

Estimating quantum mechanical effects of atomic solids using quantum molecular dynamics with dissipation

Bing Gu

Atomic solids

I. INTRODUCTION

Quantum molecular dynamics with dissipation, relevant to many processes in chemistry, physics, and biology, is a long-standing theoretical challenge. Dissipation describes interaction of the system with the bath, representing the environmental degrees of freedom. With few exceptions, the numerically exact simulations of such quantum processes occurring in condensed phase, have been performed, using path integral Monte Carlo methods for models consisting of a low-dimensional system coupled to a bath of harmonic oscillators.^{2,3} Inclusion of friction directly into the Schrödinger equation may be viewed as a simple way to mimic the effect of energy transfer from the system to the environment while limiting quantum dynamics calculations to the system degrees of freedom. Such picture is simplistic, yet it might be useful for some processes. For example, the quantum transition state theory of dissipative tunneling reproduces measurement of the H/D motion on Pt(111) surface with few adjustable parameters.

The force of friction, often taken for processes in condensed phase as linear in velocity of a particle, is most straightforwardly incorporated into equations of motion of a classical particle, characterized by position x_t and momentum p_t ,

$$\frac{dp_t}{dt} = -\frac{dV(x)}{dx} - \gamma p_t|_{x=x_t}, \quad \frac{dx_t}{dt} = \frac{p_t}{m}. \quad (1)$$

The trajectory evolves under the influence of an external potential $V(\mathbf{x})$, which is a function of the Cartesian coordinate, \mathbf{x} , parameter γ denotes the friction coefficient.

II. FORMULATION

The friction term for the time-dependent Schrödinger equation (TDSE) can be incorporated into the de Broglie-Bohm formulation of TDSE. The friction term depends on the velocity of each quantum trajectory. The resulting TDSE is nonlinear; the time-dependent wavefunction conserves normalization, while the total energy of the wavefunction decreases with time to the zero-point

energy value. The new equations of motion with friction term for quantum trajectories in the Lagrangian frame of reference are as follows:

$$\frac{dp}{dt} = -\frac{\partial}{\partial x}(V + U) - \gamma p \quad (2)$$

$$\frac{dx}{dt} = -\frac{p}{m} \quad (3)$$

Integrating Eq. (14) with respect to x , the evolution of $S(x, t)$ with friction becomes

$$-\frac{\partial S}{\partial t} = \frac{p^2}{2m} + V + U + \gamma S + C(t). \quad (4)$$

The constant of integration $C(t)$ is defined in ??,

$$C(t) = -\langle S(x, t) \rangle. \quad (5)$$

Together with continuity equation unchanged by friction, the conventional TDSE with friction becomes

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \hat{H} \psi(x, t) + \gamma(S(x, t) - \langle S(x, t) \rangle) \psi(x, t). \quad (6)$$

A. Global linear approximation to nonclassical momentum

Quantum potential, U , is responsible for all quantum mechanical effects, such as zero-point energy and quantum-mechanical tunneling. The classical limit is defined as $U \rightarrow 0$. A simple approximation can be made to compute quantum potential “fast” and accurate. Details about the linearized quantum force (LQF) methodology is described in [?]. We briefly review this method here. The essential idea is to get approximated quantum potential from the global linear least-squares fitting of the nonclassical component of the momentum operator [?],

$$r_\alpha(\mathbf{x}, t) = \frac{\nabla_\alpha A(\mathbf{x}, t)}{A(\mathbf{x}, t)} \approx \tilde{r}_\alpha(\mathbf{x}, t) \quad (7)$$

at each time step in small basis $\mathbf{f}(\mathbf{x})$, which is analytically determined. We use greek letters α, β, \dots to label an arbitrary degree of freedom.

$$U \approx \sum_\alpha \frac{-\hbar^2}{2m} (\tilde{r}_\alpha \cdot \tilde{r}_\alpha + \nabla_\alpha \tilde{r}_\alpha). \quad (8)$$

The least-squares fitting [?] minimizes $\sum_\alpha \langle (r_\alpha - \tilde{r}_\alpha)^2 \rangle$, where \tilde{r}_α is represented in a linear basis $\mathbf{f}(\mathbf{x})$

