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Considering the problem of classical hard-sphere systems, we introduce basic Monte Carlo methods: direct sampling, Markov chains, and the Metropolis algorithm. Analytical results from the virial expansion of gases are used to illustrate the power of Monte Carlo methods for high-dimensional integrals compared to traditional integration rules. We then show, how Monte Carlo methods are used in the quantum body-problem. Using the variational principle, ground state properties can be obtained by evaluating correlated (Slater-Jastrow type) wavefunctions which approximate the true ground state wavefunction, done using Variational Monte Carlo (VMC). Exact representations of the many-body density matrix at finite temperatures can be obtained by Feynman's path integral, the starting point for Path-Integral-Monte Carlo methods.

A. A simple fluid: Classical Hard-Spheres

One of the most basic models of a fluid consists of putting many classical hard spheres inside a box. These hard spheres will move around like point-like ideal particles on straight lines unless they collide. The instantaneous collision will conserve the center-off-mass momentum of the two spheres, but choose a new direction for the relative momentum. (In relative coordinates the scattering of two spheres is replaced by the collision of one sphere with a wall given by the plane tangential to the spheres when they are exactly in contact. Whereas the components of the velocity parallel to the plane are conserved, the perpenticular components change sign due to the collision.) The dynamics might be analysed by a molecular dynamics simulation, but let us look at the problem of hard spheres from a statistical mechanics point of view [1, 2].

The classical partition function of N classical particles

$$Z_N = \frac{1}{N!h^{3N}} \int d\mathbf{P} \int d\mathbf{R} e^{-\beta H}$$
(1)

$$H = \sum_{i} \frac{p_{i}^{2}}{2m} + \sum_{i < j} v(r_{ij})$$
(2)

can be integrated over all momentum and we are left with the problem of calculating the so called configuration integral

$$Q_N = \int d\mathbf{R} \exp\left[-\beta \sum_{i < j} v(r_{ij})\right]$$
(3)

For hard spheres, the potential v(r) is infinity if any of the N particles overlapp with each other and zero otherwise. Therefore, the configuration integral is independent of the temperature $T = 1/\beta$ (we use $k_B = 1$ in the following). Further, any allowed configuration **R** where none of the spheres touch any other, contributes equally to the integral. If a is the diameter of the spheres, the configuration integral is a function of na^d where n = N/V is the density of the spheres, $Q_N(na^d)$.

B. Monte Carlo Simulations: direct sampling

Direct sampling. The configuration integral seems to be difficult to evaluate even for simple models as hard spheres (in two or three dimensions). But let us try to evaluate it on a computer: just put N hard spheres of diameter a randomly in a box of volume V and count how often we obtain a legal configuration where none of the spheres overlapp with any of the others. Only legal configurations contribute to the configuration integral. A sketch of the program which calculates the partition function for all densities na^d might look like that [3]

- a) initialize counters: t = 0, z(x) = 0, chose t_{max}
- b) choose \mathbf{r}_i with $-1/2 \leq r_i^{\alpha} < 1/2$ for $i = 1, \dots N$ randomly
- c) calculate the minimum distance $r_{\min} = \min[r_{ij}, i < j]$
- d) increase counters: t = t + 1, $z(x < r_{\min}) = z(x < r_{\min}) + 1$
- e) if $t \leq t_{\text{max}}$ continue with b)

Since each configuration with minimum distance r_{\min} is a legal configurations for a hard sphere systems with diameter $a < r_{\min}$ of the spheres, it contributes for the configuration integral of systems with density $na^d < nr_{\min}^d$. Therefore we have

$$Q_N(na^d) = V^N \lim_{t_{\max} \to \infty} \frac{z(a/L)}{t_{\max}}$$
(4)

