic ($N \sim 10^3$) or macroscopic ($N \sim 10^{24}$) range, focusing in general on $d = 3$ spatial dimensions, if not stated explicitly otherwise. Further, $\hbar = k_B = 1$ is used frequently.

## II. CLASSICAL DYNAMICS

Condensed matter physics includes many systems which are close to daily live situations described within classical mechanics.

**Newton's equation of motion**. In classical mechanics, the complete description of the system is given in terms of its generalized coordinates - the spatial position $\mathbf{r}_i$ and the momentum $\mathbf{p}_i$ of each particle $i$ ($1 \leq i \leq N$). Knowing the position and momenta of all particles we can determine their future coordinates by the classical equation of motion given by Newton's law

$$\begin{aligned} \frac{d\mathbf{r}_i}{dt} &= \frac{\mathbf{p}_i}{m} \\ \frac{d\mathbf{p}_i}{dt} &= \mathbf{F}_i \end{aligned} \quad (7)$$

The force $\mathbf{F}_i$ acting on particle $i$ is due to the interaction with other particles, $v(r)$, and/or an external potential, $u(\mathbf{r})$

$$\mathbf{F}_i = -\nabla_i \left[ u(\mathbf{r}_i) + \sum_{n<m} v(r_{nm}) \right] \quad (8)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.

In generally we will not be able to solve the equations of motion analytically. However, we know exactely the equations of motion, so we can try to integrate Newton's equation of motion numerically on a computer for a finite number of particles $N \sim 10^2 - 10^7$. This approach is called *Molecular Dynamics*.

### A. Molecular Dynamics Simulations

In order to integrate numerically Newton's equations we have to discretize them in time. Therefore, we start with a Taylor expansion of a particle at time $t \pm \Delta t$

$$\mathbf{r}(t \pm \Delta t) = \mathbf{r}(t) \pm \dot{\mathbf{r}}(t)\Delta t + \frac{1}{2}\ddot{\mathbf{r}}(t)\Delta t^2 \pm \frac{1}{3!}\dddot{\mathbf{r}}(t)\Delta t^3 + \mathcal{O}(\Delta t^4) \tag{9}$$

Summing both equations and inserting Newton's law, we obtain

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{\mathbf{F}_i(t)}{m}\Delta t^2 + \mathcal{O}(\Delta t^4) \tag{10}$$

which is called *Verlet algorithm* and allows us to estimate the new position at time $t + \Delta t$ from the knowledge of the old positions at $t$ and $t - \Delta t$, and the forces at $t$. The velocity $\mathbf{v} = \mathbf{p}/m$ is not needed explicitly, but may be calculated from

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2) \tag{11}$$

It seems to be straightforward to write a small program which does the job, but at the same time we have to pose some important pratical and fundamental questions.

- Even knowing all positions/ velocities of all particles at all times, how do we visualize them? What are the observables we are interested in?
- What initial values should we use, how do they influence the results?
- Does the way we discretized the equation of motion in time modify the trajectories?
- How many particles do we actually need to describe macroscopic systems?

Answers to these questions and many more can be found in the literature on molecular dynamics [1, 2] and we might come back to them later in the cours. For the moment we will pick out some particular issues which help us to go over to a description in terms of statistical mechanics.

**Conservation laws**. In general, one considers Molecular Dynamics simulations at the same number of particles $N$, volume $V$, and energy $E$. What do these observables have in common and classify them agains others? They are all conserved quantities in an isolated system! Nature seems not to violate these symmetries, so if our simulation should reproduce nature as good as possible, we should check that these quantities are indeed conserved. This is quite trivial for $N$ and $V$, but energy is not conserved due to the time discretization of Newton's equation: some algorithms are better than others, if they conserve energy for longer times.

