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Monte Carlo Method ...

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0.1 Quantum Monte Carlo simulations: A first introduction

0.5.1 Quantum Statistical Mechanics vs. Classical Statistical Mechanics

To be specific, let us consider for the moment the problem of N atoms in a volume V at temperature T, and we wish to calculate the average of some observable A which in quantum mechanics is described by an operator $\hat{A}$. Then the answer to this problem given by quantum statistical mechanics is

$$\langle \hat{A} \rangle = Z^{-1} Tr \exp(-\hat{\mathcal{H}}/k_B T) \hat{A} = Z^{-1} \sum_n \langle n| \exp\left(-\hat{\mathcal{H}}/k_B T\right) \hat{A} |n\rangle \ , \quad (0.1)$$

where $\hat{\mathcal{H}}$ is the Hamiltonian of the system, and the trace is written here symbolically as the sum over a discrete set of states $\{|n\rangle\}$ which we assume orthonormal ($\langle n|m\rangle = \delta_{nm}$) and complete ($\sum_n |n\rangle\langle n| = \hat{1}$ where $\hat{1}$ is the identity operator). Correspondingly, the partition function Z is

$$Z = Tr \exp\left(-\hat{\mathcal{H}}/k_B T\right) = \sum_n \langle n| \exp\left(-\hat{\mathcal{H}}/k_B T\right) |n\rangle \quad (0.2)$$

The Hamiltonian $\hat{\mathcal{H}}$ can be written, assuming a situation where relativistic effects as well as explicit consideration of the spins of the particles can be neglected, and so the simple description in terms of the Schrödinger equation applies,

$$\hat{\mathcal{H}} = \sum_{j=1}^{N} \frac{\hat{\boldsymbol{p}}_j^2}{2m} + \sum_{i<j} \hat{V}\left(\hat{\boldsymbol{r}}_i - \hat{\boldsymbol{r}}_j\right) = \sum_{j=1}^{N} \hat{E}_j^{kin} + \sum_{i<j} \hat{V}_{ij} \quad (0.3)$$

where $\hat{\boldsymbol{p}}_i$ is the momentum operator of the i'th atom (all atoms are assumed to have the mass m, and $\hat{\boldsymbol{r}}_i$ is the position operator, and we have assumed pairwise interactions between the particles described by the potential V).

Now the basic reason why quantum statistical mechanics differs for this problem from classical statistical mechanics, as it was assumed in the first chapter of this book, is that momentum and position operators of a particle do not commute,

$$\left[\hat{\boldsymbol{r}}_j, \hat{\boldsymbol{p}}_j\right] = i\hbar, \quad (0.4)$$

and hence also the commutator of kinetic and potential energy of a particle is non-vanishing, $\left[\hat{E}_j^{kin}, \hat{V}_{ij}\right] \neq 0$. As a corollary of this statement, it can be easily seen - and this is worked out in most standard textbooks on statistical mechanics - that neglect of Eq. (0.4) for the evaluation of averages reduces the problem to classical statistical mechanics. Indeed: One can then write, using for $|n\rangle$ eigenstates of the position operators $\hat{\boldsymbol{x}}_i$ so $\sum_n$ becomes $\int d\boldsymbol{x}_1 \int d\boldsymbol{x}_2 \ldots \int d\boldsymbol{x}_N$,

$$Z = \int d\boldsymbol{x}_1 \ldots \int d\boldsymbol{x}_N \langle \boldsymbol{x}_1 \ldots \boldsymbol{x}_N | e^{-\sum_{j=1}^N \hat{E}_j^{kin}/k_BT} e^{-\hat{V}/k_BT} | \boldsymbol{x}_1 \ldots \boldsymbol{x}_N \rangle \ , \tag{0.5}$$

where we have used the result

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}} e^{\hat{B}} \tag{0.6}$$

for operators $\hat{A}, \hat{B}$ that commute with each other - which is true, of course, only in the limit $\hbar \to 0$, which is precisely the limit in which quantum mechanics reduces to classical mechanics. If Eq. (0.5) were true, one could furthermore use

$$\exp\left(-\sum_{j=1}^N \hat{E}_j^{kin}/k_BT\right) = \prod_{j=1}^N \exp\left(-\hat{E}_j^{kin}/k_BT\right) = \prod_{j=1}^N \exp\left(-\hat{\boldsymbol{p}}_j^2/2mk_BT\right) ,$$

and introducing then suitably complete sets in momentum representation $\int d\boldsymbol{p}_j |\boldsymbol{p}_j\rangle\langle\boldsymbol{p}_j| = \hat{1}$ the kinetic energy terms can simply be evaluated and in the end cancel out from the average in Eq. (0.1) if we consider a quantity that depends on the positions of the particles only, since the same expression results from the kinetic energy contributions both in the numerator and in the denominator of Eq. (0.1).

As we have emphasized above, details of this reasoning can be found in standard text books on statistical mechanics, and there is no need to dwell on it here. But let us recall what are the physical consequences when we indeed ignore Eq. (0.4) and evaluate all averages according to classical rather than quantum statistical mechanics. First of all, we miss spectacular effects which result from the indistinguishability of quantum particles and the resulting possibility of quantum-mechanical exchange, such as superfluidity and Bose condensation (remember that here we talk about neutral atoms, their electrons being bound to the nuclei - metals with quasi-free electrons and resulting phenomena such as superconductivity and the problem of Anderson localization etc. will not be considered here). But even in cases when we consider relatively heavy atoms (e.g., considering noble gases we exclude Helium but wish to deal with Neon, Argon, Xenon), where at low temperatures the fluid-solid transition precludes the occurency of a suprafluid phase, classical statistical mechanics at low temperatures is severely in error. "Low temperature" means here temperatures comparable to or lower than the Debye temperature Θ, as a treatment of the statistical mechanics of the crystal in terms of phonons shows. Some consequences of quantum mechanics on the low temperature properties of crystals are sketched qualitatively in Fig. 0.1: while the specific heat per atom of a (harmonic) solid would simply follow the Dulong-Petit law $C_V = 3k_B$ (in $d = 3$ dimensions), it actually vanishes for $T \to 0$ as required by the third law of thermodynamics, and follows the Debye law $C_V \propto T^3$ (in $d = 3$ dimensions) for $T \ll \Theta$; the lattice parameter according to classical statistical mechanics at low T varies linearly with T, which would mean the thermal expansion coefficient would become constant, while in reality the thermal expansion coefficient also vanishes for $T \to 0$, and the same holds for temperature derivatives of elastic constants.