This method of integration is an example of *direct sampling Monte Carlo* calculations. What have we done? We have just integrated a very simple function

$$I_a = \frac{1}{V^N} \int_{V^N} d\mathbf{R} \pi_a(\mathbf{R}) \tag{5}$$

$$\pi_a(\mathbf{R}) = \prod_{i < j} [1 - \theta(a - r_{ij})] \tag{6}$$

where $\theta(x)$ is the usual step function with $\theta(x < 0) = 0$ and $\theta(x \ge 0) = 1$. We have done the integration distributing the integration variable according to a probability density $p(\mathbf{R})$

$$I_a = \int d\mathbf{R} \pi_a(\mathbf{R}) p(\mathbf{R}) \tag{7}$$

where $p(\mathbf{R}) = V^{-N}$ is uniform in our case.

Why should the random distribution should work better than using sophistic integration rules (Simpson, Romberg, etc.) with a uniform well-defined grid? It is easy to see that the later will fail for large enough dimensions. For example, consider N hard spheres in d dimensions at a density na^d . In order to use a grid size of order δ we have to do

$$\left(\frac{L}{\delta}\right)^{dN} = \left(\frac{N}{na^d}\right)^N \left(\frac{a}{\delta}\right)^{dN} \tag{8}$$

evaluations of the integrand. However, this number is limited by the amount of computer time we can afford In order to give at least approximate results we have to choose $\delta < a$. Since $na^d < 1$, we see that already for N around 10 the task gets rapidely hopeless, independent of the size of your computer. Clearly, since any regular grid starts putting all particles in the first corner, then N - 1 in the first corner and one jut besides, etc., we waste almost all our time looking at completely unrealistic configurations, they will overlapp for sure and therefore do not contribute to the integral at all. The integrand actually is zero in a quite big amount of configurational space. Note further, that highly sophisticated integration rules of a uniform grid are based on analytic expansions of the integrand, and, therefore are not of any use in our case.

Monte Carlo error. Integrations on a regular grid is not feasable for any reasonable number of particles, but how comes that the Monte Carlo method can ever work? Clearly, random numbers will almost never put all particles in just one corner, so some problems above are clearly avoided. But to see that it really works we have to analyze the method a bit more in detail, in particular the Monte Carlo error.

In the direct sampling approach we randomly choose at each time t_i a new configuration \mathbf{R}_i where all particles are distributed uniformly inside the box of volume V. Repeating this step M times, the integral (5) is estimated by

$$I_a^M = \frac{1}{M} \sum_{i \le M} \pi_a(\mathbf{R}_i) \tag{9}$$

Clearly if $M \to \infty$ we get the exact result, $I_a^{\infty} \equiv I_a$, just like in the case we use any other integration method. What we need to know is the error of the calculation for finite M, e. g.

$$\operatorname{error}(M) \sim \sqrt{(I_a^M - I_a^\infty)^2} \tag{10}$$

We can estimate this error using only informations for finite M by calculating the variance σ_M^2

$$\sigma_M^2 = \frac{1}{M} \sum_{i \le M} \left[\pi_a(\mathbf{R}_i) \right]^2 - \left[\frac{1}{M} \sum_{i \le M} \pi_a(\mathbf{R}_i) \right]^2 \tag{11}$$

The error of our calculation can then be estimated as

$$\operatorname{error}(M) \sim \frac{\sigma_M}{\sqrt{M}}$$
 (12)

Let us assume that the distribution has a finite variance in the limit $M \to \infty$ (central limit theorem). As we can see, independent of the dimension of the integral, the error depends only on the number of evaluations M and decays as $M^{-1/2}$. For that reason, the Monte Carlo method becomes superior to any traditional integration using a fixed grid size, as soon as the dimension of the integral is large, and the variance of the distribution remains finite.