For a multi-dimensional system, $\mathbf{f}(\mathbf{x})$ can be arranged as a vector $(1, x_1, x_2, \dots)$, so the approximate nonclassical momentum component is expressed as

$$\tilde{\mathbf{r}} = \mathbf{C}\mathbf{f}, \quad (9)$$

where \mathbf{C} is a matrix of coefficients, which solves the matrix equation

$$2\mathbf{S}\mathbf{C} + \mathbf{B} = 0. \quad (10)$$

The matrices are defined by the outer product of vectors

$$\mathbf{S} = \langle \mathbf{f} \otimes \mathbf{f} \rangle, \quad \mathbf{B} = \langle \nabla \otimes \mathbf{f} \rangle^T \quad (11)$$

The approximate quantum potential defined by Eqs. (8-11) is simply a quadratic function of \mathbf{x} yielding a linear quantum force (LQF) for every trajectory. This approximation rigorously conserves energy and is exact for Gaussian wavepackets, but does not presume that $\psi(\mathbf{x}, t)$ is necessarily a Gaussian wavefunction. This simple approximation gives basic QM effects, such as wavepacket bifurcation, moderate tunneling and zero-point energy. [?]]

While studying quantum dissipation, theoretically, the expectation value of energy will decay to the ground state, which means the quantum force, $\nabla U(\mathbf{x}, t)$, will cancel the classical force so that there is no net force for quantum trajectories. The challenge here is that for an anharmonic system, the linear quantum force does not have the corresponding high order term to balance classical force, which means the trajectories will never stop. With a small friction constant, the quantum trajectories will wiggle around equilibrium position and finally become localized.

To fix this problem, a modification is proposed to account for anharmonicity.

III. POTENTIAL ENERGY AND FORCE

A pre-calculated potential describing the interaction of two helium atoms $V(r^2)$ is used to compute the potential for the whole system. The position vector \vec{r}_{ij} between two helium atoms is defined as:

$$\vec{r}_{ij} = -d\vec{r}_i + \vec{d}_{ij} + d\vec{r}_j, \quad (12)$$

where $d\vec{r}_i$, $d\vec{r}_j$ are displacement vectors for atom i and j ,

$$d\vec{r}_i = \frac{dx_i}{|dr_i|}\vec{x} + \frac{dy_i}{|dr_i|}\vec{y} + \frac{dz_i}{|dr_i|}\vec{z}. \quad (13)$$