Is there a need at all to study such low temperature properties with simulations? Isn't it good enough to work out the statistical mechanics based on the lattice dynamical phonon treatment? At this point, it must be emphasized that the simple harmonic approximation for crystals yields the Debye law but it does not yield any temperature dependence of the lattice parameters and the elastic constants at all. In order to account for these temperature dependencies, one has to use at least the self-consistent quasi-harmonic theory. The latter relies on the fact that at nonzero temperature in the NVT ensemble it is not the internal energy minimum which yields the thermal equilibrium but the free energy is a minimum, and at nonzero temperature in a crystal internal energy E and free energy F differ by the entropic contribution ($F = E - TS$) due to the disorder caused by the displacements of the atoms associated with the phonon vibrations. However, we emphasize that this quasi-harmonic theory is not exact due to the neglect of anharmonic terms. While according to classical statistical mechanics the harmonic approximation does get exact as $T \to 0$, this is not true if quantum effects are taken into account, due to zero temperature motions the anharmonicity of the potential always plays some role. These zero temperature motions are a direct consequence of Eq. (0.4) or the resulting Heisenberg uncertainty principle: a particle in a gas would be "spread out" over a linear dimension given by the thermal de Broglie wavelength,

$$\lambda_T = h/\sqrt{2\pi m k_B T}, \tag{0.7}$$

the delocalization of particles around the lattice sites of a crystal (in the potential from their neighbors) may be smaller (Fig. 0.2 [1]), but it also increases at low temperatures proportional to $T^{-1/2}$, as the thermal de Broglie wavelength does (Eq. 0.7). On the other hand, Fig. 0.2 demonstrates that for atoms such as Si or O the delocalization of atoms due to zero point motion at the temperatures of interest is only of the order of $0.1\mathring{A}$ or even smaller, i.e. much less than all interatomic spacings: therefore the neglect of quantum statistics and its consequences (exchange due to direct overlap of wave functions of particles at neighboring sites) is not a problem in practice.

The precise estimation of lattice parameters, elastic constants and other properties of crystals is of interest in materials science [2]. As an example, Fig. 0.3 [3] shows the lattice parameter of orthorhombic polyethylene versus temperature, and the fluctuation of the bond angle between three successive carbon atoms. One sees that this lattice parameter does show a behavior as anticipated qualitatively in Fig. 0.1, but even at room temperature the classical and the quantum-mechanical calculations do not yet coincide (note that polyethylene melts at about $T_m = 413K$). Quantum effects are particularly strong in solid polymers, since H and C are such light atoms, and although the bond-angle potential along the $C-C$ chain is rather stiff, there does occur an appreciable zero-point fluctuation in the bond angle. These results [3] demonstrating the importance of quantum effects in ordinary polymers such as polyethylene have come somewhat as a surprise, since polyethylene melts already at $T_m = 413K$, and usually one expects quantum effects to be strong only far below the melting temperature. However, in the case of C_nH_{2n+2} one must take into account the particular anisotropy of the crystal, the covalent forces along the backbone of the chain molecules are very much stronger than the weak van der Waals-type forces between neighboring chain molecules, and the latter forces are only responsible for melting.

Of course, many more problems of the type shown in Figs. 0.1 - 0.3 exist in the physics of condensed matter. Particular interesting are again phase transition phenomena, and indeed we encounter many transitions in solids from one crystal structure to another driven either by varying the temperature or by varying the pressure. At such structural phase transitions, the local potential experienced by atoms sometimes is of the double-well type: this allows for quantum phenomena which have no classical counterpart at all such as tunnelling. We also emphasize that interesting quantum effects in condensed matter physics not only arise from the non-commutativity of position and momentum operator Eq. 0.4, but similar considerations can be made for operators associated with other physical observables as well, e.g. (orbital) angular momentum and spin. Consider the problem of monolayers of adsorbed molecules such as N_2 on graphite [4]: In the $\sqrt{3} \times \sqrt{3}$ commensurate superstructure, one may ignore both the translational degrees of freedom and the out of plane rotation and the only degree of freedom that one must consider is the angle φ_i describing the orientation of molecule i in the xy-plane parallel to the substrate. Then the Hamiltonian is (I is the moment of inertia of the molecules, and $\hat{V}$ the intermolecular potential)

$$\hat{\mathcal{H}} = \sum_{j=1}^{N} \frac{\hat{L}_{jz}^2}{2I} + \sum_{i<j} \hat{V}\left(\hat{\varphi}_i, \hat{\varphi}_j\right) \tag{0.8}$$

For this problem the commutation relation analogous to Eq. (0.4) reads

$$\left[\hat{L}_{jz}, \hat{\varphi}_k\right] = -i\hbar\, \delta_{jk} \tag{0.9}$$

and the resulting zero-point vibrations of the angles $\hat{\varphi}_k$ cause an appreciable reduction of the orientational order parameter in comparison with its classical value at low temperature [5]. Finally, considering the classical Heisenberg model of Chapter 1 again,

$$\mathcal{H} = -J \sum_{i<j} \hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j - \mu_B H \sum_{i=1}^{N} \hat{S}_j^z \; . \tag{0.10}$$

but now rather than unit vectors the $\hat{\boldsymbol{S}}_i$ are spin operators, satisfying the commutation relation

$$\left[\hat{S}_i^\alpha ,\ \hat{S}_j^\beta\right] = i\hbar\varepsilon_{\alpha\beta\gamma}\hat{S}_j^\gamma . \tag{0.11}$$

Since the total magnetization $\hat{M} = \mu_B \sum_{i=1}^{N} \hat{S}_i^z$ commutes with the Hamiltonian, quantum effects do not lead to a reduction of the magnetization relative to its classical ground state value. But, as spin wave theory shows, the temperature dependence of internal energy and magnetization are very different in the quantum case from the classical case,

$$E(T) = \langle \hat{\mathcal{H}} \rangle = E_0 + const T^{5/2} \quad \text{, quantum case ,} \tag{0.12}$$

$$M_0 - M(T) \propto T^{3/2} \quad \text{, quantum case ,} \tag{0.13}$$

while

$$E(T) - E_0 \propto T, \quad M_0 - M(T) \propto T, \ \text{classical case.} \tag{0.14}$$

Again one sees that in the classical case a nonzero specific heat results for $T \to 0$, analogous to the Dulong-Petit result for crystals. And just as phonon theory of crystals is difficult if one wishes to include anharmonic terms, such terms exist for spin waves (magnons) too and again cannot be accounted for completely by exact analytical methods. Quantum Monte Carlo methods, however, can be applied without such restrictions.

0.5.2 The path integral quantum Monte Carlo method (PIMC)

The basic idea of the path integral representation of the partition function [6] can already be explained for the simple problem of a single quantum particle in one dimension x in an external potential $\hat{V}(x)$, where Eq. (0.3), Eq. (0.2) reduce to

$$\hat{\mathcal{H}} = \hat{E}^{kin} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}(x), \tag{0.15}$$

$$Z = \int dx \langle x | \exp(-\hat{\mathcal{H}}/k_BT) | x \rangle = \int dx \langle x | \exp(-(\hat{E}_{kin} + \hat{V})/k_BT) | x \rangle . \tag{0.16}$$