Still, to estimate if the Monte Carlo sampling is also captable to give reliable results in practice, we have to estimate roughly the variance, σ_M^2 . For the particular case of hard spheres, the probability distribution $\pi_a(\mathbf{R})$ is either one or zero, so that we have $\pi_a^2(\mathbf{R}) = \pi_a(\mathbf{R})$. Therefore we get for the variance

$$\sigma_M^2 \simeq I_a - I_a^2 \sim I_a \tag{13}$$

where we have used that $I_a < 1$. In order to obtain a reasonable answer we need an error smaller than the expected value or

$$\frac{\operatorname{error}(M)}{I_a} \simeq \frac{\sigma}{I_a M^{1/2}} \ll 1 \tag{14}$$

For the direct sampling of hard spheres we have $\operatorname{error}(M)/I_a \sim (I_a M)^{-1/2}$ and we need $M \sim 1/I_a$ in order to get sensible results from the Monte Carlo method. For a dilute gas of hard spheres the integral we can calculate $I_a < 1$ which is related to the virial expansion. In general, we expect the logarithm of the configuration integral to be extensive, $-\log I_a \sim N$, so that the direct Monte Carlo sampling fails also in the limit of large N.

C. Virial Expansion for a dilute gas

The pressure P of a system of N particles as a function of the volume V and temperature T defines the equation of state and is given by

$$P = -\frac{\partial F_N(V,T)}{\partial V}\Big|_T \tag{15}$$

where $F_N(V,T) = -T \log Z_N$ is the free energy. Since the kinetic energy of a classical gas does not depend on the volume, only the configuration integral contributes to the pressure. For an ideal gas

$$Q_N^{ideal} = V^N \tag{16}$$

and we have

$$\frac{P_{ideal}V}{NT} = 1\tag{17}$$

For real gases, the equation of state in the dilute limit is summarized as

$$\frac{PV}{NT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots$$
(18)

where B(C) is called second (third) virial coefficient. Methods developped to calculate the virial coefficients will help us to determine our integral $I_a = Q_N/V^N$.

To calculate B, let us put one extra particle in our system of N particles

$$Q_{N+1} = \int d\mathbf{R}_N e^{-\beta \sum_{i< j}^N v(r_{ij})} \int dr_{N+1} e^{-\beta \sum_{i=1}^N v(|\mathbf{r}_{N+1} - \mathbf{r}_i|)}$$
(19)

Using the N-particle density of the N-particle system

$$n(\mathbf{X}) \equiv n(\mathbf{x}_1, \mathbf{x}_2, \ldots) = \frac{N^N}{Q_N} \int d\mathbf{R}_N e^{-\beta \sum_{i< j}^N v(r_{ij})} \prod_k \delta(\mathbf{x}_k - \mathbf{r}_k)$$
(20)

we can rewrite Eq. (19) as

$$\frac{Q_{N+1}}{Q_N} = \frac{1}{N^N} \int d\mathbf{r} \int d\mathbf{X} \prod_k e^{-\beta v(|\mathbf{r}-\mathbf{x}_k|)} n(\mathbf{X})$$
(21)

To first approximation we can set $n(\mathbf{X}) = n^N$ where n = N/V is the constant density of the system

$$\frac{Q_{N+1}}{Q_N} = \frac{1}{V^N} \int d\mathbf{r} \left[\int d\mathbf{x} e^{-\beta v(|\mathbf{r}-\mathbf{x}|)} \right]^N \tag{22}$$

Now for hard spheres the integral inside of the brackets is just the reduced volume $V - 2(d-1)\pi a^d/d$ in d = 2 or d = 3 dimensions, so that we have

$$\frac{Q_{N+1}}{Q_N} = V \left(1 - \frac{\eta}{V}\right)^N \tag{23}$$

where we have defined $\eta = 2(d-1)\pi a^d/d$. We now have a recursive formula which gives

$$Q_{N} = V \left(1 - \frac{\eta}{V}\right)^{N-1} Q_{N-1} = V^{2} \left(1 - \frac{\eta}{V}\right)^{(N-1) + (N-2)} Q_{N-2} = \cdots = V^{N} \left(1 - \frac{\eta}{V}\right)^{\frac{N(N-1)}{2}}$$
(24)

where we have used $\sum_{i=1}^{N-1} i = N(N-1)/2$ For big systems we get

$$Q_N = V^N e^{-N^2 \eta/2V}$$
(25)

or for the pressure

$$\frac{PV}{NT} = \frac{V}{N} \frac{\partial \log Q_N}{\partial V} = 1 + \eta n/2 \tag{26}$$

