Bead−Fourier path integral molecular dynamics for identical particles

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The Bead–Fourier path integral molecular dynamics technique, introduced earlier [S.D. Ivanov, A.P. Lyubartsev, and A. Laaksonen, Phys. Rev. E **67** (2003) 066710] for the case of distinguishable particles is reformulated in order to achieve more efficient sampling. The reformulation is carried out on the basis of the "staging" transformation of beads' coordinates, yielding all dynamical variables to move on similar time scales. The formalism for identical particles is presented. It is shown, that the straightforward approach leads to impossibility of the sign changes. A recipe to overcome this problem is suggested. It is demonstrated, that the developed formalism for identical particles can also be reformulated, providing efficient molecular dynamics.

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1 Introduction

Path Integral (PI) simulation techniques, based on the Feynman path integral formalism [1, 2] proved to be efficient and powerful for investigations of quantum many-body systems. The simulation methods based on PI exploit the, so-called, *quantum-classical isomorphism* [3], namely, the isomorphism between the quantum partition function, presented as an imaginary time path integral [1, 2] and the classical configurational integral over closed trajectories. Properties of the quantum objects can thus be obtained by simulation of classical "ring polymers". Sampling of trajectories in PI simulations can be done either by the Monte Carlo (MC) or molecular dynamics (MD) algorithms.

The PI formalism is exact and straight-forward to use for systems of interacting quantum particles, but it requires, in principle, an infinite number of parameters to define the trajectory. Therefore finite-number approximations have to be used to treat the path integrals in numerical computer simulations.

In the mostly widespread simulation scheme the PI trajectories are approximated by a finite number of points (beads) connected by a harmonic potential [4]. The other, so-called, *Fourier* approximation [5] method describes the trajectory by a finite set of Fourier series terms. Enormous effort has been spent to determine which approach is superior and, in fact, this discussion continues up to nowadays (see e.g. [6] and references therein) with no definite winner emerged. Coalson [7] suggested that "Perhaps this is because *the two prescriptions are essentially the same*". Strictly speaking, both schemes come into perfect agreement only at very

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high orders of implementation.

Vorontsov–Velyaminov *et al.* [8] invented a combined Bead–Fourier (BF) Monte Carlo (MC) method in which the parts of the trajectory between the beads are presented as a Fourier series. It was shown in this article and in the subsequent works [9, 10] that by combining the bead and Fourier contributions in an optimal way, a substantial performance improvement can be obtained in path integral Monte Carlo (PIMC) simulations.

Recently, we developed and tested Bead–Fourier path integral molecular dynamics (BFPIMD) method [11, 12]. It was demonstrated as well, that molecular dynamics in combination with the Bead–Fourier scheme allows one to overcome serious computational difficulties present in the pure bead or pure Fourier schemes, namely, in cases requiring very large number of beads or Fourier components. The advantages of the BFPIMD scheme were especially noticeable for Coulomb systems. In [12] we pointed out, that softening of the Coulomb potential in the vicinity of the nucleus causes artificial trends in the electronic density, and suggested a recipe to overcome it.

However, the formalism presented in [11, 12] describes the distinguishable quantum particles only, neglecting the permutational symmetry. So, the first goal of this paper is to develop the formalism, that includes quantum statistics into consideration.

As it was pointed out in [13] it is important to have all molecular dynamical variables to move on the same time scales in order to achieve efficacy. So, the second aim of this paper is to reformulate the formalism developed into a more efficient one.

The paper is organized as follows. The staging ideas applied for BFPIMD, as well as the general formalism for identical particles and its reformulation into a more efficient one, are described in Sec. 2, followed by details of the molecular dynamics organisation in Sec. 3. Results and discussions are presented in Sec. 4 and concluding remarks in Sec. 5.

2 Theory

2.1 Bead−Fourier staging molecular dynamics

Bead–Fourier path integral (BFPI) scheme was suggested and developed within Monte Carlo (MC) approach by Vorontsov–Velyaminov *et al.* [8]. In our previous works [11, 12] we developed and tested Bead–Fourier path integral molecular dynamics (BFPIMD) approach for the case of distinguishable particles. Let us briefly present the BF formalism. Consider N distinguishable quantum particles in a three-dimensional system. The partition function Z reads:

$$Z = \int \prod_{i=1}^{N} \prod_{j=1}^{n} \left(\mathrm{d}\mathbf{r}_{ij} \prod_{k=1}^{k_{\max}} \mathrm{d}\mathbf{a}_{ijk} \right) \exp\left[-\beta H \left(\mathbf{r}_{ij}, \mathbf{a}_{ijk} \right) \right], \tag{1}$$

where $\beta \equiv 1/KT$ is the inversed temperature, $\mathbf{r}_{ij} = \{x_{ij}; y_{ij}; z_{ij}\}$ are coordinates of bead number j that belongs to the trajectory describing particle i. $\mathbf{a}_{ijk}$ =