The path integral representation of Eq. (0.16) can be most easily derived if one recalls the Trotter-Suzuki formula [7], [8]

$$\exp(\hat{A} + \hat{B}) = \lim_{P\to\infty} \left[\exp(\hat{A}/P)\exp(\hat{B}/P)\right]^P , \tag{0.17}$$

which holds for two non-commuting operators $\hat{A}, \hat{B}$, which satisfy another operator identity

$$\exp(\hat{A}+\hat{B}) = \exp(\hat{A})\exp(\hat{B})\exp\left(-\frac{1}{2}[\hat{A},\hat{B}]\right) \tag{0.18}$$

when the commutator of the operators $\hat{A}, \hat{B}$ is a complex number c, i.e. $[\hat{A},\hat{B}] = c$. Eq. (0.18) can be easily derived from systematic Taylor expansions of the exponential function and should be familiar to the reader from elementary text books on quantum mechanics. If we now apply Eq. (0.18) to the operator $\exp(\hat{A}' + \hat{B}')$ where $\hat{A}' = \hat{A}/P, , \hat{B}' = \hat{B}/P$, we recognize that the term $[\hat{A}', \hat{B}']$ that appears on the right hand side in the last exponential is of order P^{-2},

$$[\hat{A}', \hat{B}'] = c/P^2 \tag{0.19}$$

and thus it is plausible that in the limit $P \to \infty$ this correction can be neglected, and hence Eq. (0.17) results. In our case of the particle in the external potential we hence use

$$\exp\left[-(\hat{E}^{kin}+\hat{V})/k_BT\right] = \lim_{P\to\infty}\left[\exp(-\hat{E}^{kin}/k_BTP)\exp\left(-\hat{V}/k_BTP\right)\right]^P . \tag{0.20}$$

Using Eq. (0.20), the partition function, Eq. (0.16) becomes

$$\begin{aligned} Z = \lim_{P\to\infty} \int dx_1 \int dx_2 \ldots \int dx_P &\langle x_1|\exp(-E^{kin}/k_BTP)\exp(-\hat{V}/k_BTP)|x_2\rangle \\ &\langle x_2|\exp(-\hat{E}^{kin}/k_BTP)\exp(-\hat{V}/k_BTP)|x_3\rangle\langle x_3|\ldots\ldots|x_P\rangle \\ &\langle x_P|\exp(-\hat{E}^{kin}/k_BTP)\exp(-\hat{V}/k_BTP)|x_1\rangle \end{aligned} \tag{0.21}$$

The matrix elements appearing in Eq. (0.21) can be worked out, this is just an exercise in elementary quantum mechanics, and the result is

$$\begin{aligned} &\langle x|\exp(-\hat{E}^{kin}/k_BTP)\exp(-\hat{V}/k_BTP)|x'\rangle \\ &= \left(\frac{mk_BTP}{2\pi\hbar^2}\right)^{1/2} \exp\left[-\frac{mk_BTP}{2\hbar^2}(x-x')^2\right]\exp\left[-\frac{V(x)+V(x')}{2k_BTP}\right] \end{aligned} \tag{0.22}$$

Thus the partition function becomes

$$\begin{aligned} Z &= \lim_{P\to\infty} Z_P, \\ Z_P &= \left(\frac{mk_BTP}{2\pi\hbar^2}\right)^{P/2} \int dx_1 \int dx_2 \ldots \int dx_p \exp\{-\frac{1}{k_BT}\left[\frac{\kappa}{2}\sum_{s=1}^{P}(x_s - x_{s+1})^2\right. \\ &\quad \left. + \frac{1}{P}\sum_{s=1}^{P} V(x_s)\right]\} , \end{aligned} \tag{0.23}$$

where the boundary condition $x_{P+1} = x_1$ is implied, and as an abbreviation an effective spring constant κ was introduced,

$$\kappa = mP(k_B T/\hbar)^2 \tag{0.24}$$

¿From Eq. (0.23) one immediately recognizes that Z_P can be considered as the partition function of a problem in classical statistical mechanics with P degrees of freedom, namely a harmonic chain in an external potential $V(x_s)/P$. In this way a problem of quantum statistical mechanics Eq.(0.16) to which standard Monte Carlo methods, as described in the first chapter of this book, are readily applied. Of course, in practice we will work with several choices of large but finite P, in order to carry out the extrapolation $P \to \infty$ numerically.

This approach can be generalized straightforwardly to N particles interacting with each other according to the potential $\hat{V}(\hat{\boldsymbol{r}}_i - \hat{\boldsymbol{r}}_j)$ in 3 dimensions Eqs. (0.1)-(0.3) if we disregard the indistinguishability and statistics of the particles (later on this restriction will be removed of course). Using steps analogous to those which lead from Eq. (0.21) to Eq. (0.23), use of Eq. (0.20) now yields for Eq. (0.3) the result

$$Z_P = \left(\frac{mk_B TP}{2\pi\hbar^2}\right)^{3NP/2} \int d\boldsymbol{r}_1^{(1)} \dots \int d\boldsymbol{r}_1^{(P)} \int d\boldsymbol{r}_2^{(1)} \dots d\boldsymbol{r}_2^{(P)} \dots \int d\boldsymbol{r}_N^{(1)} \dots \int d\boldsymbol{r}_N^{(P)}$$
$$\exp\left\{-\frac{1}{k_B T}\left[\frac{\kappa}{2}\sum_{i=1}^{N}\sum_{s=1}^{P}(\boldsymbol{r}_i^{(s)} - \boldsymbol{r}_i^{(s+1)})^2 + \frac{1}{P}\sum_{i<j}\sum_{s=1}^{P} V\left(|\boldsymbol{r}_i^{(s)} - \boldsymbol{r}_j^{(s)}|\right)\right]\right\} \tag{0.25}$$

Eq. (0.25) can be interpreted as a melt of cyclic chains (”ring polymers”) with harmonic springs connecting neighboring beads along the chains, but the interactions among the beads are rather uncommon: while in a physical melt of ring polymers in principle every bead can interact with every other bead in the system, here only beads with the same Trotter index s are interacting (the coordinate along the Trotter index s plays the role of imaginary time $\tau = s\Delta\tau$ [6] and hence there is only an interaction between particles that belong to the same ”timeslice” $\Delta\tau$). This situation is sketched in Fig.0.4 for two interacting particles.

By Eq. (0.25), the problem of evaluating the partition function, Eq. (0.2), within the framework of quantum statistical mechanics has indeed been reduced to an equivalent problem in classical statistical mechanics, although one must be careful since the effective Hamiltonian $\mathcal{H}p$ of the $N \times P$ particles in Z_P

$$Z_P = \left(\frac{mk_B TP}{2\pi\hbar^2}\right)^{3NP/2} \int d\boldsymbol{r}_1^{(1)} \dots \int d\boldsymbol{r}_N^{(P)} \exp\left\{-\frac{1}{k_B T}\mathcal{H}_P\right\} \tag{0.26}$$

depends explicitly on temperature (via the spring constant κ, see Eq. (0.24)) [6, 9, 10, 11, 12]. Thus Monte Carlo simulations can be applied rather straightforwardly to estimate corresponding averages [9, 10, 11, 12]

$$\langle A \rangle_P = Z_P^{-1} \int d\boldsymbol{r}_1^{(1)} \dots \int d\boldsymbol{r}_N^{(P)} \exp\left\{ -\frac{1}{k_B T} \mathcal{H}_P \right\} A. \tag{0.27}$$