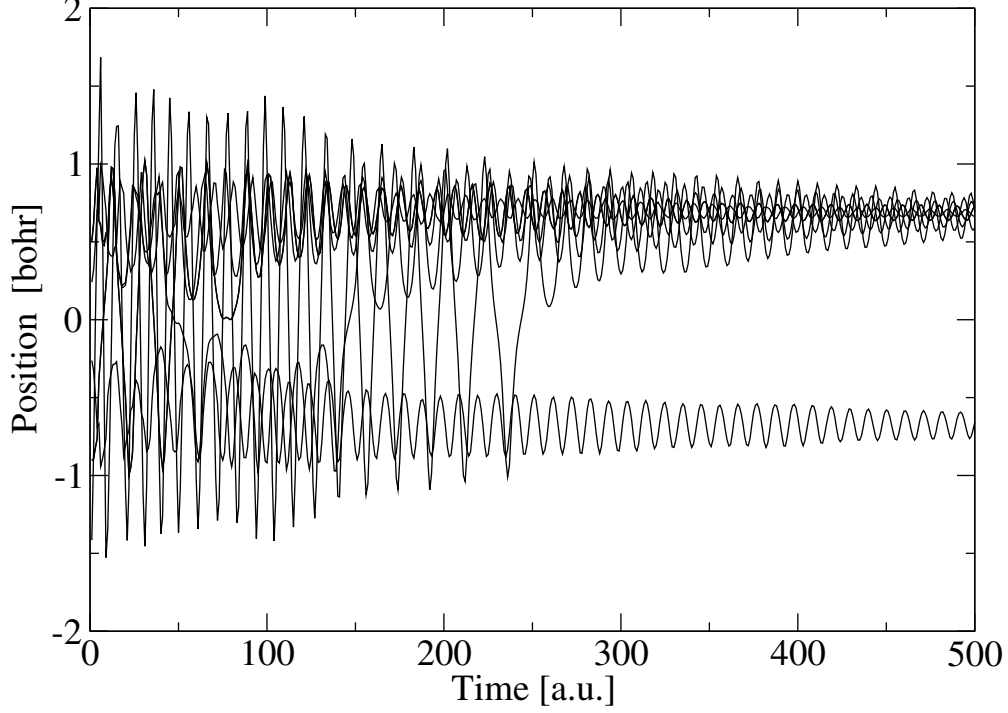


FIG. 1: Quantum trajectories for one-dimensional anharmonic potential, $V(x) = \frac{x^2}{2} + 0.1x^4$, LQF is applied, $\alpha_0 = 1$, $\gamma = 0.05$

The two-body potential is computed over a grid of the square of the distance between two atoms, the classical force over each DOF is computed as

$$\frac{\partial V}{\partial dx_i} = \frac{\partial V}{\partial r_{ij}^2} \frac{\partial r_{ij}^2}{\partial dx_i}, \quad (14)$$

$$r_{ij}^2 = (-dx_i + x_{ij} + dx_j)^2 + (-dy_i + y_{ij} + dy_j)^2 + (-dz_i + z_{ij} + dz_j)^2, \quad (15)$$

$$\frac{\partial r_{ij}^2}{\partial dx_i} = 2(-dx_i + x_{ij} + dx_j). \quad (16)$$

$$\frac{\partial V}{\partial dx_i} = 2(-dx_i + x_{ij} + dx_j) \frac{\partial V}{\partial r_{ij}^2} \quad (17)$$

IV. LONG-RANGE INTERACTIONS CORRECTION

Long-range interactions are calculated in the same way as for the short-range interactions. The long-range interaction for each atom is approximated by a polynomial $P_{N_b}(x, y, z)$ on the basis of,

$$\mathbf{b} = \{1, x, y, z, x^2, y^2, z^2, xy, yz, xz\}^T, \quad (18)$$

$$P_{N_b}(x, y, z) = \mathbf{b}^T \mathbf{c} \quad (19)$$

. We set up a three-dimensional grid of the displacements of atom on space and for each point (x_i, y_i, z_i) , we obtain the value of the long-range interaction $V_l(x_i, y_i, z_i)$ which is convergent to the number of atoms being used for the computation. Finally, we will get $N_p = N_x \times N_y \times N_z$ values and use these values to obtain the coefficients

$$\mathbf{c} = \{c_1, c_2, \dots, c_{N_b}\}^T \quad (20)$$

before the each basis term. N_b is the number of basis terms, which in this case is 10. The coefficients can be obtained by solving the matrix equation

$$\mathbf{M}\mathbf{c} = \mathbf{V}_l, \quad (21)$$

where \mathbf{M} is an $N_p \times N_b$ matrix, for each line, the elements are

$$\mathbf{M}(i, j = 1, \dots, N_b) = \{1, x_i, y_i, z_i, x_i^2, y_i^2, z_i^2, x_i y_i, y_i z_i, x_i z_i\}. \quad (22)$$

and \mathbf{V}_l is the vector of the interaction values at all points,

$$\mathbf{V}_l(i) = V_l(x_i, y_i, z_i). \quad (23)$$

Since it is an overdetermined system, the matrix equation is solved under Least-Squares algorithm.

V. EQUATIONS OF MOTION FOR (x, p, r)

Starting from continuity equation

$$\frac{\partial \rho(\mathbf{x}, t)}{\partial t} + \nabla \cdot \left(\rho(\mathbf{x}, t) \frac{\mathbf{p}}{m} \right) = 0 \quad (24)$$

substitute $\rho = A^2$ into the continuity equation, we will obtain

$$2A\partial_t A + \sum_{\alpha} (2A\nabla_{\alpha} A m_{\alpha}^{-1} p_{\alpha} + A^2 \nabla_{\alpha} p_{\alpha} m_{\alpha}^{-1}) = 0 \quad (25)$$

divide by $2A^2$,

$$\partial_t \log A = - \sum_{\alpha} \left(\nabla_{\alpha} \log A p_{\alpha} m_{\alpha}^{-1} + \frac{\nabla_{\alpha} p_{\alpha}}{2m_{\alpha}} \right) \quad (26)$$

use partial derivative operator ∇_{α} operate on both sides of the last equation and notice $r_{\alpha} = \nabla_{\alpha} \log A$, we will get

$$\dot{r}_{\alpha} = - \left(\sum_{\beta} \frac{\nabla_{\alpha} p_{\beta}}{m_{\beta}} r_{\beta} + \sum_{\beta} \frac{\nabla_{\alpha} \nabla_{\beta} p_{\beta}}{2m_{\beta}} \right) \quad (27)$$