$\{a_{xijk}; a_{yijk}; a_{zijk}\}$ are the corresponding k-th Fourier harmonics amplitudes, n is the number of beads, N is the number of particles (trajectories), $k_{\max}$ is the number of the last term of the truncated Fourier sine series taken into consideration. The Hamiltonian H is defined by:

$$H = \sum_{i=1}^{N} \sum_{j=1}^{n} \left\{ \frac{m\omega_n^2}{2} \left[(\mathbf{r}_{ij+1} - \mathbf{r}_{ij})^2 + \sum_{k=1}^{k_{\max}} \frac{(k\pi)^2}{2} \mathbf{a}_{ijk}^2 \right] + \frac{1}{n} \int_0^1 \mathrm{d}\xi V \left[\mathbf{r}_{ij}(\xi) \right] \right\}, \quad (2)$$

where $V[\mathbf{r}_{ij}(\xi)]$ is the interaction potential, which depends on the system studied, the "chain frequency" ω_n being:

$$\omega_n \equiv \frac{\sqrt{n}}{\beta\hbar} \quad (3)$$

and $\mathbf{r}_{ij}(\xi)$ describes "i"-trajectory between beads "j" and "$j+1$":

$$\mathbf{r}_{ij}(\xi) = \mathbf{r}_{ij} + (\mathbf{r}_{ij+1} - \mathbf{r}_{ij})\xi + \sum_{k=1}^{k_{\max}} \mathbf{a}_{ijk} \sin(k\pi\xi)\,. \quad (4)$$

Note that in expressions (2, 4) the trajectories are closed, i.e. $\mathbf{r}_{i,n+1} = \mathbf{r}_{i,1}$.

Eqs. (1) and (2) are suitable for MC, not for MD. Following [11,12] we treat the Hamiltonian (2) as a potential energy and introduce corresponding kinetic terms. Then, the total BF Hamiltonian reads:

$$H^{\mathrm{BF}} = \sum_{i=1}^{N} \sum_{j=1}^{n} \left(\frac{p_{ij}^2}{2\tilde{m}_{ij}} + \sum_{k=1}^{k_{\max}} \frac{p_{ijk}^2}{2\tilde{m}_{ijk}} \right) + U_{\mathrm{eff}}^{\mathrm{BF}} \left(\{\mathbf{r}_{ij}, \mathbf{a}_{ijk}\} \right), \quad (5)$$

where $U_{\mathrm{eff}}^{\mathrm{BF}}(\{\mathbf{r}_{ij}, \mathbf{a}_{ijk}\})$ coincides with the Hamiltonian from Eq. (2), while $\mathbf{p}_{ij}$ and $\mathbf{p}_{ijk}$ are the momenta, conjugated to $\mathbf{r}_{ij}$ and $\mathbf{a}_{ijk}$, respectively. The Hamiltonian H^{BF} can be used for derivation of Hamiltonian equations of motion with both beads' coordinates and Fourier amplitudes treated as generalized coordinates, with their momenta treated as generalized momenta. For details, see [11,12].

Direct application of the scheme described above makes both beads and Fourier amplitudes oscillate on very different time scales. Indeed, the harmonic coupling of beads $(\mathbf{r}_{ij+1} - \mathbf{r}_{ij})^2$ induces characteristic frequencies (normal modes) to cover many time scales. The prefactor $\frac{1}{2}(k\pi)^2$ at the quadratic Fourier term a_{ijk}^2 explicitly presents the wide spectrum of frequencies for Fourier amplitudes. Although it is possible to use BFPIMD as is, i.e., ignoring this problem, as we have done in [11,12], it may be not very efficient and can lead to convergence problems in certain cases. Hence, we suggest a recipe to avoid it and reformulate the BF scheme in order to force all degrees of freedom oscillate on the same time scale.

The harmonic coupling can be resolved exactly in the same manner, as in the pure bead case. Historically, there appeared two variants of a variable transform, that uncouple the beads. One is called *staging* and was initially developed for MC [14,15]. Tuckerman *et al.* [13] developed staging MD scheme. The other is called normal mode transformation (see e.g. [16,17]). Staging seems preferable for us, since the corresponding formulas have simple recursive form as presented below. Consider a change of variables of the form:

$$\mathbf{u}_{i1} = \mathbf{r}_{i1}\,, \qquad \mathbf{u}_{ij} = \mathbf{r}_{ij} - \frac{(j-1)\mathbf{r}_{ij+1} + \mathbf{r}_{i1}}{j}\,. \tag{6}$$

This transformation is known as the staging transformation.

Note that beads and Fourier amplitudes are coupled only by the potential energy term (2). Hence, we can consider Fourier amplitudes as parameters and perform exactly the same staging transformation (6) as was done by Tuckerman *et al.* in the pure bead case, resulting in:

$$\begin{aligned} &U_{\mathrm{eff}}^{\mathrm{stage}}\left(\{\mathbf{u}_{ij}, \mathbf{a}_{ijk}\}\right) = \\ &= \sum_{i=1}^{N}\sum_{j=1}^{n} \frac{\omega_n^2}{2}\left[m_{ij}u_{ij}^2 + m\sum_{k=1}^{k_{\max}} \frac{(k\pi)^2}{2}\,a_{ijk}^2\right] + \frac{1}{n}\,l\phi\left(\{\mathbf{u}_{ij}(\{\mathbf{r}_{ij}\}), \mathbf{a}_{ijk}\}\right), \end{aligned} \tag{7}$$

where ω_n was defined in (3), masses m_{ij} are the staging masses defined as: $m_{i1} = 0$; $m_{ij} = \dfrac{m_i j}{j-1}$ $\forall j > 1$, with index i pointing the particles. The potential energy term $\phi\left(\{\mathbf{u}_{ij}(\{\mathbf{r}_{ij}\}), \mathbf{a}_{ijk}\}\right)$ is a denotation for:

$$\phi\left(\{\mathbf{u}_{ij}(\{\mathbf{r}_{ij}\}), \mathbf{a}_{ijk}\}\right) \equiv \sum_{i=1}^{N}\sum_{j=1}^{n}\int_0^1 \mathrm{d}\xi V\left[\mathbf{r}_{ij}(\xi)\right]. \tag{8}$$

Now the quadratic term in Eq. (7) is completely uncoupled in the terms of the staging coordinates $\mathbf{u}_{ij}$. Note, that the variables $\mathbf{u}_{i1}$ do not appear in the transformed harmonic term, since $m_{i1} = 0$. This illustrates the well known fact, that n coupled oscillators can be presented as $n-1$ uncoupled ones.