Let us now briefly discuss the physical interpretation of these results. If the potential in Eq. (0.25) could be neglected completely, we could infer from the equipartition theorem of classical statistical mechanics that the energy carried by each spring is (in d dimensions)

$$\frac{\kappa}{2} \langle (\boldsymbol{r}_i^{(s)} - \boldsymbol{r}_i^{(s+1)})^2 \rangle = \frac{d}{2} k_B T \tag{0.28}$$

Using Eqs.(0.24), (0.28), we conclude that the average mean square distance between neighboring particles in a ring polymer is

$$\ell^2 \equiv \langle (\boldsymbol{r}_i^{(s)} - \boldsymbol{r}_i^{(s+1)})^2 \rangle = d k_B T/\kappa = \hbar^2 d/(m k_B T P) \tag{0.29}$$

Of course, this result does not depend on s, all particles in a ring polymer are equivalent. Now the gyration radius of a ring polymer containing P monomers for large P scales as

$$\langle R_g^2 \rangle = \ell^2 P/12 = (d/12)(\hbar^2/(m k_B T)) \tag{0.30}$$

As could have been expected, this is of the same order as the square of the thermal de Broglie wavelength, $\lambda_T^2 = h^2/(2\pi m k_B T)$, and the "Trotter number" P has cancelled out from this result. As is well known from the quantum statistical mechanics of an ideal, noninteracting gas, integrating out the momenta the Heisenberg uncertainty principle $(\Delta p)^2 (\Delta x)^2 \approx h^2$ requires that the delocalization of a particle in space is $\langle (\Delta x)^2 \rangle \approx h^2/\langle (\Delta p)^2 \rangle \approx \hbar^2/(m k_B T)$, omitting prefactors of order unity here. Eq. (0.30) thus again illustrates that quantum effects become the more important the lower the temperature and the lighter the particle (i.e., the smaller the mass m). Of course, Eq. (0.29) no longer is accurate when interactions among the particles occur, but qualitatively it still predicts correctly the order of magnitude of the quantum mechanical delocalization due to zero point motions at low temperatures; Fig. 0.2 gives an explicit example for the case of SiO_2 [1].

Now it is clear that in order to take into account quantum effects correctly one has to perform the extrapolation towards $P \to \infty$ (cf. Eq. (0.23)). From Eqs. (0.17)-(0.20) one can infer that the quantum corrections of physical observables scale as P^{-2} (cf. Eq. (0.19)). This result implies that one should compute observables for several values of P and try an extrapolation of the results as a function of P^{-2}. Of course, in general it is a nontrivial question to judge how large P must be chosen in order to reach the asymptotic scaling limit. From Eq. (0.5) it is clear that the distance between effective monomers in the ring polymer scales as $\ell \propto \hbar/\sqrt{m k_B T P}$. We need to keep this distance fixed at a value that is small in comparison to the length scale on which the potential acting on the particles changes appreciably. In order to keep ℓ fixed it thus obviously is necessary to keep the product mk_BTP fixed - the lower the temperature, the larger P must be chosen. In practice, there does not exist a simple recipe that tells how large P has to be in a specific case; rather one has to find the appropriate range of P values by trial and error. Fig. 0.5 shows that in favorable cases rather small values of P suffice to reach the asymptotic limit [13] where the scaling of data linearly with P^{-2} actually is observed. This figure also demonstrates that PIMC is able to identify typical quantum-mechanical effects such as "isotope effects": the two isotopes ^{20}Ne and ^{22}Ne of the Lennard-Jones-system differ only by their mass - in classical statistical mechanics there would be no difference in static properties whatsoever. However, Fig. 0.5 shows there is is a clear distinction between the lattice constants of the two isotopes, and the difference observed in the simulation in fact is rather close to the value found in experiments [14]. However, other examples exist when even Trotter numbers as large as $P = 100$ are not large enough to ensure that the asymptotic limit of the P^{-2} scaling has been reached.

As mentioned above, the treatment so far has completely neglected the effects of quantum statistics. This approximation is o.k. for crystals, ensuring furthermore that the typical inter-particle distance is large in comparison with the linear dimension of the ring polymers. As expected, this approximation breaks down when the linear dimension of the ring polymer describing a particle $\left(\sqrt{\langle R_g^2 \rangle}\right)$ becomes comparable to inter-particle distances: then the wave functions show appreciable overlap and the effects of quantum statistics need to be properly taken into account. This problem needs to be handled when one wishes to treat quantum crystals such as solid ^3He or solid ^4He, as well as the corresponding quantum fluids [11, 12]. Here we shall only discuss Bose systems (such as ^4He). Only totally symmetric eigenfunctions contribute to the density matrix, and hence we introduce a permutation operator $\hat{P}$ such that $\hat{P}\boldsymbol{R}$ is a permutation of particle labels if we use the shortened notation $\boldsymbol{R} \equiv (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ for the set of particle coordinates. Then we have for any eigenfunction $\Phi_\alpha(\hat{R})$

$$\hat{P}\Phi_\alpha(\boldsymbol{R}) = \frac{1}{N!}\sum_P \Phi(\hat{P}\boldsymbol{R}) \ , \tag{0.31}$$

and the partition function for a Bose system therefore takes the form

$$Z_{Bose} = \left(\frac{mk_BTP}{2\pi\hbar^2}\right)^{dNP/2} \frac{1}{N!}\int d\boldsymbol{r}_1^{(1)} \ldots \int d\boldsymbol{r}_N^{(P)} \exp(-\mathcal{H}_P/k_BT) \ . \tag{0.32}$$

Now the boundary condition is not $\boldsymbol{r}_i^{(P+1)} = \hat{r}_i^{(1)}$ as it was in Eqs. (0.25),(0.26), but one has to obey only the condition that

$$\hat{P}\boldsymbol{R}^{(P+1)} = \boldsymbol{R}^{(1)} \tag{0.33}$$

This means that paths are allowed to close on any permutation of their starting positions, and contributions from all $N!$ closures are summed over in the partition function. At high temperatures the contribution from the identity permutation will dominate, while at zero temperature all permutations contribute equally. In the classical isomorphic polymer system, this means that "cross links" can form between chains and open up again; of course, this has nothing to do with the chemical kinetics of cross-linking and polymerization in real polymers. Thus, a two atom system with P effective monomers per ring polymer can be in two possible permutation states: either two separate ring polymers, each with P springs (this is the situation described in Fig. 0.4) or one larger ring polymer with 2P springs.

It is illuminating to ask what superfluidity means in this formalism ([15]), since this actually occurs in ^4He: A macroscopic polymer is formed which involves on the order of N atoms and stretches over the entire system. From Fig. 0.4, it is clear that this "cross-linking" among ring polymers can set in only when the linear dimension of a ring polymer becomes of the same order as the "ring polymer spacing"; from this argument one can get a rough estimate of the superfluid transition temperature, by putting the thermal de Broglie wavelength $\lambda_T = h/\sqrt{2\pi m k_B T}$ equal to the classical inter-particle spacing, $\rho^{-1/d}$ in d dimensions, ρ being the density. The "degeneracy temperature" T_D found from $\lambda_T = \rho^{-1/d}$ is $T_D = \rho^{2/d}h^2/(2\pi k_B m)$, and this sets the temperature scale on which important quantum effects occur.