The second virial coefficient writes

$$B = N\eta/2 \tag{27}$$

D. Monte Carlo methods: Markov chains, detailed balance, and Metropolis algorithm

From the virial expansion we know the value of our integral I_a in the dilute limit

$$I_a = Q_N / V^N = e^{-Nn\eta/2} \tag{28}$$

where $N\eta$ is the total excluded volume due to the hard spheres. For the direct sampling method we therefore need at least

$$M \sim 1/I_a \sim e^{Nn\eta/2} \tag{29}$$

number of evaluations of the integrand. For dilute systems $n\eta \ll 1$ we can therefore integrate much more particles N than using any sophisticated method with fixed grids, however, our methods severly fails for denser systems.

Markov chains. It is clear that for dense systems, random configurations of the spheres will in general lead to overlapping spheres, and only very occasionally a legal configuration is picked up. It is therefore tempting to try only

small, local changes of the configuration once a legal configuration is found. However, at this point we introduce an (artificial) Monte Carlo dynamic in the system and we have to analyse the dynamics to make sure to get what we want. We consider the conditional probability that the system is in state \mathbf{R}_{t_n} at time t_n

$$P(\mathbf{R}_{t_n}|\mathbf{R}_{t_{n-1}},\mathbf{R}_{t_{n-2}},\ldots,\mathbf{R}_{t_1})$$

$$(30)$$

given that at the preceding time it was in state $\mathbf{R}_{t_{n-1}}$ at t_{n-1} , $\mathbf{R}_{t_{n-2}}$ at t_{n-2} , etc. Our direct sampling algorithm was just the most simplest case where this conditional probability is just given statistically uncorrectated samples, or

$$P_{\text{direct sampling}}(\mathbf{R}_{t_n}|\mathbf{R}_{t_{n-1}},\mathbf{R}_{t_{n-2}},\ldots,\mathbf{R}_{t_1}) = p(\mathbf{R}_{t_n})p(\mathbf{R}_{t_{n-1}})\cdots p(\mathbf{R}_{t_1})$$
(31)

A particular dynamics which is still simple to analyse are obtained by Markov chains: we choose certain transition probabilities from one state to another which do not depend on the particular state

$$P_n(\mathbf{R}_{t_n}|\mathbf{R}_{t_{n-1}},\mathbf{R}_{t_{n-2}},\ldots,\mathbf{R}_{t_1}) = p(\mathbf{R}_{t_1})T(\mathbf{R}_{t_1}\to\mathbf{R}_{t_2})T(\mathbf{R}_{t_2}\to\mathbf{R}_{t_3})\cdots T(\mathbf{R}_{t_{n-1}}\to\mathbf{R}_{t_n})$$
(32)

The basic object in Markov chains is the transition probability $T(\mathbf{R} \to \mathbf{R}')$ which depends on both states \mathbf{R} and \mathbf{R}' but is independent of time. The transition probability must be normalized

$$\sum_{\mathbf{R}'} T(\mathbf{R} \to \mathbf{R}') = \sum_{\mathbf{R}} T(\mathbf{R} \to \mathbf{R}') = 1$$
(33)