**Ergodicity**. What do we want to measure? Important observables are the one-body and two-body densities

$$\hat{\rho}^{(1)}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \tag{12}$$

$$\hat{\rho}^{(2)}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N} \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j) \tag{13}$$

and in Molecular Dynamics simulations we might measure time averaged quantities, e.g.

$$\overline{\hat{\rho}^{(1)}(\mathbf{r})} = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' \hat{\rho}^{(1)}(\mathbf{r}(t')) \tag{14}$$

In writing down this equation, we implicitly assule that the limit on the rhs exists. In particular, this means that the time-averaged quantities are independant of the initial positions of the particles at time $t = 0$. This assumption is not true in general. In the *ergodic hypothesis* one merely assumes that in the dynamical evolution the systems will reach any point in phase space $(\mathbf{R}, \mathbf{P})$ which is compatible with the energy $E$ in a long enough time intervall, and that it spends equal time in all possible regions of phase space. In order to enforce the ergodic behavior on the observables, we might run many Molecular dynamics simulations seperately with different initial conditions, but same total energies.

**Thermodynamic limit**. Which system sizes do we need? In order to compare with real experiments one should simulate $N \sim 10^{24}$ particles, obviously an impossible task, since we cannot even store all initial positions in any existing computer. Nevertheless, we can try to simulate different system sizes between $N \sim 10^2$ to $N \sim 10^6$ and extrapolate numerically some observable to the limit $N \to \infty$. This, of course, makes only sense if we compare obserables in a way that this limit exists, e.g. the energy per partcle etc.

**Ensemble average**. At this point it is quite natural to formulate the fundamental principle of statistical mechanics: In an (energetically) isolated system any state with total energy $E$ is equally likely to be observed. Therefore, instead of doing a very long Molecular dynamics calculation starting from one single set of initial conditions, we do an ensemble average over short runs starting with different initial conditions having the same energies.

Statistical mechanics is easily formulated using the language of quantum mechanics right from the beginning, so we will give a brief reminder of quantum mechanics before continuing statistical physics.

## III. QUANTUM MECHANICS

**Single partice quantum mechanics**. The state of the system is characterized by by a vector $|\Psi\rangle$, and the mean value of an observable with operator $\hat{O}$ in this state is given by

$$\langle\Psi|\hat{O}|\Psi\rangle \tag{15}$$

The state can be representated using any complete basis set, e.g. $\hat{r}|r\rangle = r|r\rangle$ is the position representation

$$\langle\Psi|\hat{O}|\Psi\rangle = \int d\mathbf{r} \int d\mathbf{r}' \Psi^*(\mathbf{r})\langle\mathbf{r}|\hat{O}|\mathbf{r}'\rangle\Psi(\mathbf{r}) \tag{16}$$

$$\Psi(\mathbf{r}) = \langle\mathbf{r}|\Psi\rangle, \quad \Psi^*(\mathbf{r}) = \langle\Psi|\mathbf{r}\rangle \tag{17}$$

In the The time evolution of the system's state is determined by Schrödinger's equation

$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle \tag{18}$$

where $\hat{H}$ is the Hamiltonian of the system, and operators are time-independant. Eigenstates of $\hat{H}$ with energies $E_i$ are stationary, and form a basis $|E_i\rangle$ with $\hat{H}|E_i\rangle = E_i|E_i\rangle$.

**Many particle quantum mechanics: Bosons and Fermions**. We can form a basis for many quantum particles by labelling each of them as we do for classical particles. If we have single particle states, e.g. energy eigenstates of a single particle hamiltonian $|E_i\rangle$ we can form a many-body state

$$|\Psi_N\rangle = |E_1\rangle_1 \times |E_2\rangle_2 \times \ldots |E_N\rangle_N \tag{19}$$

putting the first particle in an energy state $E_1$, the second into $E_2$, etc.. However, there is no possibility of distinguishing quantum particles, e.g. all Hamiltonians known up to now are symmetric with respect to particle permutations. Therefore, all wavefunctions needed to describe the world so far are seperated in two main classes which do not mix: Total symmetric and total antisymmetric wavefunctions

$$|\Psi_N\rangle_{S/A} = \frac{1}{\sqrt{N!}}\sum_P (\pm)^{|P|}|E_{P(1)}\rangle_1 \times |E_{P(2)}\rangle_2 \times \ldots |E_{P(N)}\rangle_N \tag{20}$$

where the summation is over all possible $N!$ permutations $P$ of particle labels. Particles which are described by symmetrical wavefunctions are called Bosons, antisymmetric wavefunctions describe Fermions. The framework for formal calculations with symmetric/antisymmetric many-body wavefunctions is called *second quantization*.