In practice, use of Eq. (0.25) and (0.30) would not work for the study of superfluidity in ^4He: although the formalism in principle is exact, too large values of P would be required in order to obtain reasonable results. In order to make progress one must not use the so-called "primitive action" defined in Eq. (0.25) but must use the so-called "improved actions" for $\mathcal{H}_P$. We refer the reader to the original literature for details [11].

0.5.3 Quantum Monte Carlo for Lattice Models

One follows again the strategy to decompose the Hamiltonian of the considered model $\mathcal{H}$ into two parts, $\hat{\mathcal{H}} = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2$, that can be diagonalized separately so that the use of the Trotter-Suzuki-formula [7, 8] is helpful, cf. Eq. (0.17),

$$\exp[-(\hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2)/k_BT] = \lim_{P\to\infty}[\exp(-\hat{\mathcal{H}}_1/k_BTP)\exp(-\hat{\mathcal{H}}_2/k_BTP)]^P \ . \tag{0.34}$$

Unfortunately, there is no general recipe how this splitting of the Hamiltonian into parts is best done in practice - what is best depends very much on the model that is considered. Therefore many different variants of this approach can be found in the literature [16, 17, 18]; we hence cannot attempt to explain all these various methods, but only attempt to convey the spirit of the general approach here. At this point, we also mention that it is possible to consider higher-order decompositions of $\hat{\mathcal{H}}$, where application of the Trotter formula with a finite Trotter number P does not imply a scaling of the error as P^{-2} but according to a higher power of $1/P$ [19].

As a first example, we treat the one-dimensional Ising model in a transverse field of strength $H_\perp$, taking [20]

$$\hat{\mathcal{H}}_1 = -J \sum_{i=1}^{N} \hat{\sigma}_i^z \hat{\sigma}_{i+1}^z \ , \quad \hat{\mathcal{H}}_2 = -H_\perp \sum_{i=1}^{N} \hat{\sigma}_i^x \ , \tag{0.35}$$

where $\hat{\sigma}_i^\alpha (\alpha = x, y, z)$ denote the Pauli spin matrices at lattice site i. Periodic boundary conditions $\hat{\sigma}_{N+1}^\alpha = \hat{\sigma}_1^\alpha$ are assumed as usual. As a state representation let us use eigenstates of $\hat{\sigma}_z$ and label them by Ising spin variables, $s = \pm 1$, i.e.

$$\hat{\sigma}^z |s\rangle = s|s\rangle \tag{0.36}$$

Of course, $\hat{\mathcal{H}}_1$ is diagonal in this representation, while $\hat{\mathcal{H}}_2$ is not. Now the P'th approximant Z_P to the partition function can be written as

$$\begin{aligned} Z_P = Tr \left\{ \exp(-\hat{\mathcal{H}}_1/k_BTP) \exp(-\hat{\mathcal{H}}_2/k_BTP) \right\}^P &= \\ = \sum_{\left\{S_i^{(s)}\right\}} \prod_{s=1}^{P} \prod_{i=1}^{N} \exp\left[\frac{J}{k_BTP} S_i^{(s)} S_{i+1}^{(s)}\right] \langle S_i^{(s)}| \exp\left(\frac{H_\perp \hat{\sigma}_i^x}{k_BTP}\right) |S_i^{(s+1)}\rangle \end{aligned} \tag{0.37}$$

In this trace we have to take periodic boundary conditions in the imaginary time direction as well, $S_i^{(P+1)} = S_i^{(1)}$. Using the results for the ... spin operators, one easily obtains the following result for the matrix element in Eq. (0.38)

$$\langle s| \exp(a\hat{\sigma}^x |s'\rangle = (\frac{1}{2} \sinh 2a)^{1/2} \exp\left(\frac{1}{2} \log \coth a\right) ss' \ , \tag{0.38}$$

where a is an abbreviation for $H_\perp/(k_BTP)$. Using Eq. (0.38) in Z_P one obtains an expression that is formally equivalent to the partition function of an anisotropic two-dimensional Ising model in the absence of any fields, namely

$$Z_P = \left[\frac{1}{2} \sinh(2H_\perp/k_BTP)\right]^{PN/2}$$

$$\sum_{\{S_i^{(k)}\}} \exp\left[\sum_{k=1}^{P}\sum_{i=1}^{N}(K_P S_i^{(k)} S_i^{(k+1)} + \frac{J}{k_B T P} S_i^{(k)} S_{i+1}^{(k)}\right] \tag{0.39}$$

with a coupling constant K_P in the "Trotter direction" that depends both on the temperature T and the linear dimension P in this direction,

$$K_P = \frac{1}{2}\log\{\coth(H_\perp/k_B T P)\}\ . \tag{0.40}$$

Eq. (0.40) is analogous to the coupling with the spring constant κ in Eq. (0.24). Again it turns out necessary to choose P such that one works in the limit of large K_P, i.e. one must have $k_B T P/H_\perp \gg 1$, the lower the temperature the larger the Trotter dimension P must be. As in the off-lattice case, the original interaction (here the exchange interaction J), acts only between spins with the same Trotter index (denoted as k here).

The partition function of the two-dimensional Ising square lattice can be solved exactly also for anisotropic exchange couplings, and hence there is no need to deal with this problem by Monte Carlo methods. However, the same method as shown in Eqs. (0.35) - (0.40) straightforwardly applies to higher - dimensional Ising models with transverse fields as well - always the quantum effects lead to the occurrence of this extra dimension, and the linear dimension P in this direction needs to be extrapolated to infinity in order to render this method as an exact one. In practice, the recipe is to carry out a series of simulations for finite values of P, and extrapolate physical properties as function of P^{-2} towards $P \to \infty$.

As a second and physically more interesting example where the Trotter formalism is applied to a spin problem on a lattice is the anisotropic Heisenberg chain with spin quantum number $s = 1/2$. The Hamiltonian of this model is given by (periodic boundary conditions again being implied)

$$\mathcal{H} = \sum_{i=1}^{N}(J_x \hat{S}_i^x \hat{S}_{i+1}^x + J_y \hat{S}_i^y \hat{S}_{i+1}^y + J_z \hat{S}_i^z \hat{S}_{i+1}^z)\ . \tag{0.41}$$

There have been several distinct ways in which the quantum Hamiltonian can be split into parts such that the Trotter formula {Eq. (0.17)} can be applied in a useful way. We describe here only the procedure first suggested by Suzuki and by Barma and Shastry [21, 22],

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_A + \hat{\mathcal{H}}_B\ , \tag{0.42}$$

where

$$\hat{\mathcal{H}}_0 = -\sum_{i=1}^{N} J_z \hat{S}_i^z \hat{S}_{i+1}^z\ , \quad \hat{\mathcal{H}}_A = \sum_{i\ \text{odd}} \hat{\mathcal{H}}_i\ , \quad \hat{\mathcal{H}}_B = \sum_{i\ \text{even}} \hat{\mathcal{H}}_i\ , \tag{0.43}$$

where $\hat{\mathcal{H}}_i$ is the local transverse part of the Hamiltonian,

$$\hat{\mathcal{H}}_i = -\left(J_x \hat{S}_i^x \hat{S}_{i+1}^x + J_y \hat{S}_i^y \hat{S}_{i+1}^y\right) . \tag{0.44}$$