Detailed balance. We can write down a master equation for the probability, $p(\mathbf{R}, t+1)$, to find \mathbf{R} at t+1 knowing the distribution at t by considering all possible processes

$$p(\mathbf{R}, t+1) = \sum_{\mathbf{R}' \neq \mathbf{R}} p(\mathbf{R}', t) T(\mathbf{R}' \to \mathbf{R}) + T(\mathbf{R} \to \mathbf{R}) p(\mathbf{R}, t)$$
(34)

or using the normalization (33)

$$p(\mathbf{R},t+1) - p(\mathbf{R},t) = \sum_{\mathbf{R}' \neq \mathbf{R}} p(\mathbf{R}',t) T(\mathbf{R}' \to \mathbf{R}) - \sum_{\mathbf{R}' \neq \mathbf{R}} T(\mathbf{R} \to \mathbf{R}') p(\mathbf{R},t)$$
(35)

$$= \sum_{\mathbf{R}'} p(\mathbf{R}', t) T(\mathbf{R}' \to \mathbf{R}) - \sum_{\mathbf{R}'} p(\mathbf{R}, t) T(\mathbf{R} \to \mathbf{R}')$$
(36)

The stationary state $\pi(\mathbf{R}) = \lim_{t \to \infty} p(\mathbf{R}, t)$ then satisfied the so called detailed balance condition

$$\sum_{\mathbf{R}'} \pi(\mathbf{R}') T(\mathbf{R}' \to \mathbf{R}) = \sum_{\mathbf{R}'} \pi(\mathbf{R}) T(\mathbf{R} \to \mathbf{R}')$$
(37)

which can be enforced for each term in the summation since all elements are non negative

$$\pi(\mathbf{R}')T(\mathbf{R}' \to \mathbf{R}) = \pi(\mathbf{R})T(\mathbf{R} \to \mathbf{R}')$$
(38)

This condition just ensures that once equilibrium is reached it remains unchanged, since losses and gains just compensate.

Exponential convergence. How can be assure that the Markov process is really converging to the stationary distribution $\pi(\mathbf{R})$ and what is the time scale associated to reach stationarity? Let us start from an arbitrary distribution $p(\mathbf{R}_0, t = 0)$, after time t = n we have

$$p(\mathbf{R}_n, t=n) = \sum_{\mathbf{R}_0} \sum_{\mathbf{R}_1} \sum_{\mathbf{R}_2} \cdots \sum_{\mathbf{R}_{n-1}} p(\mathbf{R}_0, t=0) T(\mathbf{R}_0 \to \mathbf{R}_1) T(\mathbf{R}_1 \to \mathbf{R}_2) \cdots T(\mathbf{R}_{n-1} \to \mathbf{R}_n)$$
(39)

which can be simply written as a matrix product introducing a huge vecor to represent the probabilities $p(\mathbf{R}, t)$ and a matrix for $T(\mathbf{R} \to \mathbf{R}')$

$$p(\mathbf{R}_n, t=n) = \langle \mathbf{R}_n, t=n | T^n | \mathbf{R}_0, t=0 \rangle p(\mathbf{R}_0, t=0)$$
(40)

Diagonalizing the matrix T and denoting $|\lambda_i\rangle$ the eigenvector with eigenvalue λ_i we have

$$p(\mathbf{R}_n, t=n) = \sum_i \lambda_i^n \langle \mathbf{R}_n, t=n | \lambda_i \rangle \langle \lambda_i | \mathbf{R}_0, t=0 \rangle p(\mathbf{R}_0, t=0)$$
(41)

$$\simeq \lambda_0^n a_0 [1 + (\lambda_1/\lambda_0)^n a_1 + \ldots]$$
(42)

where λ_0 is the largest eigenvector. For large *n* we will have exponential convergence to this eigenvector since the contributions of the other eigenvectors will decay with e.g.

$$(\lambda_1/\lambda_0)^n = e^{-n\log\lambda_0/\lambda_1} \tag{43}$$

for the first eigenstate.