## IV. STATISTICAL MECHANICS

**Micro-canonical ensemble**. Since any energy eigenstate is equally probably in the micro-canonical ensemble, ($N$, $V$, $E$ are constant), the expectation value of an obersable, e.g. the one-body density, is given by

$$\langle\rho^{(1)}\rangle = \frac{\mathrm{Tr}\left[\delta_{\hat{H},E}\rho^{(1)}(\mathbf{r})\right]}{\mathrm{Tr}\left[\delta_{\hat{H},E}\right]} \tag{21}$$

$$= \frac{\sum_i \delta_{E,E_i}\langle E_i|\rho^{(1)}(\mathbf{r})|E_i\rangle}{\sum_i \delta_{E,E_i}} \tag{22}$$

where $\hat{H}$ is the Hamiltonian of the system and $E_i$ are its eigenvalues.

The denominator counts just the degeneracy of the energy level under consideration, and it is common to define the entropy $S$ of the system which is proportional to that degeneracy

$$S(E,N,V) = k_B \log \mathrm{Tr}\delta_{\hat{H},E} \tag{23}$$

$$= k_B \log \sum_i \delta_{E,E_i} \tag{24}$$

**Canonical ensemble**. Let us consider now that the system is connected to a bigger bath and can exchange energy with the bath. Bath and system together form an isolated system which can be described by the micro-canonical ensemble. Both, system and bath are sufficiently large systems such that the total energy of bath and system is additive such that surface effects can be neglected. The probability, $p_i$, to find the system at energy $E_i$ is equal to the probability that the bath has energy $E - E_i$

$$p_i = \frac{\text{number of states of energy } E - E_i \text{ in the bath}}{\text{total number of states in the bath}} = \frac{e^{S_B(E-E_i)/k_B}}{\sum_i e^{S_B(E-E_i)/k_B}} \tag{25}$$

where $S_B(E)$ is the entropy of the bath for a given bath-energy $E$ (notice that we sum over each energy states independent of degeneracies). If the bath is much bigger than the system, we can expand $S_B(E-E_i)$ around $E_i = 0$. We get

$$S_B(E - E_i) = S_B(E) - \frac{dS_B(E)}{dE} E_i + \dots \tag{26}$$

or

$$p_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \tag{27}$$

where we have defined the inverse temperature from the thermodynamic relation $1/T = \frac{\partial S}{\partial E}\Big|_{V,N}$, and $\beta = 1/k_B T$,. Since the total entropy $S_B(E-E_S) + S(E_S)$ must be maximal for the most likely energy of the system $E_s$ (assuming a large enough system), the temperature of the bath must equal the temperature of the system in equilibrium.

The canonical ensemble describes a system in contact with an energy bath. It is therefore characterized by the temperature $T$ (instead of the energy), and the probability $p_\alpha$ to find the system in a state $|\alpha\rangle$,

$$p_\alpha = \langle\alpha|\hat{\rho}(\beta)|\alpha\rangle \tag{28}$$

The probability is expressed introducing the density operator

$$\hat{\rho}(\beta) = \frac{e^{-\beta\hat{H}}}{Z(\beta)} = \frac{\sum_i |E_i\rangle\langle E_i| e^{-\beta E_i}}{Z(\beta)} \tag{29}$$

The normalisation factor $Z(\beta)$ is called partition function of the canonical ensemble

$$Z(\beta) = \sum_i e^{-\beta E_i}. \tag{30}$$

The mean value, $\langle\hat{O}\rangle$, of some obersable $\hat{O}$ can now be calculated

$$\langle\hat{O}\rangle = \mathrm{Tr}\left[\hat{O}\hat{\rho}(\beta)\right] = \sum_\alpha \langle\alpha|\hat{O}\hat{\rho}(\beta)|\alpha\rangle \tag{31}$$