The resulting Hamiltonian H^{stage} is similar to the one defined in (5), with the only substitution: $U_{\mathrm{eff}}^{\mathrm{BF}} \to U_{\mathrm{eff}}^{\mathrm{stage}}$. We would like to stress, that H^{stage} generates a different dynamics, that samples the configuration space more effectively, although yields the same result.

As we already mentioned, the forces, $\partial\phi/\partial\mathbf{u}_{ij}$ can also be retrieved in a recurrent manner:

$$\begin{aligned} \frac{\partial\phi}{\partial\mathbf{u}_{i1}} &= \sum_{j=1}^{n}\frac{\partial\phi}{\partial\mathbf{x}_{ij}}\,, \\ \frac{\partial\phi}{\partial\mathbf{u}_{ij}} &= \frac{\partial\phi}{\partial\mathbf{x}_{ij}} + \frac{j-2}{j-1}\,\frac{\partial\phi}{\partial\mathbf{u}_{ij-1}}\,. \end{aligned} \tag{9}$$

This form is especially convenient, since the bead forces $\partial\phi/\partial\mathbf{x}_{ij}$ can be computed directly, given the form of the potential, without any additional effort.

The next target is the prefactor of the Fourier quadratic term. Consider a variable transform:

$$\tilde{\mathbf{a}}_{ijk} \equiv \frac{k\pi}{\sqrt{2}}\,\mathbf{a}_{ijk}\,. \tag{10}$$

Then, the BF trajectory representation (4) changes as:

$$\mathbf{r}_{ij}\left(\xi\right)=\mathbf{r}_{ij}+\left(\mathbf{r}_{ij+1}-\mathbf{r}_{ij}\right)\xi+\sum_{k=1}^{k_{\max}}\frac{\sqrt{2}}{k\pi}\,\tilde{\mathbf{a}}_{ijk}\sin(k\pi\xi)\,. \qquad (11)$$

In the matter of fact, nothing except re-denotation has been done. Gathering all together, for the partition function we get:

$$Z(\beta)\approx\int\exp\left[-\beta H^{\mathrm{BF}}\left(\{\mathbf{u}_{ij},\tilde{\mathbf{a}}_{ijk}\}\right)\right]\prod_{i=1}^{N}\prod_{j=1}^{n}\biggl(\mathrm{d}\mathbf{u}_{ij}\prod_{k=1}^{k_{\max}}\mathrm{d}\tilde{\mathbf{a}}_{ijk}\biggr). \qquad (12)$$

We used proportionality sign instead of equality, since the normalizing term was omitted. The Hamiltonian H^{BF} is defined in (5), with $U_{\mathrm{eff}}^{\mathrm{BF}}$:

$$U_{\mathrm{eff}}^{\mathrm{BF}}\left(\{\mathbf{u}_{ij},\tilde{\mathbf{a}}_{ijk}\}\right)=\sum_{i=1}^{N}\sum_{j=1}^{n}\frac{\omega_n^2}{2}\biggl(m_{ij}u_{ij}^2+m\sum_{k=1}^{k_{\max}}\tilde{a}_{ijk}^2\biggr)+\frac{1}{n}\,\phi\left(\{\mathbf{u}_{ij}(\{\mathbf{r}_{ij}\}),\tilde{\mathbf{a}}_{ijk}\}\right). \qquad (13)$$

The system moves in the phase space, according to the Hamiltonian equations of motion, with the generalized coordinates$^{1)}$ $\mathbf{u}_{ij}$, $\mathbf{a}_{ijk}$ and conjugated momenta $\mathbf{p}_{ij}$, $\mathbf{p}_{ijk}$. Again, the BFPIMD derived from Eqs. (12) and (13) is not the same as the one derived from Eqs. (1) and (2), though it yields the same result. Beads' coordinates and Fourier amplitudes should now oscillate on the similar time scales.

2.2 General formalism for system of N identical particles

Now, let us proceed with BFPIMD for identical particles. Previously, PIMD approach for identical particles was considered by Miura and Okazaki [18] for the pure bead case. We shall develop the BF scheme following their ideas. PIMD [18] is based on the (anti)symmetric propagator approach of Takahashi and Imada [19]. The difference with the "permutational sampling" used by Vorontsov–Velyaminov *et al.* [8] is in the order of operations, namely, the Trotter expansion and summing over permutations. Although, the result doesn't depend on their order, the microscopic picture is clearly different.

The partition function for fermionic systems reads:

$$Z\approx\frac{1}{(N!)^n}\int\mathrm{d}\tau\prod_{j=1}^{n}\det A_j\times\exp\biggl[-\frac{\beta m\omega_n^2}{2}\sum_{i=1}^{N}\sum_{j=1}^{n}\sum_{k=1}^{k_{\max}}\frac{(k\pi)^2}{2}\,a_{ijk}^2\biggr]. \qquad (14)$$

We used proportionality sign, since we omitted the normalizing term in Eq. (14). The denotation $\mathrm{d}\tau$ is introduced for compactness of formulas, being:

$$\mathrm{d}\tau\equiv\prod_{i=1}^{N}\prod_{j=1}^{n}\biggl(\mathrm{d}\mathbf{r}_j^{(i)}\prod_{k=1}^{k_{\max}}\mathrm{d}\mathbf{a}_{ijk}\biggr). \qquad (15)$$