We apply the Trotter formula to obtain the P'th approximant Z_P of the partition function in the following form,

$$Z_P = Tr\left(e^{-\hat{\mathcal{H}}_0/2k_BTP}\; e^{-\hat{\mathcal{H}}_A/k_BTP}\; e^{-\hat{\mathcal{H}}_0/2k_BTP}\; e^{-\hat{\mathcal{H}}_B/k_BTP}\right)^P \tag{0.45}$$

As in the previous case, we use eigenstates of $\hat{S}^z$ and hence of the Hamiltonian $\hat{\mathcal{H}}_0$, the Ising-like part. We now insert into the above trace operation altogether $2P$ complete sets of such states in such a way that there is just one complete set between each term $e^{-\hat{\mathcal{H}}_A/k_BTP}$,$e^{-\hat{\mathcal{H}}_B/k_BTP}$.

$$\begin{aligned} Z_P = Tr_{\{S_i^{(k)}\}} \exp\Bigg\{ &-\frac{1}{2k_BTP}\sum_{k=1}^{2P}\mathcal{H}_0^{(k)} - \frac{1}{k_BT}\sum_{i\in A}\sum_{k=1}^{2P} h(i,k) \\ &- \frac{1}{k_BT}\sum_{i\in B}\sum_{k=1}^{2P} h(i,k) \Bigg\} , \end{aligned} \tag{0.46}$$

with

$$\exp\left[-h(i,k)/k_BT\right] = \langle S_i^{(k)} S_{i+1}^{(k)} | \exp(-\mathcal{H}_i/k_BTP) | S_i^{(k,i)} S_{i+1}^{(k)} \rangle . \tag{0.47}$$

Also the spins $S_i^{(k)}$ have values $S_i^{(k)} = \pm 1/2$. Eq. (0.46) can be interpreted as the partition function of a lattice of size $N \times 2P$ with periodic boundary conditions in both directions and a very anisotropic interaction: these are just the two-spin couplings described by $\mathcal{H}_0^{(k)} = -\sum_{i=1}^{N} J_z S_i^{(k)} S_{i+1}^{(k)}$ in the real space direction, and temperature-dependent four-spin couplings on alternating elementary plaquettes, which couple neighboring sites in both real space and the Trotter direction. This one can recognize from Eq. (0.47), which defines the four-spin couplings implicitly.

For more details on this problem defined by Eq. (0.41) and results obtained in numerical studies of Eq. (0.46) by Monte Carlo methods we refer to the literature [20, 23]. Here we turn to a very brief discussion of other models that have been intensively studied, that involve fermionic degrees of freedom explicitly. The simplest case are spinless fermions in one dimension [20, 23] with the Hamiltonian being

$$\hat{\mathcal{H}} = -t\sum_{i=1}^{N}(\hat{c}_i^{+}\hat{c}_{i+1} + \hat{c}_{i+1}^{+}\hat{c}_i) + V\sum_{i=1}^{N}\hat{n}_i\hat{n}_{i+1} . \tag{0.48}$$

As is well known, the fermion operators $\hat{c}_i^{+}, \hat{c}_i$ create (or annihilate) a particle at lattice site i, and satisfy the anticommutation relation

$$[\hat{c}_i^+, \hat{c}_j]_+ = \hat{c}_i^+ \hat{c}_j + \hat{c}_j \hat{c}_i^+ = \delta_{ij} \ . \tag{0.49}$$

The particle number operator

$$\hat{n}_i \equiv \hat{c}_i^+ \hat{c}_i \tag{0.50}$$

has only the two eigenvalues $n_i = 0$ or $n_i = 1$,

$$\hat{n}_i |1\rangle = 1|1\rangle \ , \quad \hat{n}_i |0\rangle = 0.|0\rangle = o, \tag{0.51}$$

expressing the Pauli principle that never can be two fermions in the same state. The total number of particles in the system is then related to the operator

$$\hat{\mathcal{N}} = \sum_{i=1}^{N} \hat{n}_i \tag{0.52}$$

and the particle density is defined as

$$\hat{\rho} = \hat{\mathcal{N}}/N \ . \tag{0.53}$$

In Eq.(0.48) one can choose the hopping energy t as unity, leaving v_1 as the only nontrivial energy scale in the model. Since $\hat{c}_i^+|n_i\rangle = |1\rangle$ if $n_i = 0$, $\hat{c}_{i+1}|n_{i+1}\rangle = |0\rangle$ if $n_{i+1} = 1$, the term $\hat{c}_i^+ c_{i+1}$ in Eq. (0.48) yields a non-vanishing contribution if a particle is destroyed at site $i+1$ and simultaneously a particle is created at site i, which physically may be interpreted as a hopping process of the particle from site $i+1$ to site i.

It turns out that the present model, Eq. (0.48), can be essentially mapped to the previous model, Eq. (0.41), by a clever transformation: this approach is one of the standard tricks to deal with quantum problems, by which one tries to make the problem more tractable! Thus, one first defines spin-raising $(\hat{\sigma}_\ell^+)$ and spin-lowering $(\hat{\sigma}_\ell^-)$ operators in terms of the Pauli matrices $\hat{\sigma}_\ell^\alpha(\alpha = x, y, z)$,

$$\hat{\sigma}_\ell^+ = (\hat{\sigma}_\ell^x + i\hat{\sigma}_\ell^y)/2, \quad \hat{\sigma}_\ell^- = (\hat{\sigma}_\ell^x - i\hat{\sigma}_\ell^y)/2. \tag{0.54}$$

Now the fermion operators can be expressed in terms of the operators $\hat{\sigma}_\ell^+, \hat{\sigma}_\ell^-, \hat{\sigma}_\ell^z$ by the so-called Jordan-Wigner transformation,

$$\hat{c}_\ell^+ = \hat{\sigma}_\ell^+ exp[\frac{i\pi}{2}\sum_{p=1}^{\ell-1}(1+\hat{\sigma}_p^z)] \ , \quad \hat{c}_\ell^- = \hat{\sigma}_\ell^- exp[-\frac{i\pi}{2}\sum_{p=1}^{\ell-1}(1+\hat{\sigma}_p^z)] \tag{0.55}$$

While this nonlocal transformation looks fairly complicated, the resulting Hamiltonian becomes rather simple, if we neglect boundary terms, which are unimportant for $N \to \infty$,

$$\hat{\mathcal{H}} = -\frac{t}{2}\sum_{i=1}^{N}(\hat{\sigma}_i^x \sigma_{i+1}^x + \hat{\sigma}_i^y \hat{\sigma}_{i+1}^y) - \frac{V}{2}\sum_{i=1}^{N}(\hat{\sigma}_i^z \hat{\sigma}_{i+1}^z + 2\hat{\sigma}_i^z + 1) \tag{0.56}$$

This problem can be solved by the method described for Eq. (0.41) in Eqs. (0.42)-(0.51), or a similar decomposition [20, 24]. Here we do not discuss further the methodological aspects of this problem, but rather show results [24] for the structure factor

$$S_T(q) = \sum_{j=1}^{N}(\langle \hat{n}_i \hat{n}_{i+j}\rangle - \langle \hat{n}_i\rangle\langle \hat{n}_{i+j}\rangle)\cos(jqa), \tag{0.57}$$

where a is the lattice spacing and q the wave number (Fig. 0.6). One can see that for such fermion models even in $d = 1$ dimensions nontrivial results are obtained. But even in this case statistical errors at low temperatures become appreciable already for moderately large N (the largest N included in Fig. 0.6 is $N = 100$), and the finite-size behavior needs to be carefully analyzed (not the logarithmic scaling with N).