One important observable is the energy $E$ itself and the mean energy of the system at temperature $T$ writes

$$\langle E\rangle = \frac{\sum_\alpha E_\alpha e^{-\beta E_\alpha}}{\sum_\alpha e^{-\beta E_\alpha}} = -\frac{\partial \log Z(\beta)}{\partial\beta} \tag{32}$$

can be calculated directly from the partition function. The partition function, indeed, plays a central role in statistical mechanics and the connections to thermodynamics is made by introducing the free energy, $F(\beta)$, via

$$Z(\beta) = \exp\left[-\beta F(\beta)\right]. \tag{33}$$

From the thermodynamic definition of the free energy,

$$F = \langle E\rangle - TS \tag{34}$$

we can define the entropy $S$ from thermodynamics. Again, we see that $e^S$ is connected to the typical number of states with energy $E$ in the system.

## V. THERMODYNAMICS OF IDEAL GASES

Assuming thermodynamic equilibrium, statistical averages of any observable $A$ are given by

$$\langle A\rangle \equiv \frac{1}{Z}\mathrm{Tr}Ae^{-\beta H} \tag{35}$$

where the normalization is given by partition function $Z$

$$Z = \mathrm{Tr}e^{-\beta H} \tag{36}$$

Here, $H = K + V + U$ is the Hamiltonian and $\beta = 1/k_BT$ the inverse temperature. Neglecting any relativistic effects, kinetic and potential energy writes

$$K = \sum_i \frac{\mathbf{p}_i^2}{2m}, \quad V = \sum_{i<j} v(r_{ij}), \quad U = \sum_i u(\mathbf{r}_i) \tag{37}$$

where $\mathbf{r}_i$ denotes the coordinate of particle $i$, $i = 1,\dots N$, and $\mathbf{p}_i$ is the corresponding momentum operator, $m$ is the particles mass, $v(r)$ the interparticle interaction ($r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$), and $u(\mathbf{r})$ any external potential.

**Classical particles**. For classical distinguishable particles, we can neglect the operator character of the momentum, such that the partition function splits into two parts

$$Z \sim \left[\prod_i \int d^3p_i e^{-\beta p_i^2/2m}\right] \times \int d\mathbf{R} e^{-\beta[V(\mathbf{R})+U(\mathbf{R})]} \tag{38}$$

where $\mathbf{R} = (\mathbf{r}_1,\dots,\mathbf{r}_N)$, and the gaussian integrals over momentum can be explicitly performed. As an immediate consequence, the momentum/velocity distribution is gaussian, and we obtain the equipartition theorem

$$\langle p_{\alpha,i}^2\rangle = mk_BT \tag{39}$$

where $\alpha = x, y, z$. Any deviation from a gaussian velocity distribution indicates either velocity dependent forces or the involvement of quantum mechanics and/or quantum statistics of the particles (or that the assumption of thermal equilibrium is violated).

**Configuration integral - Monte Carlo sampling.** After performing the integration over momenta for the partition function, we have to face the configuration integral $\sim \int d\mathbf{R}\exp[-\beta V(\mathbf{R}) - \beta U(\mathbf{R})]$. This is a $dN$-dimensional integral. Monte Carlo methods are a standard computational tool sampling the propability distribution

$$p(\mathbf{R}) = \frac{e^{-\beta[V(\mathbf{R})+U(\mathbf{R})]}}{\int d\mathbf{R} e^{-\beta[V(\mathbf{R})+U(\mathbf{R})]}} \tag{40}$$

e.g. via Markov chains. This allows us to compute Expectation values of observables up to a (controlled) statistical error.

For classical statistical mechanics the choice between molecular dynamics and Monte Carlo methods is a question of efficiency and taste. For quantum systems, we do not (yet) have a real choice, only Monte Carlo methods suitable extended are available so far to describe quite generally a broad class of generic quantum many-body problems.

**Quantum particles**. In quantum mechanics, momentum and position operator do not commute, so that $\exp[-\beta(K+V)] \neq \exp[-\beta K]\exp[-\beta V]$ in general, and there is no reason for the momentum distribution to be gaussian with a variance determined uniquely by temperature times the mass of the particles. For exmple, at low temperature the momentum distribution of a particle in an harmonic trapping potential will approach $\sim |\varphi_0(p)|^2 \sim \exp[-2p^2/m\hbar\omega]$ with a variance depending on the trap frequency $\omega$. More general, denoting $E_n$ the $n$th energy eigenstate of the system,

$$Z = \mathrm{Tr}e^{-\beta H} = \sum_n e^{-E_n/k_BT} \tag{41}$$

quantization effects reflecting the discreteness of the energy levels occur for $k_BT \lesssim \hbar\omega$ where $\hbar\omega \approx E_{n+1} - E_n$ is a typical excitation energy, e.g. for rotation or vibrational excitations of a molecules.

