

I. BASICS OF STATISTICAL MECHANICS AND QUANTUM MECHANICS

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We introduce basic concepts of classical and quantum statistical mechanics. Starting from the classical equation of motion using the example of vibrations of atoms in a crystal, we shortly discuss the numerical approach using Molecular Dynamics for liquids and solids. We then introduce the basic concepts of statistical mechanics: partition function, free energy, density operators. As examples we work out the partition function of phonons in a solid in the Debye approximation and the classical limit of the quantum partition function of a gas/ liquid of particles.

We want to describe basic properties of systems containing a large number N of particles, from mesoscopic ($N \sim 10^3$) up to macroscopic ($N \sim 10^{24}$) systems in d spatial dimensions. (In general we have $d = 3$.) Liquids and solids are typical many-body systems. In many cases, the atoms/ molecules of the system are very well described by classical dynamics. Only at very low temperatures, the quantum nature of the particles becomes important. Liquid helium has been for long time “the example” of a quantum liquid. In the last years, experiments on alkaline gases have achieved the necessary densities/ temperatures to reach quantum degeneracy. Whereas observation of quantum effects for “real particles” necessitates quite some experimental efforts, a different kind of quantum liquid is dominating every day’s life, at least for condensed matter and solid state physicists: the electron gas.

Many body properties are best described in the framework of statistical mechanics, and we will give a short (and incomplete) introduction in classical and quantum statistics.

A. Classical dynamics

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

$$\begin{aligned}\frac{d\mathbf{r}_i}{dt} &= \frac{\mathbf{p}_i}{m} \\ \frac{d\mathbf{p}_i}{dt} &= \mathbf{F}_i\end{aligned}\tag{1}$$

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

$$\mathbf{F}_i = -\nabla_i \left[u(\mathbf{r}_i) + \sum_{j \neq i} v(r_{ij}) \right]\tag{2}$$

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

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 $i = 1, \dots, N$ ($\mathbf{R} \equiv \mathbf{L}$), which minimize the total potential energy

$$V(\mathbf{R}) = \frac{1}{2} \sum_{i \neq j} v(r_{ij})\tag{3}$$

$$\nabla_j V(\mathbf{R}) \Big|_{\mathbf{R}=\mathbf{L}} = 0, \quad j = 1, \dots, N\tag{4}$$

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 $\delta_{i\alpha} = r_{i\alpha} - l_{i\alpha}$,

$\alpha = 1, \dots, d$, we may expand the potential energy and introduce the matrix of the harmonics

$$A_{i\alpha,j\beta} = \frac{\partial^2 V(\mathbf{R})}{\partial r_{i\alpha} \partial r_{j\beta}} \Big|_{\mathbf{R}=\mathbf{L}} \quad (5)$$

and the equations of motion write

$$m \frac{d^2 \delta_{i\alpha}}{dt^2} + \sum_{j\beta} A_{i\alpha,j\beta} \delta_{j\beta} = 0 \quad (6)$$

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

$$A_{i\alpha,j\beta} = \sum_{k\gamma} U_{i\alpha,k\gamma}^* \frac{\omega_{k\gamma}^2}{m} U_{j\beta,k\gamma} \quad (7)$$

$$\sum_{k\gamma} U_{i\alpha,k\gamma}^* U_{j\beta,k\gamma} = \delta_{i,j} \delta_{\alpha,\beta} \quad (8)$$

Using normal coordinates

$$q_{k\gamma} = \sum_{i\alpha} U_{i\alpha,k\gamma} \delta_{i\alpha} \quad (9)$$

we obtain a set of uncoupled harmonic oscillators

$$\frac{d^2 q_{i\alpha}(t)}{dt^2} + \omega_{i\alpha}^2 q_{i\alpha}(t) = 0 \quad (10)$$

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

Fluids. If we consider a system with higher total energy (higher temperature), where the particles fluctuate wildly around their lattice positions, the harmonic approximation will fail. At some point, the particles will leave their lattice position and the crystal melts. The liquid/gas state is characterized that the kinetic energy dominates and the particles might move a certain distance before colliding (interacting) with other particles.

In generally we will not be able to solve the equations of motion analytically. However, we know exactly 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*.