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1) From here and further tildes upon Fourier amplitudes are omitted

Note, that in the case of bosons determinant should be substituted by permanent. The Fourier amplitudes' quadratic terms are collected outside the determinant, since each column contains the same set of them. Matrix A_j is $N \times N$ matrix, whose matrix elements are defined as:

$$A_j^{(il)} \equiv \exp\left[-\frac{\beta m\omega_n^2}{2}\left(\mathbf{r}_j^{(i)} - \mathbf{r}_{j+1}^{(l)}\right)^2 - \frac{\beta}{n}\int_0^1 \mathrm{d}\xi V\left[\mathbf{r}_j^{(il)}(\xi)\right]\right], \tag{16}$$

where $\mathbf{r}_j^{(il)}(\xi)$ is the part of the trajectory, linking bead j of trajectory i with bead $j+1$ of trajectory l:

$$\mathbf{r}_j^{(il)}(\xi) = \mathbf{r}_j^{(i)} + \left(\mathbf{r}_{j+1}^{(l)} - \mathbf{r}_j^{(i)}\right)\xi + \sum_{k=1}^{k_{\max}} \mathbf{a}_{ijk}\sin(k\pi\xi). \tag{17}$$

Note, that in contrary to the pure bead case, the potential energy term enters the determinant. Since the determinant can be negative, the following trick [19] is used. Consider an observable, represented by the operator $\hat{O}$ with the corresponding estimator $\epsilon_O\left(\{\mathbf{r}_j^{(i)}(\xi)\}\right)$. Then the canonical average of the observable $\hat{O}$:

$$\begin{aligned}
\langle\hat{O}\rangle &= \frac{\int \mathrm{d}\tau \prod\limits_{j=1}^{n} \det A_j \times \epsilon_O\left(\{\mathbf{r}_j^{(i)}(\xi)\}\right)\exp\left[-\frac{\beta m\omega_n^2}{2}\sum\limits_{i=1}^{N}\sum\limits_{j=1}^{n}\sum\limits_{k=1}^{k_{\max}}\frac{(k\pi)^2}{2}a_{ijk}^2\right]}{\int \mathrm{d}\tau \prod\limits_{j=1}^{n} \det A_j \exp\left[-\frac{\beta m\omega_n^2}{2}\sum\limits_{i=1}^{N}\sum\limits_{j=1}^{n}\sum\limits_{k=1}^{k_{\max}}\frac{(k\pi)^2}{2}a_{ijk}^2\right]} \\
&= \frac{\int \mathrm{d}\tau \prod\limits_{j=1}^{n} \left|\det A_j\right| \mathrm{sgn}(\det A_j) \times \epsilon_O\left(\{\mathbf{r}_j^{(i)}(\xi)\}\right)\exp\left[-\frac{\beta m\omega_n^2}{2}\sum\limits_{i=1}^{N}\sum\limits_{j=1}^{n}\sum\limits_{k=1}^{k_{\max}}\frac{(k\pi)^2}{2}a_{ijk}^2\right]}{\int \mathrm{d}\tau \prod\limits_{j=1}^{n} \left|\det A_j\right| \mathrm{sgn}(\det A_j)\exp\left[-\frac{\beta m\omega_n^2}{2}\sum\limits_{i=1}^{N}\sum\limits_{j=1}^{n}\sum\limits_{k=1}^{k_{\max}}\frac{(k\pi)^2}{2}a_{ijk}^2\right]} \\
&= \frac{\left\langle \epsilon_O\left(\{\mathbf{r}_j^{(i)}(\xi)\}\right)\mathrm{sgn}(\det A_j)\right\rangle_{||}}{\left\langle \mathrm{sgn}(\det A_j)\right\rangle_{||}},
\end{aligned} \tag{18}$$

where $\langle\ldots\rangle_{||}$ means averaging with respect to artificial probability distribution:

$$\prod_{j=1}^{n}\left|\det A_j\right| \times \exp\left[-\frac{\beta m\omega_n^2}{2}\sum_{i=1}^{N}\sum_{j=1}^{n}\sum_{k=1}^{k_{\max}}\frac{(k\pi)^2}{2}a_{ijk}^2\right], \tag{19}$$

sgn being the sign function. In other words, we perform a simulation according to always positive artificial probability distribution (19) (which is the modulus of the original distribution) and recover true thermodynamic averages from this "unphysical" MD trajectory. Note, that the origin of the sign problem is clearly pointed out in Eq. (18). When the exchange effect is strong, all permutations have approximately the same probabilities, tending the average sign to zero. Thus, we have a very small number in the denominator, resulting in a dramatic uncertainty growth. In an attempt to write down the partition function in a more convenient form, the effective potential W_{eff} is introduced, defined as:

$$W_{\text{eff}} \equiv \frac{m\omega_n^2}{2} \sum_{i=1}^{N} \sum_{j=1}^{n} \sum_{k=1}^{k_{\max}} \frac{(k\pi)^2}{2}\, a_{ijk}^2 - \frac{1}{\beta} \sum_{j=1}^{n} \ln\left|\det A_j\right| \tag{20}$$

resulting in the following expression for the partition function:

$$Z \approx \int \mathrm{d}\tau \exp\left[-\beta W_{\text{eff}}\left(\{\mathbf{r}_j^{(i)}\}\right)\right]. \tag{21}$$

Thus, W_{eff} is the effective potential indeed. Note a very important property of the effective potential (20):

$$\left|\det A_j\right| \to 0 \Rightarrow \; W_{\text{eff}} \to +\infty\,. \tag{22}$$

It means, that there exists an infinite energy barrier, at "nodal surfaces" defined as $\det A_j = 0$. Since molecular dynamics is continuous, it would not be able to cross the barrier under any circumstances. Note, that this feature does not depend on the scheme used, i.e., it exists in both BF scheme and the one of Miura and Okazaki [18]. Thus, the approach described above is, in fact, similar to restricted path integral approach of Ceperley [20], which applicability is doubtful, since it gives an incorrect result, e.g., for the ideal Fermi gas [21]. Miura and Okazaki have tested their approach for the fermionic case, only on a system, consisting of three particles in a one-dimensional harmonic well. The remarkable feature of antisymmetric propagator approach, applied to one-dimensional systems is, that sign is always positive. Hence, they were not able to notice the failure of the approach.