Considering purely translational degrees of freedom for particles confined in a (periodic) box, the single particle energy levels are given by $\varepsilon_n = (2\pi\hbar)^2(n_x^2 + n_y^2 + n_z^2)/2mL^2$ where $L$ is the box size and $n_\alpha = 0, \pm1, \dots$ are integers. For a gas of non-interacting particles, the energy levels of the total system, $E_n$, can then be easily constructed from

the single particle energy levels $\varepsilon_n$. If the particles are different (distinguishable), we can simply attribute to one energy level to each particle independently

$$Z = \left[\sum_n e^{-\beta\varepsilon_n}\right]^N \tag{42}$$

Approching the thermodynamic limit, $N, L \to \infty$ keeping the density $n = N/L^3$ constant, quantization effects of energy levels are thus restricted to extremely low temperatures $\sim \hbar^2/2mL^2 = N^{-2/3}\hbar^2 n^{2/3}/2m$. Approximating the summation over $n$ by an integral,

$$\sum_n e^{-\beta\varepsilon_n} \simeq L^3 \int \frac{d^3p}{(2\pi\hbar)^3} e^{-\beta p^2/2m} \tag{43}$$

we again obtain a gaussian velocity/momentum distribution. Quantum effects amount to the difference between the integral and the summation of the discrete energy levels. However, already for moderate particle numbers, they are only important in a very small window, approaching zero temperature with increasing particle number.

**Quantum statistics (Bosons)**. In the case of indistinguishable particles, only fully symmetric (Bosons) or fully antisymmetric (Fermions) wave functions with respect to particle exchanges are allowed. For ideal Bosons, the total energies $E_n = \sum_i N_i\varepsilon_k$ can be expressed in terms of occupation numbers, where $N_i = 0, 1, \ldots$ denotes the number of particles in the single particle state $i$, and we have

$$Z_N = \prod_i \sum_{N_i=0}^{\infty} \delta_{\sum_i N_i, N} e^{-\beta N_i \varepsilon_i} \tag{44}$$

The constraint due to the fixed number of particles, $N = \sum_i N_i$, is usually circumvented by switching to the grand canonical esemble,

$$Z = \sum_N e^{\beta\mu N} Z_N = \sum_{N_1=0}^{\infty} e^{-\beta N_1(\varepsilon_1-\mu)} \sum_{N_2=0}^{\infty} e^{-\beta N_2(\varepsilon_1-\mu)} \cdots = \prod_i \frac{1}{1-e^{-\beta(\varepsilon_i-\mu)}} \tag{45}$$

where $\mu$ is the chemical potential. The mean occupation of the single particle state $i$ is then given by the usual Bose distribution

$$\langle N_i\rangle = -\frac{d\log Z}{d(\beta\varepsilon_i)} = \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1} \tag{46}$$

Effects of (bosonic) quantum statistics can now be observed at low, but finite temperatures of macroscopic systems in the thermodynamic limit, e.g. in the momentum distribution or

$$\langle p_x^2\rangle \;=\; \frac{\sum_{\mathbf{p}} p_x^2 \langle N_{\mathbf{p}}\rangle}{\sum_{\mathbf{p}}\langle N_{\mathbf{p}}\rangle} \tag{47}$$

Since we have (going over from the summation to the integral)

$$\int d^dp\, p_x^2 \frac{1}{e^{\beta(p^2/2m-\mu)}-1} \;=\; \sum_{n=1}^{\infty} \int d^dp\, p_x^2 e^{-n\beta(p^2/2m-\mu)} \tag{48}$$

$$= \sum_{n=1}^{\infty} \frac{mk_BT}{n} \int d^dp\, e^{-n\beta(p^2/2m-\mu)} \tag{49}$$

$$< \; mk_BT \sum_{n=1}^{\infty} \int d^dp\, e^{-n\beta(p^2/2m-\mu)} \tag{50}$$

we can see that the classical equipartition theorem is violated for Bosons at any finite temperature

$$\langle p_x^2\rangle < mk_BT \tag{51}$$

due to the deviations of the Bose-Einstein distribution with respect to the Boltzmann distribution. Still, deviations are small at high temperatures where the Bose distribution is well approximated by the Boltzmann distribution, and increase smoothly lowering the temperature.