One of the most famous models for interacting electrons on a lattice is the single-band Hubbard model [25]

$$\hat{\mathcal{H}} = -t\sum_{\langle i,j\rangle}(\hat{c}_{j,\sigma}^{+}\hat{c}_{i,\sigma} + \hat{c}_{j,\sigma}^{+}\hat{c}_{i,\sigma}) + U\sum_i \hat{n}_{i\downarrow}\hat{n}_{i\uparrow}\ , \tag{0.58}$$

where now $\hat{c}_{i,\sigma}^{+}(\hat{c}_{i,\sigma})$ denotes a creation (annihilation) operator for a fermion spin σ at lattice site i, with $\sigma =\uparrow$ or $\sigma =\downarrow$ denoting the two orientations of the electron spin. Comparing Eq. (0.58) with (0.48), we note that we have made two generalizations: from one dimension to general dimension, but the hopping is still restricted to nearest neighbor pairs $\langle i,j\rangle$; and the fermions are treated as spin $\frac{1}{2}$ particles, as they should, rather than ignoring the spin, as done in Eq. (0.48). Electrons are negatively charged, of course, and so in principle we should have a Coulomb interaction: as a crude approximation, all interactions are neglected apart from the on-site interaction between two electrons with opposite spin on the same site in Eq. (0.48), for the case of "spinless fermions", at most one particle per site is possible, and hence the simplest choice of an interaction is a nearest-neighbor interaction. Although the model Eq. (0.58) is not a realistic description of any physical system, it still captures some essential features of the physics of strongly correlated electrons. Originally the Hubbard model was studied intending applications to the metal-insulator transition, and to the problem of itinerant magnetism in narrow bands in metallic crystals. During the last 15 years, it became a very popular starting point (in its two-dimensional version) to describe the electrons in the Cu_2O-planes of high temperature superconducting materials.

Although it has been studied so intensively with a variety of methods, important aspects of its properties are still incompletely understood, and thus the model Eq. (0.58) still is an active area of research.

For higher-dimensional systems, the transformation of Eq.(0.55) does not help, and thus a different approach for dealing with the fermion operators is needed. One strategy is to integrate out the fermionic degrees of freedom by introducing auxiliary bosonic fields. For this purpose one uses the identity

$$\int_{-\infty}^{+\infty} \exp(-a\phi^2 - b\phi)d\phi = \sqrt{\pi/a}\exp(b^2/4a), \qquad (0.59)$$

where a, b are real numbers, and $a > 0$ is required. Suppose now we wish to calculate the grand-canonical partition function Z_{gc} with the Trotter-Suzuki formula,

$$\begin{aligned} Z_{gc} = Tr\exp[-\frac{1}{k_BT}(\hat{\mathcal{H}} - \mu\hat{\mathcal{N}})] &= \lim_{P\to\infty} Z_{gc}^P, \\ Z_{gc}^P \quad = \quad Tr\{(\exp[-\frac{1}{k_BTP}(\hat{E}^{kin} - \mu\hat{\mathcal{N}})] &\exp(-\frac{1}{k_BTP}\hat{V}))^P\} \ , \end{aligned} \qquad (0.60)$$

μ being the chemical potential, and we have made use of the Trotter formula to disentangle terms which are quadratic in the fermion operators $(\hat{E}^{kin} - \mu\hat{\mathcal{N}})$ from quartic terms ($\hat{V}$ thus contains the terms $U\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} = U\hat{c}^+_{i\uparrow}\hat{c}_{i\uparrow}\hat{c}^+_{i\downarrow}\hat{c}_{i\downarrow}$). Now one can express $\exp(-\hat{V}/k_BTP)$ as an exponent of a quadratic form, if one uses Eq. (0.59) as follows:$(U > 0)$

$$\exp[-\frac{U}{k_BTP}\sum_{i=1}^{N}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}] \propto \prod_{i=1}^{N}\int_{-\infty}^{+\infty} d\phi_i \exp[-\frac{k_BTP\phi_i^2}{2U} - \phi_i(\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow}) - \frac{U(\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow})}{2k_BTP}] \qquad (0.61)$$

Symbolically, the P'th approximant $\mathcal{Z}_{gc}^P$ to the grandcanonical partition function can be written as follows, involving a quadratic form of the fermion operators in the exponential,

$$\mathcal{Z}_{gc}^P = \prod_{i=1}^{N}\int_{-\infty}^{+\infty} d\phi_i Tr\{\exp[\hat{c}^+_{i\sigma}A^{(1)}_{ij}\hat{c}_{j\sigma}]\dots\exp[\hat{c}^+_{i\sigma}A^{(2P)}_{ij}\hat{c}_{j\sigma}]\} \ , \qquad (0.62)$$

where the $A^{(k)}_{ij}$ (which depend on the ϕ_i and σ, of course) are elements of $N \times N$-matrices $\underline{A}^{(k)}$. However, for quadratic forms in the fermion operators as appearing in Eq. (0.62) the trace over the fermionic degrees of freedom can be carried out analytically to yield [18]

$$Tr\{\exp[\hat{c}^+_i\hat{A}^{(1)}_{ij}\hat{c}_j]\dots\exp[\hat{c}^+_i\hat{A}^{(P)}_{ij}\hat{c}_j]\} = \det\{1 + \exp(\underline{A}^{(1)})\dots\exp(\underline{A}^{(P))}\} \qquad (0.63)$$

As a result, the partition function becomes [18]

$$
\begin{aligned}
Z_{gc}^{(P)} \propto \prod_{i,s} \int d\phi^{(s)} \exp[-\frac{k_BTP(\phi_i^{(s)})^2}{2U}] \det[\underline{1} + \exp(-\widetilde{K}/k_BTP)\exp(-\widetilde{V}(\phi_i^{(1)}))\\
\exp(-\widetilde{K}/k_BTP)\ldots\exp(-\widetilde{K}/k_BTP)\exp(-\widetilde{V}(\phi_i^{(P)}))]\det[\underline{1}+\\
\exp(-\widetilde{K}/k_BTP)\exp(-\widetilde{V}(-\phi_i^{(1)}))\exp(-\widetilde{K}/k_BTP)\ldots\ldots\\
\exp(-\widetilde{K}/k_BTP)\exp(-\widetilde{V}(-\phi_i^{(P)}))]
\end{aligned}
\qquad (0.64)
$$

Here $\widetilde{K}$ is an abbreviation for $\widetilde{K} = E_{kin} - (\mu - V/2)\mathcal{N}$, the kinetic energy matrix for a single-particle matrix on a lattice, and $\widetilde{V}(\phi_\ell)$ is a diagonal matrix depending on the $\phi_{\ell j}$ which we do not write out in detail here.