Below we suggest a recipe to overcome the problem of the infinite energy barrier. Let us start from Eq. (14). Again, consider an observable, represented by the operator $\hat{O}$ with the corresponding estimator $\epsilon_O\left(\{\mathbf{r}_j^{(i)}\}\right)$. But, instead of splitting of the determinant into a product of its modulus and sign we perform another trick: we multiply and divide it on $\sqrt{(\det A_j)^2+\delta}$, where δ is a positive number. Then, the canonical average of the observable $\hat{O}$ becomes:

$$\begin{aligned}\langle\hat{O}\rangle &= \frac{\displaystyle\int \mathrm{d}\tau \prod_{j=1}^{n} \frac{\det A_j \sqrt{(\det A_j)^2+\delta}}{\sqrt{(\det A_j)^2+\delta}} \exp\left[-\frac{\beta m\omega_n^2}{2} \sum_{i=1}^{N}\sum_{j=1}^{n}\sum_{k=1}^{k_{\max}} \frac{(k\pi)^2}{2}\, a_{ijk}^2\right] \epsilon_O\left(\{\mathbf{r}_j^{(i)}\}\right)}{\displaystyle\int \mathrm{d}\tau \prod_{j=1}^{n} \frac{\det A_j \sqrt{(\det A_j)^2+\delta}}{\sqrt{(\det A_j)^2+\delta}} \exp\left[-\frac{\beta m\omega_n^2}{2} \sum_{i=1}^{N}\sum_{j=1}^{n}\sum_{k=1}^{k_{\max}} \frac{(k\pi)^2}{2}\, a_{ijk}^2\right]} \\ &= \frac{\left\langle \epsilon_O\left(\{\mathbf{r}_j^{(i)}\}\right) \dfrac{\det A_j}{\sqrt{(\det A_j)^2+\delta}} \right\rangle_f}{\left\langle \dfrac{\det A_j}{\sqrt{(\det A_j)^2+\delta}} \right\rangle_f}\,,\end{aligned} \tag{23}$$

where $\langle \ldots \rangle_f$ means averaging with respect to artificial probability distribution f:

$$f \equiv \prod_{j=1}^{n} \sqrt{(\det A_j)^2 + \delta} \times \exp\Big[-\frac{\beta m \omega_n^2}{2} \sum_{i=1}^{N} \sum_{j=1}^{n} \sum_{k=1}^{k_{\max}} \frac{(k\pi)^2}{2}\, a_{ijk}^2 \Big]. \tag{24}$$

Again, we introduce the effective potential W_{eff}:

$$W_{\text{eff}} \equiv \frac{m\omega_n^2}{2} \sum_{i=1}^{N} \sum_{j=1}^{n} \sum_{k=1}^{k_{\max}} \frac{(k\pi)^2}{2}\, a_{ijk}^2 - \frac{1}{\beta} \sum_{j=1}^{n} \ln \sqrt{(\det A_j)^2 + \delta}\,. \tag{25}$$

When $\delta > 0$ the effective potential[2] reaches only a finite maximum at nodal surface. Thus, the problem of infinite potential barrier disappears. The height of the finite energy barrier at nodal surface is determined by the particular value of the parameter δ. Again, we perform a simulation according to always positive artificial probability distribution f (24) and recover true thermodynamic averages according to (23). The expression for the partition function coincides with Eq. (21).

Note, that $\sqrt{(\det A_j)^2 + \delta}$ is not the only function class, that solves the problem. For instance, $(\det A_j)^2 + \delta$ would manage, as well. We choose it to be the square root, because:

$$\frac{\det A_j}{\sqrt{(\det A_j)^2 + \delta}} \to \operatorname{sgn}(\det A_j)\,, \quad |\det A_j| \gg \delta\,. \tag{26}$$

Note, that if we set $\delta = 0$ the approach becomes identical to the original one of Miura and Okazaki [18]. The expression for the partition function coincides with Eq. (21) with the effective potential W_{eff} determined by (25).

As we discussed in the previous subsection, one desires to have all dynamical variables to move on the similar time scales. It was found possible to reformulate the formalism for identical particles achieving this goal. Let us investigate the structure of the determinant $\det A_j$ for the case of free particle:

$$\det \begin{vmatrix} \exp\Big[-\frac{1}{2}\,\beta m\omega_n^2 \Big(\mathbf{r}_j^{(1)} - \mathbf{r}_{j+1}^{(1)}\Big)^2\Big] & \ldots & \exp\Big[-\frac{1}{2}\,\beta m\omega_n^2 \Big(\mathbf{r}_j^{(1)} - \mathbf{r}_{j+1}^{(N)}\Big)^2\Big] \\ \multicolumn{3}{c}{\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots} \\ \exp\Big[-\frac{1}{2}\,\beta m\omega_n^2 \Big(\mathbf{r}_j^{(N)} - \mathbf{r}_{j+1}^{(1)}\Big)^2\Big] & \ldots & \exp\Big[-\frac{1}{2}\,\beta m\omega_n^2 \Big(\mathbf{r}_j^{(N)} - \mathbf{r}_{j+1}^{(N)}\Big)^2\Big] \end{vmatrix}. \tag{27}$$