Using the normalization, Eq. (33), we have

$$\sum_{\mathbf{R}'} \pi(\mathbf{R}) T(\mathbf{R} \to \mathbf{R}') = \pi(\mathbf{R})$$
(44)

Substituting the detailed balance inside the lbs we get

$$\sum_{\mathbf{R}'} \pi(\mathbf{R}') T(\mathbf{R}' \to \mathbf{R}) = \pi(\mathbf{R})$$
(45)

we see that the stationary distribution $\pi(\mathbf{R})$ is an eigenstate of the transition matrix with eigenvalue one. If we can show that all other eigenvalues are smaller than one we indeed reach the desired equilibrium. This can indeed be assured if it is possible to go from any of the configurations to all others in a finite number of steps.

Metropolis algorithm. A particular solution for the transition matrix which satisfies detailed balance is the Metropolis algorithm using

$$T(\mathbf{R} \to \mathbf{R}') = \min\left[1, \frac{\pi(\mathbf{R}')}{\pi(\mathbf{R})}\right]$$
(46)

To prove detailed balance for general values of $\pi(\mathbf{R})$ and $\pi(\mathbf{R}')$ we write down the tranition matrix $T(\mathbf{R} \to \mathbf{R}')$ and $T(\mathbf{R}' \to \mathbf{R})$. Assume $\pi(\mathbf{R}') > \pi(\mathbf{R})$ first. In that case we have $T(\mathbf{R} \to \mathbf{R}') = 1$, but $T(\mathbf{R}' \to \mathbf{R}) = \pi(\mathbf{R})/\pi(\mathbf{R}')$. We immediately find $\pi(\mathbf{R})T(\mathbf{R} \to \mathbf{R}') = \pi(\mathbf{R})'T(\mathbf{R}' \to \mathbf{R})$ to be fullfilled. The case $\pi(\mathbf{R}) > \pi(\mathbf{R}')$ goes through just the same.

A priori probabilities. Sometimes it is useful to choose a-priori probabilities to propose moves from \mathbf{R} to \mathbf{R}' which are different from the a-priori probability for the return move \mathbf{R}' to \mathbf{R} . In this case we write

$$T(\mathbf{R} \to \mathbf{R}') = \mathcal{A}(\mathbf{R} \to \mathbf{R}')p(\mathbf{R} \to \mathbf{R}')$$
(47)

where $\mathcal{A}(\mathbf{R} \to \mathbf{R}')$ is the a-priori probability and $p(\mathbf{R} \to \mathbf{R}')$ the final acceptance probability. Enforcing detailed balance we are led to a generalized Metropolis algorithm for the acceptance probability

$$p(\mathbf{R} \to \mathbf{R}') = \min\left[1, \frac{\pi(\mathbf{R}')}{\mathcal{A}(\mathbf{R} \to \mathbf{R}')} \frac{\mathcal{A}(\mathbf{R}' \to \mathbf{R})}{\pi(\mathbf{R})}\right]$$
(48)

The a-priori probability is choosen such that it is fast to evaluate and bigger moves can be done for a reasonable acceptance probability.

Hard Spheres Monte Carlo. It is natural to choose a stationary probability $\pi(\mathbf{R}) \propto \pi_a(\mathbf{R})$ for our gas of hard spheres with diameter a. The simplest choice for the a-priori probability is to randomly choose one particle and to displays it by a random vector within a box of dimension δ . The acceptance probability for this move using the Metropolis algorithm is simple: if we obtain a legal position we accept the attempted move, otherwise we reject and stay at the same place.

The practical experience with Markov chain Monte Carlo shows that it is able to simulate very large system sizes even for dense liquids undergoing phase transitions. Unfortunantely, I'm not able to estimate the (exponential) speed of convergence towards equilibrium for hard spheres