B. 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 $t \pm \Delta t$

$$\mathbf{r}(t \pm \Delta t) = \mathbf{r}(t) \pm \dot{\mathbf{r}}(t) \Delta t + \frac{1}{2} \ddot{\mathbf{r}}(t) \Delta t^2 \pm \frac{1}{3!} \dddot{\mathbf{r}}(t) \Delta t^3 + \mathcal{O}(\Delta t^4) \quad (11)$$

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

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{\mathbf{F}_i(t)}{m} \Delta t^2 + \mathcal{O}(\Delta t^4) \quad (12)$$

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

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2) \quad (13)$$

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 course. 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 against 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

$$\hat{\rho}^{(1)}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (14)$$

$$\hat{\rho}^{(2)}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \sum_{j \neq i}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \quad (15)$$

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

$$\overline{\hat{\rho}^{(1)}(\mathbf{r})} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t dt' \hat{\rho}^{(1)}(\mathbf{r}(t')) \quad (16)$$

In writing down this equation, we implicitly assume that the limit on the rhs exists. In particular, this means that the time-averaged quantities are independent 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 interval, 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 separately 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 $N \rightarrow \infty$. This, of course, makes only sense if we compare observables in a way that this limit exists, e.g. the energy per particle 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.

C. Quantum Mechanics

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

$$\langle \Psi | \hat{O} | \Psi \rangle \quad (17)$$

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

$$\langle\Psi|\hat{O}|\Psi\rangle = \int d\mathbf{r} \int d\mathbf{r}' \Psi^*(\mathbf{r}) \langle\mathbf{r}|\hat{O}|\mathbf{r}'\rangle \Psi(\mathbf{r}) \quad (18)$$

$$\Psi(\mathbf{r}) = \langle\mathbf{r}|\Psi\rangle, \quad \Psi^*(\mathbf{r}) = \langle\Psi|\mathbf{r}\rangle \quad (19)$$

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

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle \quad (20)$$

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

$$|\Psi_N\rangle = |E_1\rangle_1 \times |E_2\rangle_2 \times \dots |E_N\rangle_N \quad (21)$$

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 separated in two main classes which do not mix: Total symmetric and total antisymmetric wavefunctions

$$|\Psi_N\rangle_{S/A} = \frac{1}{\sqrt{N!}} \sum_P (\pm)^{|P|} |E_{P(1)}\rangle_1 \times |E_{P(2)}\rangle_2 \times \dots |E_{P(N)}\rangle_N \quad (22)$$

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*.

D. 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 observable, e.g. the one-body density, is given by

$$\langle\rho^{(1)}\rangle = \frac{\text{Tr} [\delta_{\hat{H},E} \rho^{(1)}(\mathbf{r})]}{\text{Tr} [\delta_{\hat{H},E}]} \quad (23)$$

$$= \frac{\sum_i \delta_{E,E_i} \langle E_i | \rho^{(1)}(\mathbf{r}) | E_i \rangle}{\sum_i \delta_{E,E_i}} \quad (24)$$

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

$$S(E, N, V) = k_B \log \text{Tr} \delta_{\hat{H},E} \quad (25)$$

$$= k_B \log \sum_i \delta_{E,E_i} \quad (26)$$

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. The probability, p_i , to find the system at energy E_i is equal to the probability that the bath has energy $E - E_i$

$$p_i = \frac{e^{S_B(E-E_i)/k_B}}{\sum_i e^{S_B(E-E_i)/k_B}} \quad (27)$$

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

$$S_B(E - E_i) = S_B(E) - \frac{dS_B(E)}{dE} E_i + \dots \quad (28)$$

or

$$p_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \quad (29)$$

where we have defined the inverse temperature from the thermodynamic relation $1/T = \left. \frac{\partial S}{\partial E} \right|_{V,N}$, 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 , 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_α to find the system in a state $|\alpha\rangle$,

$$p_\alpha = \langle \alpha | \hat{\rho}(\beta) | \alpha \rangle \quad (30)$$

The probability is expressed introducing the density operator

$$\hat{\rho}(\beta) = \frac{e^{-\beta \hat{H}}}{Z(\beta)} = \frac{\sum_i |E_i\rangle \langle E_i| e^{-\beta E_i}}{Z(\beta)} \quad (31)$$

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

$$Z(\beta) = \sum_i e^{-\beta E_i}. \quad (32)$$

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

$$\langle \hat{O} \rangle = \text{Tr} [\hat{O} \hat{\rho}(\beta)] = \sum_\alpha \langle \alpha | \hat{O} \hat{\rho}(\beta) | \alpha \rangle \quad (33)$$

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

$$\langle E \rangle = \frac{\sum_\alpha E_\alpha e^{-\beta E_\alpha}}{\sum_\alpha e^{-\beta E_\alpha}} = - \frac{\partial \log Z(\beta)}{\partial \beta} \quad (34)$$

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

$$Z(\beta) = \exp [-\beta F(\beta)]. \quad (35)$$

From the thermodynamic definition of the free energy,

$$F = \langle E \rangle - TS \quad (36)$$

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.