We suggest to decompose quadratic expressions under exponents. Matrix elements of A_j:

$$A_j^{(il)} = \exp\Big[-\frac{\beta m\omega_n^2}{2} \Big((r_j^{(i)})^2 - 2\mathbf{r}_j^{(i)} \cdot \mathbf{r}_{j+1}^{(l)} + (r_{j+1}^{(l)})^2 \Big) \Big]. \tag{28}$$

The exponent in the right hand side of Eq. (28) can be split into product of three exponents. Note now, that all exponents in the first column contain the

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[2] Strictly speaking, not the effective potential itself, but its second term in (25).

term: $\exp\left[-\frac{1}{2}\,\beta m\omega_n^2 (r_{j+1}^{(1)})^2\right]$, while all exponents in the first row contain the term: $\exp\left[-\frac{1}{2}\,\beta m\omega_n^2 (r_j^{(1)})^2\right]$. The generalization of the latter statement is obvious. Row or column with number i contains the Gaussian with $(r_j^{(i)})^2$ or $(r_{j+1}^{(i)})^2$, correspondingly. Thus, using the well known property of the determinants, that multiplication of a determinant by a factor is equivalent to multiplication of any its row/column by the same factor, one gets:

$$\prod_{j=1}^{n} \det A_j = \exp\left[-\beta m\omega_n^2 \sum_{i=1}^{N}\sum_{j=1}^{n}\left(r_j^{(i)}\right)^2\right] \times \prod_{j=1}^{n} \det B_j \,, \tag{29}$$

where B_j is $N \times N$ matrix, whose matrix elements are:

$$B_j^{(il)} = \exp\left[-\beta m\omega_n^2 \mathbf{r}_j^{(i)} \cdot \mathbf{r}_{j+1}^{(l)}\right]. \tag{30}$$

In the general case, the matrix elements would contain the potential energy terms, as in Eq. (16):

$$B_j^{(il)} = \exp\left[-\beta m\omega_n^2 \mathbf{r}_j^{(i)} \cdot \mathbf{r}_{j+1}^{(l)} - \frac{\beta}{n}\int_0^1 \mathrm{d}\xi V\left[\mathbf{r}_j^{(il)}(\xi)\right]\right]. \tag{31}$$

The effective potential W_{eff} reads:

$$W_{\text{eff}} = m\omega_n^2 \sum_{i=1}^{N}\sum_{j=1}^{n}\left[\left(r_j^{(i)}\right)^2 + \sum_{k=1}^{k_{\max}} \frac{(k\pi)^2}{4}\, a_{ijk}^2\right] - \frac{1}{\beta}\sum_{j=1}^{n} \ln\sqrt{(\det B_j)^2 + 1}\,. \tag{32}$$

One sees, that the first term is the sum of uncoupled oscillators with twice bigger masses^{3}) than the particles' mass. The last step is to perform the transform of Fourier amplitudes, analogously to (10):

$$\tilde{\mathbf{a}}_{ijk} \equiv \frac{k\pi}{2}\,\mathbf{a}_{ijk} \tag{33}$$

resulting in the new expression for the trajectory description:

$$\mathbf{r}_j^{(il)}(\xi) = \mathbf{r}_j^{(i)} + \left(\mathbf{r}_{j+1}^{(l)} - \mathbf{r}_j^{(i)}\right)\xi + \sum_{k=1}^{k_{\max}} \frac{2}{k\pi}\,\tilde{\mathbf{a}}_{ijk}\sin(k\pi\xi)\,. \tag{34}$$

Finally, the expression for the effective potential in new variables:

$$W_{\text{eff}} = \frac{\tilde{m}\omega_n^2}{2}\sum_{i=1}^{N}\sum_{j=1}^{n}\left[\left(r_j^{(i)}\right)^2 + \sum_{k=1}^{k_{\max}} \tilde{a}_{ijk}^2\right] - \frac{1}{\beta}\sum_{j=1}^{n}\ln\sqrt{(\det B_j)^2 + 1}\,. \tag{35}$$

The similarity of the obtained formula with the staging one (13) is clear.

Miura and Okazaki also tried to achieve the dynamics of the similar time scales using the other reformulation of the method (see [18] for details). It seems important to mention, that in contrary to their approach, we did not choose any "privileged" permutation.

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^{3}) This can be considered as frequencies being greater by the factor $\sqrt{2}$), but we prefer to treat it as the mass increase.

3 Organising molecular dynamics

In the previous section, we developed two variants of BFPIMD, namely, the staging variant of BFPIMD, for distinguishable particles, and the version for identical particles. Both were designed in order to have all MD variables to move on the similar time scales.

As it was already mentioned, one of the benefits of staging approach is, that knowledge of forces in terms of Cartesian coordinates is enough for organising the staging MD. Moreover, since the staging transform (6) as well as the inverse transform can be carried out by simple recurrent relations, the estimators can also be computed in Cartesian coordinates. The derivation of Cartesian forces was discussed in details in [12].

As it was also pointed out in [12], softening the Coulomb potential in the close vicinity of the nucleus is a necessary, but tricky task. The correction potential, invented in [12]:

$$V^{\mathrm{corr}}(r) = -\frac{1}{\beta}\ln\left[\frac{\rho_{\mathrm{ex}}(r)}{\rho(r)}\right], \tag{36}$$

was used for staging MD. It leads only to appearance of additional force in Cartesian coordinates, which was used to compute forces, acting on the staging beads in the standard manner (9).