Pair correlation function and Structure factor. The Markov chain construction does not allow us to obtain the full configuration integral Q_N any more, but the pair correlation function, g(r), defined as [5]

$$g(\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2) = \frac{N(N-1)}{n^2} \frac{1}{Q_N} \int d\mathbf{r}_3 \int d\mathbf{r}_4 \cdots \int d\mathbf{r}_N \, e^{-\beta \sum_{i < j} v(r_{ij})} \tag{49}$$

or the structure factor

$$S(\mathbf{k}) = \frac{1}{N} \frac{1}{Q_N} \int d\mathbf{R} \, e^{-\beta \sum_{i < j} v(r_{ij})} \rho_{\mathbf{k}} \rho_{-\mathbf{k}}$$
(50)

$$\rho_{\mathbf{k}} = \sum_{i} e^{i\mathbf{k}\cdot\mathbf{r}_{i}} \tag{51}$$

are important quantities which can be calculated directly. Both are related by a Fourier transform

$$S(\mathbf{k}) = 1 + n \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} g(\mathbf{r})$$
(52)

and clearly distinguish a liquid where they are isotrop from a crystal-like state with sharp and strongly angular dependant peaks.

E. Quantum many-body systems

In contrast to classical dynamics, there exists no reliable method to calculate the dynamics of an interacting quantum many-body system. Since we cannot perform a "Quantum Molecular Dynamics" simulation for almost any quantum many-body system, Monte Carlo methods naturally play a much more important role there. We distinguish between ground state Quantum Monte Carlo to obtain ground state properties as the energy or wavefunction, and finite temperature Path-Integral Monte Carlo for thermodynamic properties at non-zero temperature. Both rely on a mapping of the quantum problem to a classical system.

Variational principle. The ground state energy of any quantum system can be bounded from above using the variational principle: The energy expectation value of any *reasonable* wavefunction, $|\Psi\rangle$, is always higher than the ground state energy, E_0

$$E_0 \le \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{53}$$

Using eigenstates of the Hamiltonian, we can easily prove this inegality

$$\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_{i} |\langle \Psi | E_i \rangle|^2 E_i}{\sum_{i} |\langle \Psi | E_i \rangle|^2} \ge \frac{\sum_{i} |\langle \Psi | E_i \rangle|^2 E_0}{\sum_{i} |\langle \Psi | E_i \rangle|^2} = E_0$$
(54)

since $E_i \ge E_0$ by definition. Reasonable wavefunctions are wavefunctions continuous in space and with a continuous derivative satisfying the boundary conditions of our system.

Variational Monte Carlo (VMC). We will use the position representation for our trial wavefunction, $\Psi(\mathbf{R})$, and get

$$E_0 \le \frac{\int d\mathbf{R} |\Psi(\mathbf{R})|^2 E_L(\mathbf{R})}{\int d\mathbf{R} |\Psi(\mathbf{R})|^2} \tag{55}$$

where we have introduced the local energy

$$E_L(\mathbf{R}) = \frac{H\Psi(\mathbf{R})}{\Psi(\mathbf{R})} \tag{56}$$

The representation (55) is the starting point for numerical approaches: just parametrize your wavefunction and minimize the energy!

Jastrow wavefunction. The simplest wavefunction which captures the basic features of the ground state of homogeneous quantum liquids is a Jastrow wavefunction [4]

$$\Psi(\mathbf{R}) = e^{-\sum_{ij} u(r_{ij})} \tag{57}$$

where u(r) is a one dimensional function which is either given by some approximate theory (Quantum Cluster expansions, Correlated Basis Function) or which can be parametrized with few parameters which are then optimized to lower the energy.

However, already the evaluation of the wavefunction, or the energy, using the Jastrow approximation cannot be done analytically in most cases (and we have not yet optimized it). However, notice that the form (57) is formally just the same as the integrand of the configuration integral of a classical fluid, Eq (3), with a corresponding inter-particle potential given by $u(r) = \beta v(r)$. We have shown before how to solve this problem using Monte Carlo methods and it is naturally to extend it to the classical problem.