Example: Phonons in a crystal. We have seen before, that classical particles will condense in a crystal at low enough temperatures, and the vibration of the atoms around their lattice sites is described using normal modes by dN independent harmonic oscillators of strength $\omega_{k\alpha}$. The total energy of the classical systems writes

$$E_{cl} = \sum_{k\alpha} \left[\frac{1}{2} \dot{q}_{k\alpha}^2 + \frac{1}{2} \omega_{k\alpha}^2 q_{k\alpha}^2 \right] \quad (37)$$

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

$$E_{ph}(\{n_{k\alpha}\}) = \sum_{k\alpha} \left[n_{k\alpha} + \frac{1}{2} \right] \hbar\omega_{k\alpha} \quad (38)$$

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

$$Z_{ph}(\beta) = \sum_{\{n_{k\alpha}\}} e^{-\beta E_{ph}(\{n_{k\alpha}\})} \quad (39)$$

$$= \sum_{n_{11}=0}^{\infty} e^{-\beta(n_{11}+1/2)\hbar\omega_{11}} \sum_{n_{12}=0}^{\infty} e^{-\beta(n_{12}+1/2)\hbar\omega_{12}} \dots \sum_{n_{Nd}=0}^{\infty} e^{-\beta(n_{Nd}+1/2)\hbar\omega_{Nd}} \quad (40)$$

$$= \prod_{k\alpha} \frac{e^{-\beta\hbar\omega_{k\alpha}/2}}{1 - e^{-\beta\hbar\omega_{k\alpha}}} \quad (41)$$

or the free energy

$$F_{ph} = T \sum_{k\alpha} \log(1 - e^{-\beta\hbar\omega_{k\alpha}}) + E_0 \quad (42)$$

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 $C_v = dN$, independent 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 $\mathbf{k} \rightarrow 0$ and we expect that the modes are given by the speed of sound c . In the Debye approximation we assume

$$\omega_{\mathbf{k}\alpha} = \theta(K_m - |\mathbf{k}|)c|\mathbf{k}| \quad (43)$$

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

$$N = \frac{1}{V} \sum_{\mathbf{k} \leq K_m} = \int_0^{K_m} \frac{d^d k}{(2\pi)^d} \quad (44)$$

The internal energy is then given by

$$\frac{U}{V} = \frac{E_0}{V} + \frac{1}{V} \sum_{k\alpha} \frac{\hbar\omega_{k\alpha}}{e^{\beta\hbar\omega_{k\alpha}} - 1} \simeq \frac{E_0}{V} + d \int_0^{K_m} \frac{d^d k}{(2\pi)^d} \frac{\hbar ck}{e^{\beta\hbar ck} - 1} \quad (45)$$

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

$$\frac{U}{V} = \frac{E_0}{V} + AT^{d+1} \int_0^{\Theta/T} \frac{x^d dx}{e^x - 1} \quad (46)$$

and one can convince oneself that we obtain $C_v \sim T^d$ at low temperatures, $T \ll \Theta$, since A is temperature independent.

Classical Statistical Mechanics. The classical limit of the partition function for a system with Hamiltonian

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2m} + \sum_i u(\hat{\mathbf{r}}_i) + \sum_{i < j} v(\hat{\mathbf{r}}_{ij}) \quad (47)$$

can be obtained by assuming that the momentum and position operators commute. In this limit we have

$$e^{-\beta \hat{H}} \simeq e^{-\beta \sum_i \frac{\hat{p}_i^2}{2m}} e^{-\beta [\sum_i u(\mathbf{r}_i) + \sum_{i < j} v(r_{ij})]} \quad (48)$$

Using momentum eigenfunctions $|\mathbf{p}_i\rangle$ as basis of indistinguishable particles to evaluate the trace, we get for the partition function

$$Z(\beta) = \frac{1}{N!^2} \sum_P \sum_{P'} (-1)^{|P+P'|} \sum_{\mathbf{p}_1} \langle \mathbf{p}_{P(1)} |_1 \times \sum_{\mathbf{p}_2} \langle \mathbf{p}_{P(2)} |_2 \dots \sum_{\mathbf{p}_N} \langle \mathbf{p}_{P(N)} |_N e^{-\beta \sum_i \frac{p_i^2}{2m}} \int d\mathbf{r}_1 |\mathbf{r}_1\rangle_1 \langle \mathbf{r}_1|_1 \times \int d\mathbf{r}_2 |\mathbf{r}_2\rangle_2 \langle \mathbf{r}_2|_2 \times \dots \int d\mathbf{r}_N |\mathbf{r}_N\rangle_N \langle \mathbf{r}_N|_N \quad (49)$$

$$e^{-\beta [\sum_i u(\mathbf{r}_i) + \sum_{i < j} v(r_{ij})]} |\mathbf{p}_{P'(1)}\rangle_1 \times |\mathbf{p}_{P'(2)}\rangle_2 \times \dots |\mathbf{p}_{P'(N)}\rangle_N \quad (50)$$