In the case of identical particles, the formalism, providing the efficient⁴) MD, follows naturally from the original formulation of the antisymmetric propagator approach in the BF case, by some reorganisation of formulas. The expressions for forces differ only by derivation of the additional potential energy term:

$$\ln\sqrt{(\det B_j)^2+\delta}\,.$$

For instance, beads' forces coming from this term reads:

$$\frac{1}{\beta}\sum_{j=1}^{n}\frac{\det B_j}{(\det B_j)^2+\delta}\,\frac{\partial(\det B_j)}{\partial \mathbf{r}_{ij}}\,.$$

Thus, one has to take the derivatives of the determinant, which is definitely, the bottleneck of the approach. Technically, it can be done using the following expression [19]:

$$\frac{\partial}{\partial x}\det B_j = \det B_j\cdot\mathrm{Tr}\left(B_j^{-1}\frac{\partial}{\partial x}B_j\right).$$

Both inverting matrixes and calculation of the determinants can be done with the amount of operations required, proportional to N^3. However, the efficacy of the forces' calculations is still under consideration. Unfortunately, we don't know any fast way to compute permanents, which appear in the case of Bose–Einstein statistics.

We used time reversible molecular dynamics algorithm [22] with Nosé–Hoover chains [23] of two thermostats each in all calculations.

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4) By "efficient" we mean the MD with all characteristic frequencies of the same order, in other words, all MD variables moving on the similar time scales.

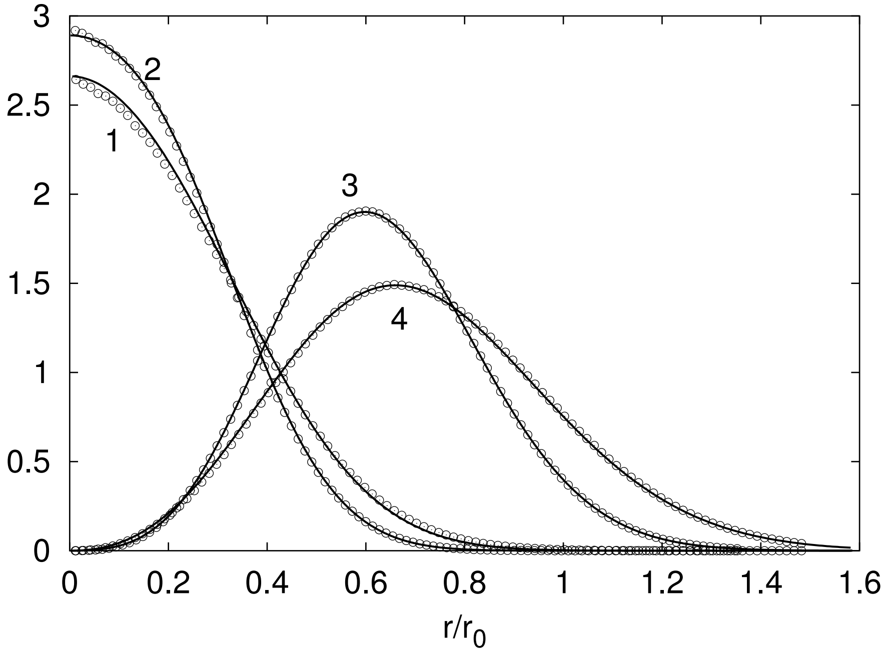

Fig. 1. Electron density and pair correlation function for the harmonic helium atom. Solid lines stay for the analytical solutions, circles – for the simulation results. 1, 2 – electron density for $n = 2, 3$; 3, 4 – pair correlation function for $n = 2, 3$, correspondingly.

4 Results and discussion

Staging BFPIMD algorithm for distinguishable particles was tested for systems considered in [11,12]. Since, the results of the tests were similar to those, described in details [11,12] we comment on some of them. In order to test the harmonic type potentials, we considered "harmonic Helium atom": two electrons, confined in the harmonic potential. This system does have analytical solutions for the discrete set of frequencies (see [12, 24] for details). The results are presented on Fig 1. One can see, that simulation results demonstrate almost perfect agreement with the analytical ones.

As for Coulomb systems, it seems instructive to present the results for Helium ion. In [12] we introduced the function f, which integral was equal to the error in potential energy, induced by deviations of the electronic density from the exact one:

$$f(r) \equiv \frac{e^2 \left[\rho_{\mathrm{ex}}(r) - \rho(r)\right]}{4\pi\epsilon_0 r}\,, \tag{37}$$

$\rho(r)$ and $\rho_{\mathrm{ex}}(r)$ are the simulated and exact RDFs, respectively. Functions $f(r)$ before and after correction are plotted in Fig. 2. Note, that the integral of $f(r)$ after correction is very small, since positive and negative contributions are nearly