Slater-Jastrow. The Jastrow ansatz, Eq. (57), is symmetric with respect to particle exchanges and therefore can approximate Bosonic wavefunctions. In order to treat Fermions, we have to use an antisymmetric ansatz for the wavefunction. This is conviniently done using an additional term - a Slater determinant of single particle orbitals

$$D(\mathbf{R}) = \det_{ki} \phi_k(\mathbf{r}_i). \tag{58}$$

For homogeneous systems we are forced to use plane wave orbitals $\phi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$ inside the determinant, typically the first N plane-waves with energies $\hbar^2 k^2/2m$ less than the Fermi-energy ϵ_F . The simplest non-trivial ansatz for the fermionic wavefunction, the Slater-Jastrow form, is thus

$$\Psi_F(\mathbf{R}) = \det_{ki} \phi_k(\mathbf{r}_i) e^{-\sum_{ij} u(r_{ij})}$$
(59)

and is still one of the most used forms for precise Fermion calculations up to date.

Feynman's path integral. Now we look at the quantum many-body-problem at finite temperture $T = 1/\beta$. The partition function (neglecting the symmetry of the particles using "Boltzmann quantum particles") can be written as

$$Z = \int d\mathbf{R} \left\langle \mathbf{R} | e^{-\beta H} | \mathbf{R} \right\rangle \tag{60}$$

and the natural object for Monte Carlo simulation is the N-body density matrix, ρ , in the position representation

$$\rho(\mathbf{R}, \mathbf{R}, \beta) = \left\langle \mathbf{R} | e^{-\beta H} | \mathbf{R} \right\rangle \tag{61}$$

which is positive semi-definite for any Hamiltonian with time-reversal symmetry. For many thermal properties, only the diagonal elements are neccessary. Nevertheless, we have no explicit form for $\rho(\mathbf{R}, \mathbf{R}, \beta)$ for any interacting quantum system at low temperature, so we cannot apply any Monte Carlo strategy directly. But any density matrix satisfies a convolution equation, as we can see, writing

$$e^{\beta H} = \left(e^{-\beta H/M}\right)^M = e^{-\beta H/M} e^{-\beta H/M} \cdots e^{-\beta H/M}$$
(62)

and inserting a complete set of states in between any of the exponentials on the rhs. We get

$$\rho(\mathbf{R}, \mathbf{R}', \beta) = \int d\mathbf{R}_1 \int d\mathbf{R}_2 \cdots \int d\mathbf{R}_{M-1} \left\langle \mathbf{R} | e^{-\tau H} | \mathbf{R}_1 \right\rangle \left\langle \mathbf{R}_1 | e^{-\tau H} | \mathbf{R}_2 \right\rangle \cdots \left\langle \mathbf{R}_{M-1} | e^{-\tau H} | \mathbf{R}' \right\rangle$$
(63)

$$= \int d\mathbf{R}_1 \int d\mathbf{R}_2 \cdots \int d\mathbf{R}_{M-1} \rho(\mathbf{R}, \mathbf{R}_1, \tau) \rho(\mathbf{R}_1, \mathbf{R}_2, \tau) \cdots \rho(\mathbf{R}_{M-1}, \mathbf{R}', \tau)$$
(64)

using $\tau = \beta/M$ What did we gain? At the prize of doing a lot of integrals more, we have found an expression which involves only density matrix at higher temperature or $\tau = \beta/M \ll \beta$. We can now use explicit expressions known for density matrices at high temperature, and use a Monte Carlo method to sample all the integrals. This is known as Path-Integral-Monte Carlo, since in the limit of $\tau \to 0$ we obtain Feynman's path integral in Eq. (64). It is at the moment one of the most powerful tools for quantum many-body calculations.

- [1] R.P. Feynman, Statistical Mechanics
- [2] W. Krauth, Statistical Mechanics: Algorithms and Computations
- [3] Many algorithm, programs, etc. used in Ref. [2] and some more are available on the web page of the book: http://www.smac.lps.ens.fr
- [4] E. Feenberg, Theory of Quantum Fluids
- [5] J.P. Hansen and I.R. McDonald, Theory of Simple Liquids