**Bose-Einstein condensation: ideal gas**. As the chemical potential approaches the single particle ground state energy, $\mu \to \varepsilon_0$, a singularity appears as $\langle N_0 \rangle \simeq T/(\varepsilon_0 - \mu)$ diverges. For a homogeneous ideal Bose gas in 3 dimensions, for any $\mu < 0$, the density of particles $n = \frac{1}{V}\sum_i \langle N_i \rangle$ remains finite for $T > 0$, so that the singularity at $\mu = 0$ is approached at the finite phase space density of Bose-Einstein condensation (BEC)

$$n\lambda^3\Big|_{\mu=0} = \frac{1}{V}\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{3/2} \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\hbar^2k^2/2mk_BT} - 1} \simeq 2.61\ldots \tag{52}$$

where $\lambda = \sqrt{2\pi\hbar^2/mk_BT}$ is the thermal wave length. At higher phase space densities, it can be shown that only the single particle ground state becomes macroscopically occupied, $\langle N_0 \rangle \simeq (n - 2.61\lambda^{-3})V \sim N$.

Bose-Einstein consensation of an ideal gas thus occurs abruptly at a the BEC transition temperature $T_c \simeq (n/2.61)^{2/3}2\pi\hbar^2/mk_B$, which remains finite in the macroscopic limit. Due to the macroscopic occupation of the zero momentum state, below $T_c$, some observables may even show macroscopic deviations with respect to the classiclly expected behavior.

*Example: Phonons*

**Solid state: lattice vibrations**. In a solid state, the potential energy dominates and the particles are localized around lattice vectors $\mathbf{l}_i$ in the absence of any external potential ($u \equiv 0$). We distribute the particles at the lattice sites, $\mathbf{r}_i = \mathbf{l}_i$ with $i = 1, \ldots N$ ($\mathbf{R} \equiv \mathbf{L}$), which minimize the total potential energy

$$V(\mathbf{R}) = \frac{1}{2}\sum_{i \neq j} v(r_{ij}) \tag{53}$$

$$\nabla_j V(\mathbf{R})\Big|_{\mathbf{R}=\mathbf{L}} = 0, \quad j = 1, \ldots N \tag{54}$$

so that no force is acting on the particles. At zero temperature we expect that classical particles form a perfect crystal. At non-zero temperatures, particles will move around their equilibrium position. Introducing $\delta_{i\alpha} = r_{i\alpha} - l_{i\alpha}$, $\alpha = 1, \ldots, d$, we may expand the potential energy and introduce the matrix of the harmonics

$$A_{i\alpha,j\beta} = \frac{\partial^2 V(\mathbf{R})}{\partial r_{i\alpha}\partial r_{j\beta}}\Big|_{\mathbf{R}=\mathbf{L}} \tag{55}$$

and the equations of motion write

$$m\frac{d^2\delta_{i\alpha}}{dt^2} + \sum_{j\beta} A_{i\alpha,j\beta}\delta_{j\beta} = 0 \tag{56}$$

These equations are still coupled. We can decouple them by diagonalizing the matrix $A$ (using that it is real, symmetric, and positiv semi-definitite)

$$A_{i\alpha,j\beta} = \sum_{k\gamma} U^*_{i\alpha,k\gamma}\frac{\omega^2_{k\gamma}}{m}U_{j\beta,k\gamma} \tag{57}$$

$$\sum_{k\gamma} U^*_{i\alpha,k\gamma}U_{j\beta,k\gamma} = \delta_{i,j}\delta_{\alpha,\beta} \tag{58}$$