By eliminating the fermionic degrees in favor of Gaussian fields $\phi_i^{(s)}$ (or in favor of Ising spin variables, which is an even more useful alternative for the Hubbard model [26]), one has managed to express the partition function entirely in terms of real numbers, so it looks suitable for a Monte Carlo evaluation. However, in order to be able to interpret the result in terms of an effective classical Hamiltonian, i.e.

$$
Z_{gc}^{(P)} \propto \prod_{i,s} \int d\phi_i^{(s)} \exp\left[-\mathcal{H}_{eff}^{(P)}(\phi_i^{(s)})/k_BT\right] \qquad (0.65)
$$

it is mandatory that the integrand in Eq. (0.65) is always non-negative, and this is not the case! This problem - which is quite typical for quantum Monte Carlo simulations of fermionic systems - is called the "minus-sign problem" [27]. So when we want to calculate an average of a quantity $A(x)$ with a measure $\rho(x)$,

$$
\langle A \rangle = \int A(x)\rho(x)dx / \int \rho(x)dx \ , \qquad (0.66)
$$

we can no longer interpret $\rho(x)$ as probability density, if $\rho(x)$ is not positive semi-definite, and so the basis for Metropolis importance sampling is no longer valid. Of course, this difficulty can be circumvented formally by the trick to use the probability density $\widetilde{\rho} = |\varphi(x)|/\int|\rho(x)|dx$ and absorb the sign of $\rho(x)$ in the quantity that one wishes to estimate,

$$
\langle A \rangle = \frac{\int A(x) sign(\rho(x))\widetilde{\rho}(x)dx}{\int sign(\rho(x))\widetilde{\rho}(x)dx} = \frac{\langle A\hat{s}\rangle}{\langle \hat{s}\rangle} \ , \qquad (0.67)
$$

where $\hat{s}$ is the sign operator. But it is unlikely that this importance sampling based on $|\rho(x)|$ will really sample the important regions of phase space when N gets large. Indeed, for the Hubbard Hamiltonian one estimates that [18]

$$\langle \hat{s} \rangle \propto \exp(-\gamma N U / k_B T) \ , \tag{0.68}$$

where γ is a constant of order unity. Thus it is clear that for low temperatures and large N the denominator $\langle \hat{s} \rangle$ in Eq. (0.67) gets extremely small, and hence it becomes impossible to sample $\langle A \rangle$ by Eq. (0.67) with meaningful accuracy.

While many schemes have been devised to alleviate this problem, a fully satisfactory solution to this "minus sign problem" is unknown to the authors of this book at the time of writing. In view of these difficulties, we have confined ourselves to a rather sketchy description of the quantum Monte Carlo approach to fermions on lattices, since this is still an active area of research. Also the treatment of quantum spin models still is under development: in particular, substantial improvement has been obtained by combining cluster algorithms with PIMC Monte Carlo methods for quantum spin systems [28].

0.6 Concluding remarks

Quantum Monte Carlo simulation is a particularly rich field, and many aspects are still under development. In this chapter, we have emphasized the path integral quantum Monte Carlo technique and even for this method only the flavor of the approach could be given, and typical applications were sketched. There are also important Monte Carlo methods addressing the problem of solving the many-body Schrödinger equation, in order to find ground state energy and associated wave function [18]. We refer the interested reader to the literature where he can find very concise accounts of "variational Monte Carlo (VMC)", "Green's function Monte Carlo (GFMC)", "Projector Quantum Monte Carlo (PQMC)", etc. [18]. Path integral simulations of "rotors" (rotating rigid molecules) have recently been reviewed in [29].

Fig. 0.1. Qualitative sketch of the specific heat C_v (upper part), the lattice constant a (middle part) and an elastic constant $C_{\ell m}$ (lower part) plotted vs temperature T. The corresponding behavior given by classical statistical mechanics are the broken straight lines. Significant differences between classical and quantum statistical mechanics occur for temperature T below the Debye temperature Θ.

Fig. 0.2. Radii of "ring polymers" representing quantum-mechanically treated silicon and oxygen atoms in two crystalline structures of SiO_2, β-cristobalite and β-quartz, plotted as function of temperature, using a Trotter number P = 30. For comparison, the thermal de Broglie wavelength for free oxygen and silicon atoms are also shown. From Rickwardt et al. [1].

Fig. 0.3. a) Temperature dependence of the lattice constant a for orthorhombic polyethylene (C_nH_{2n+2}). Results of a path-integral Monte Carlo calculation are compared with the values for a classical system and with experiment. After Martonak et al. [3] b) Temperature dependence of the average fluctuation $\langle(\delta\Phi_{CCC})^2\rangle^{1/2}$ of the C-C-C bond angle in polyethylene, according to the classical Monte Carlo simulation (full dots, yielding $\langle(\delta\Phi_{CCC})^2\rangle^{1/2} \propto T^{1/2}$ at low T, and according to path integral Monte Carlo simulations (open symbols). Two choices of chain length n are used, $n = 12$ and $n = 24$, respectively. After Martonak et al. [3]

Fig. 0.4. Schematic representation of two interacting quantum particles i,j in two dimensions: each particle (i) is represented by a "ring polymer" composed of $P = 10$ effective monomers at positions $\boldsymbol{r}_i^{(s)}$, with $s = 1, 2, \ldots, P$. Harmonic springs (of strength κ) only connect "monomers" of the same "polymer" while interatomic forces join different monomers with the same Trotter index s, indicated by the thin straight lines. In the absence of such interactions, the size of such a ring polymer would be of the order of the thermal de Broglie wavelength $\lambda_T = h/\sqrt{2\pi m k_B T}$, where h is Planck's constant.

Fig. 0.5. Trotter scaling plot for the lattice parameter a of solid Neon. The upper curve corresponds to ^{20}Ne at $T = 16K$, the lower curve to ^{22}Ne at $T = 16K$. From Müser et al. (1995).

Fig. 0.6. (a) Points showing Monte Carlo data for the structure factor $S(q)$ versus q, for the case of $N = 40$ and 20 non-interacting electrons ($t = 1, V = 0$) at a low temperature, $k_B T = 1/4$. Solid line is the analytical solution, which can trivially be found for this non-interacting system. (b) Monte Carlo results for the structure factor $S(q)$ vs q, for the case of $N = 40$ but 20 interacting electrons ($t = 1, V = 2, k_B T = 1/4$). Note the difference in scale between parts (a) and (b). (c) Maximum structure factor for the half-filled case ($\langle \hat{\rho} \rangle = 1/2$), $S(q_\pi)$, plotted versus the logarithm of the lattice size for $t = 1, V = 2, k_B T = 1/4$. From Hirsch et al [24].

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