where we have inserted a complete set of position eigenfunctions (of distinguishable particles). (Note that one of $N!$ is coming that we overcount states the states, since any permutation of the integration labels correspond to exactly the same many-body state.) Using

$$\langle \mathbf{p} | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{p}' \rangle = \frac{1}{V} e^{i(\mathbf{p}' - \mathbf{p}) \cdot \mathbf{r} / \hbar} \quad (51)$$

and assuming that the relevant momenta are high enough so that we can set

$$\langle \mathbf{p} | \mathbf{r} \rangle \langle \mathbf{r} | \mathbf{p}' \rangle \approx \frac{1}{\hbar^d V} \delta_{\mathbf{p}, \mathbf{p}'} \quad (52)$$

This condition implies that the potential must vary slowly on the scale of the mean thermal wavelength $\lambda_T \sim \hbar p^{-1} \sim (\hbar^2/mT)^{1/2}$. Collecting terms together we obtain the classical partition function

$$Z(\beta) = \frac{1}{N! \hbar^{dN}} \int \frac{d\mathbf{P}}{(2\pi)^{dN}} \int d\mathbf{R} e^{-\beta E(\mathbf{R}, \mathbf{P})} \quad (53)$$

where the energy writes

$$E(\mathbf{R}, \mathbf{P}) = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i=1}^N u(r_i) + \sum_{i<j}^N v(r_{ij}) \quad (54)$$

The coordinates $\mathbf{R} \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ and momenta $\mathbf{P} \equiv (\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$ define the phase space of the classical system, and the probability of finding the particles at the point (\mathbf{R}, \mathbf{P}) is given by

$$\rho(\mathbf{R}, \mathbf{P}) d\mathbf{R} d\mathbf{P} = \frac{e^{-\beta E(\mathbf{R}, \mathbf{P})} d\mathbf{R} d\mathbf{P}}{Z(\beta)} \quad (55)$$

where $d\mathbf{R} \equiv \prod_i d\mathbf{r}_i$. The momentum integration in the partition function

$$Z(\beta) = \frac{1}{N! \hbar^{dN}} \int d\mathbf{R} \int d\mathbf{P} e^{-\beta E(\mathbf{R}, \mathbf{P})} \quad (56)$$

can be done explicitly in d spatial dimensions,

$$Z(\beta) = \left(\frac{m}{2\pi\hbar^2\beta} \right)^{dN/2} \frac{1}{N!} \int d\mathbf{R} e^{-\beta[U(\mathbf{R}) + V(\mathbf{R})]} \quad (57)$$

and only the configuration integral over the potential energy in position space remains, $U(\mathbf{R}) \equiv \sum_i u(r_i)$ and $V(\mathbf{R}) \equiv \sum_{i<j} v(r_{ij})$

It is an important feature of a classical system, that kinetic and potential energy separates in the partition function. Independantly of strength and form of the interactions, the distribution of momenta is always gaussian

$$\rho(\mathbf{P}) d\mathbf{P} \sim \int \rho(\mathbf{R}, \mathbf{P}) d\mathbf{R} d\mathbf{P} \sim e^{-\beta \sum_i p_i^2 / 2m} \quad (58)$$

and the kinetic energy is a direct measure of the temperature

$$\frac{d}{2} k_B T = \left\langle \frac{1}{N} \sum_i \frac{p_i^2}{2m} \right\rangle \quad (59)$$

This result is the equipartition theorem for classical particles. This relation allows us to determine the temperature in a Molecular Dynamics simulation of in experiments.

Appendix: gaussian integrals

Gaussian integrals play a central role in statistical mechanics, in d dimensions we have

$$I_d(\gamma) = \int d^d x e^{-\gamma \mathbf{x}^2} \quad (60)$$

where $\mathbf{x}^2 = x_1^2 + x_2^2 + \dots + x_d^2$. We can easily relate the integrals between different dimensions using

$$I_d(\gamma) = [I_1(\gamma)]^d \quad (61)$$

In $d = 2$ dimensions, the integral can be calculated easily changing to radial variables, $r = \sqrt{x_1^2 + x_2^2}$ and $\cos \theta = x_1/r$,

$$I_2 = \int_{-1}^1 d \cos \theta \int dr r e^{-\gamma r^2} = \pi \int d(r^2) e^{-\gamma r^2} = \frac{\pi}{\gamma} \quad (62)$$

So we get the general result

$$I_d(\gamma) = \left(\frac{\pi}{\gamma} \right)^{d/2} \quad (63)$$

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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*
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 - [4] L.P. Kadanoff, *Statistical Mechanics*
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