Using normal coordinates

$$q_{k\gamma} = \sum_{i\alpha} U_{i\alpha,k\gamma}\delta_{i\alpha} \tag{59}$$

we obtain a set of uncoupled harmonic oscillators

$$\frac{d^2q_{k\alpha}(t)}{dt^2} + \omega^2_{k\alpha}q_{k\alpha}(t) = 0 \tag{60}$$

From the initial conditions, $r_{i\alpha}(t=0)$ and $p_{i\alpha}(t=0)$ we obtain $q_{k\alpha}(0)$ and $\dot{q}_{k\alpha}(0)$ and we can integrate analytically the equations of motion in the harmonic approximation.

Since, we have independent oscillators,

$$q_{k\alpha}(t) = q_{k\alpha}(0)\cos(\omega_{k\alpha}t) + \dot{q}_{k\alpha}(0)\sin(\omega_{k\alpha}t) \tag{61}$$

and total energy of the classical systems writes

$$E_{cl} = \sum_{k\alpha}\left[\frac{1}{2}\dot{q}_{k\alpha}^2 + \frac{1}{2}\omega_{k\alpha}^2 q_{k\alpha}^2\right] \tag{62}$$

From the mean square fluctuations averaged over time

$$\overline{q_{k\alpha}^2(t)} = \frac{1}{2}\left[q_{k\alpha}^2(0) + \dot{q}_{k\alpha}^2(0)\right] \tag{63}$$

and

$$\overline{\dot{q}_{k\alpha}^2(t)} = \omega_{k\alpha}^2\overline{q_{k\alpha}^2(t)} \tag{64}$$

we see that the mean potential energy equals the mean kinetic energy. Since for classical particles the kinetic energy is $k_BT/2$ per degree of freedom at thermal equilibrium, the total energy is simply given by $3Nk_BT$.

**Quantum mechanics: Phonons**. The quantized energy levels of an harmonic oscillator of strength $\omega$ are given by $E_n = (n+1/2)\hbar\omega$, and we can write down the total energy of the quantized lattice vibrations (Phonons):

$$E_{ph}(\{n_{k\alpha}\}) = \sum_{k\alpha}\left[n_{k\alpha} + \frac{1}{2}\right]\hbar\omega_{k\alpha} \tag{65}$$

as a function of the occupation numbers $n_{k\alpha}$ of each oscillator. The partition function is the trace over all possible occupation numbers

$$\begin{aligned} Z_{ph}(\beta) &= \sum_{\{n_{k\alpha}\}} e^{-\beta E_{ph}(\{n_{k\alpha}\})} && (66)\\ &= \sum_{n_{11}=0}^{\infty} e^{-\beta(n_{11}+1/2)\hbar\omega_{11}} \sum_{n_{12}=0}^{\infty} e^{-\beta(n_{12}+1/2)\hbar\omega_{12}} \cdots \sum_{n_{Nd}=0}^{\infty} e^{-\beta(n_{Nd}+1/2)\hbar\omega_{Nd}} && (67)\\ &= \prod_{k\alpha}\frac{e^{-\beta\hbar\omega_{k\alpha}/2}}{1-e^{-\beta\hbar\omega_{k\alpha}}} && (68) \end{aligned}$$

or the free energy

$$F_{ph} = T\sum_{k\alpha}\log\left(1 - e^{-\beta\hbar\omega_{k\alpha}}\right) + E_0 \tag{69}$$

where $E_0 = \sum_{k\alpha}\hbar\omega_{k\alpha}/2$ is the zero-point energy.