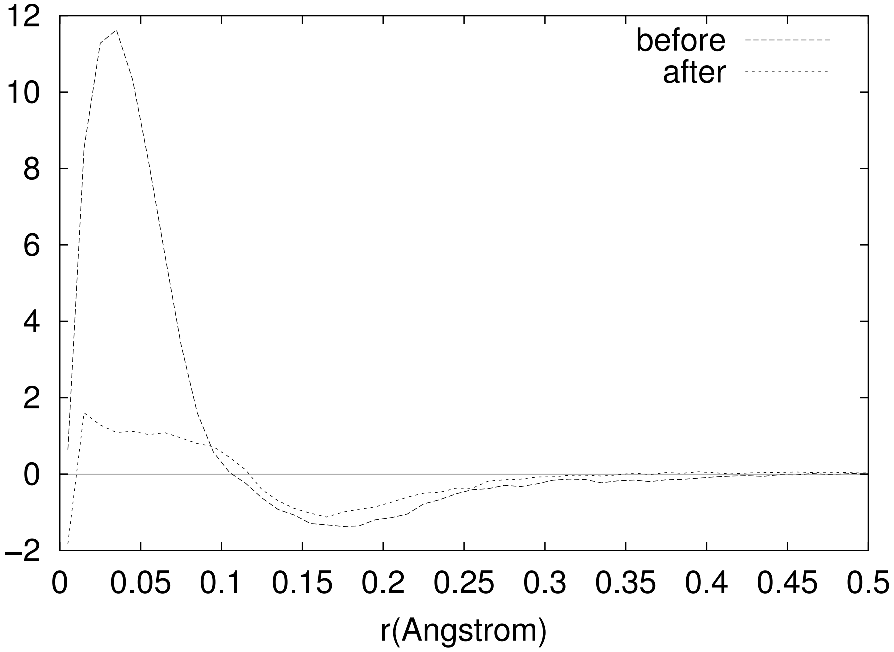

Fig. 2. Function $f(r)$ for Helium ion defined in (37) before and after correction potential was applied.

equal. Moreover, even the integral of the absolute value of $f(r)$ is not that big and is comparable by the order of magnitude with the accuracy of simulations.

The correction force derived from the correction potential (36) according to:

$$\mathbf{f}^{\mathrm{corr}}\left(r_{ij}\right) = -\frac{\partial V^{\mathrm{corr}}\left(r_{ij}\right)}{\partial r_{ij}} \sum_{l=1}^{L} \frac{\mathbf{x}_{ijl}}{x_{ijl}} \tag{38}$$

is presented in Fig. 3. Note, that it differs from the one, presented in [12] mainly by the height of the peak near zero. As it was pointed out in [12] this height strongly depends on the bins' size of the electronic density histogram. Here the bins' size was bigger than in [12], resulting in a lower peak.

The important feature of staging approach is, that, e.g., for Helium ion and Hydrogen atom, it allows us to increase the time step at least twice.

The simulations of systems of identical particles are under way and the results would be presented in the subsequent publication. We are considering BFPIMD for identical particles as a tool for accurate computation of the electronic structure, following the ideas of recent work [25], where a way for the simulation of excited states was demonstrated.

In conclusion, we would like to mention, that the solution of the problem of

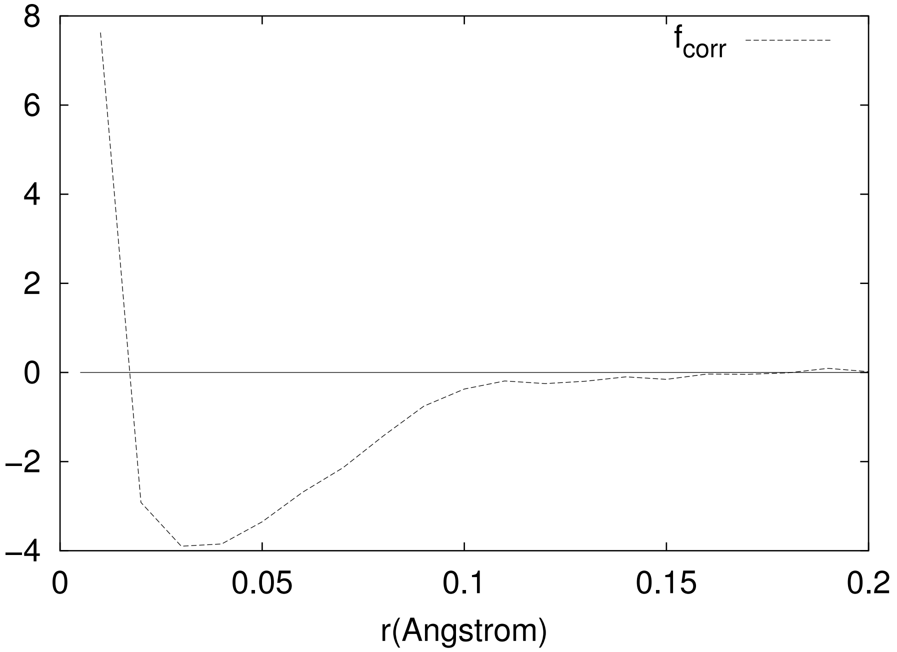

Fig. 3. Correction force defined in (38) for Helium ion.

Coulomb singularity in Monte Carlo methods can be provided by the, so-called, partial averaging [26, 27], (see, e.g. [28] for details)

5 Conclusion

We developed formalism for two variants of Bead–Fourier path integral molecular dynamics, both providing similar time scales for all dynamical variables. The first one, based on the staging transformation of beads coordinates, describes distinguishable particles. The other, derived from the antisymmetric propagator approach, deals with identical particles.

We have tested the first formalism on the simple systems with analytical solutions known, such as: harmonic Helium atom, Hydrogen atom, Helium ion and atom, Hydrogen molecule and molecular ion. The approach demonstrated more stable behaviour of the algorithm, which allowed bigger time steps, than the one, used before [11, 12].

We have shown, that the approach suggested earlier by Miura and Okazaki [18] within pure bead molecular dynamics leads to impossibility of the sign changes. A recipe overcoming the latter problem is suggested. Testing of the BFPIMD variant for identical particles is a subject for the ongoing research.

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