From the free energy we can obtain the internal energy $U = \langle E\rangle$ and the heat capacity $C_v = \partial U/\partial T$. At high temperatures, expanding the free energy around $\beta = 0$, we obtain $C_v = dN$, independant of the oscillator strength. For low temperature, we need more information about the mode structure. From translational invariance, we expect that the normal modes are characterized by wavevectors $\mathbf{k}$. Translations of the whole lattice correspond to the limit $\mathbf{k} \to 0$ and we expect that the modes are given by the speed of sound $c$. In the Debye approximation we assume

$$\omega_{\mathbf{k}\alpha} = \theta(K_m - |\mathbf{k}|)c|\mathbf{k}| \tag{70}$$

where $\alpha = 1, \ldots d$ counts the number of polarizations, and the cut-off vector $K_m$ is choosen to obtain the right degrees of freedom

$$N = \frac{1}{V}\sum_{\mathbf{k}\leq K_M} = \int_0^{K_m}\frac{d^dk}{(2\pi)^d} \tag{71}$$

The internal energy is then given by

$$\frac{U}{V} = \frac{E_0}{V} + \frac{1}{V}\sum_{k\alpha}\frac{\hbar\omega_{k\alpha}}{e^{\beta\hbar\omega_{k\alpha}}-1} \simeq \frac{E_0}{V} + d\int_0^{K_m}\frac{d^dk}{(2\pi)^d}\frac{\hbar ck}{e^{\beta\hbar ck}-1} \tag{72}$$

Making the integrand dimensionless and introducing the Debye temperature $\Theta = \hbar c K_m / k_B$ we can write

$$\frac{U}{V} = \frac{E_0}{V} + AT^{d+1} \int_0^{\Theta/T} \frac{x^d dx}{e^x - 1} \tag{73}$$

and one can convince oneself that we obtain $C_v \sim T^d$ at low temperatures, $T \ll \Theta$, since $A$ is temperature independant. Measurements of the specific heat of various solids show deviations from the classical prediction of a constant specific heat. Even at room temperature quantum mechanics is needed!

**Finite size effects.** Interested in bulk properties, we are interested in the extrapolation to the thermodynamic limit, $V \to \infty$. Let us focus on the ground state energy per volume

$$\frac{E_0^N}{V} = \frac{1}{V} \sum_{k\alpha} \frac{\hbar \omega_{k\alpha}}{2} \tag{74}$$

Computation of a finite size system with $N$ will have a systematic bias with respect to the thermodynamic limit

$$\Delta_N = \frac{E_0^\infty}{V} - \frac{E_0^N}{V} = \sum_\alpha \left[ \int \frac{d^d k}{(2\pi)^d} - \frac{1}{V} \sum_k \right] \frac{\hbar \omega_{k\alpha}}{2} \tag{75}$$

using the standard recipy of thermodynamic limit extrapolations, replacing discrete sums by integrals. Finite size effects then correspond to a mere quadrature error.

Quadrature errors depend on the analytic properties of the integrand. In the asymptotic limit, $V \to \infty$, the error is dominated by non-analytic points of the integral. We quite generally have $\omega_{k\alpha} \sim |k|$ for the acoustic modes at small k which is non analytic ($|k| = \sqrt{k_x^2 + k_y^2 + k_z^2}$) at $k = 0$. Our finite size error can then be estimated by the "missing volume" around the origin

$$\Delta_N \approx \sum_\alpha \int_{|k| \le 2\pi/L} \frac{d^d k}{(2\pi)^d} \frac{\hbar \omega_{k\alpha}}{2} \sim (2\pi/L)^{d+1} \tag{76}$$

We can now argue that the asymptotic form of the finite size error $\sim N^{-(d+1)/d}$ is more general, and also expected to be valid for interacting fluids and solids. From hydrodynamics we can expect long living modes with $\omega_k \sim |k|$ (for non-singular interaction potentials, important exception: Coulomb interaction) to entirely describe the long wave length behavior of solids and fluids. Further, we can expect that the frequency of the modes in the finite system, $\omega_k^N$, rapidly become independent of system size, once our simulation box exceeds the physical correlation length, $\omega_k^N \to \omega_k^\infty$, an assumption which can be explicitly checked, if needed. Notice that the $N^{-4/3}$ behavior in $d = 3$ is slightly different from a (wrong) $1/N$ extrapolation frequently used in numerical thermodynamic limit extrapolation (exception: Coulomb).

Further, since we have harmonic modes, finite size error of the potential energy equals that of the kinetic energy. Often, it is easier to understand the finite size corrections of the potential energy, but we know that we must have an equal contribution from the kinetic energy (at zero temperature!).

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[1] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids*
[2] D. Frenkel and B. Smit, *Understanding Molecular Simulation*