Then in Lagrangian frame of reference, the exact equations of motion for (x, p, r) will be

$$\dot{x}_\alpha = \frac{p_\alpha}{m_\alpha} \quad (28)$$

$$\dot{p}_\alpha = -\nabla_\alpha (V(\mathbf{x}) + U(\mathbf{x}, t)) \quad (29)$$

$$\dot{r}_\alpha = -\left(\sum_\beta \frac{\nabla_\alpha p_\beta}{m_\beta} r_\beta + \sum_\beta \frac{\nabla_\alpha \nabla_\beta p_\beta}{2m_\beta} \right) \quad (30)$$

where

$$\tilde{U}(x, t) = \sum_\alpha (\tilde{r}(x, t)_\alpha^2 + \nabla_\alpha \tilde{r}) \quad (31)$$

\mathbf{x}, \mathbf{p} are position and momentum vectors with dimensionality of $3N$, N is the number of particles.

Instead of applying linear basis, cubic basis $(1, x, x^2, x^3)$ is used to approximate non-classical momentum r , as well as classical momentum p . By doing this, we kind of add some freedom to the formula of quantum force but constraint to the motion of trajectories. The new equations of motion with fitted terms in Lagrangian frame of reference, \tilde{p}, \tilde{r} will be

$$\dot{x}_\alpha = \frac{\tilde{p}_\alpha}{m_\alpha} \quad (32)$$

$$\dot{p}_\alpha = -\nabla_\alpha (V(\mathbf{x}) + \tilde{U}(\mathbf{x}, t) - \gamma p_\alpha) \quad (33)$$

$$\dot{r}_\alpha = -\left(\sum_\beta \frac{\nabla_\alpha \tilde{p}_\beta}{m_\beta} \tilde{r}_\beta + \sum_\beta \frac{\nabla_\alpha \nabla_\beta \tilde{p}_\beta}{2m_\beta} \right) \quad (34)$$

VI. MODIFICATION OF APPROXIMATION FOR QUANTUM FORCE

Fitting with larger basis can cause a dramatic increase in computational cost. The size of the basis $x_i x_j$ will be $1 + 3N_{atom} + \frac{3N_{atom}(3N_{atom}-1)}{2}$ if we want to include cubic basis for each DoF and all the linear coupling terms. To save computational efforts, the least-square fitting procedure is decomposed into two steps after we realize for each DoF, there are some terms that are of little contribution to the fitting, which means the coefficients before these terms remains a small number close to 0.

- The first step is to apply a linear basis $(1, x, y, \dots)$ to do least-square fitting of (\mathbf{p}, \mathbf{r}) to minimize $\sum_\alpha \|(r_\alpha(x, t) - \tilde{r})_\alpha(x, t)\|_2$ and $\sum_\alpha \|(p_\alpha(x, t) - \tilde{p})_\alpha(x, t)\|_2$, the fitted terms can be expressed by

- The second step is to fit the remainder with a cubic basis for each degree of freedom, $(1, x_\alpha, x_\alpha^2, x_\alpha^3)$. The other terms in the basis include linear terms of other DoFs, $(x_\beta, \beta = 1..N_c)$, and linear coupling terms $(x_\alpha x_\beta)$. N_c is the number of the coupling DoFs that will be included.

A. Two-dimensional model

We design a two-dimensional potential, which represent two linearly coupled anharmonic vibrational mode.

$$V(x, y) = \frac{1}{2}(x^2 + x^4) + \frac{1}{2}(y^2 + y^4) + \epsilon xy \quad (35)$$

ϵ is a parameter that can be used to control the coupling between two degrees of freedom.

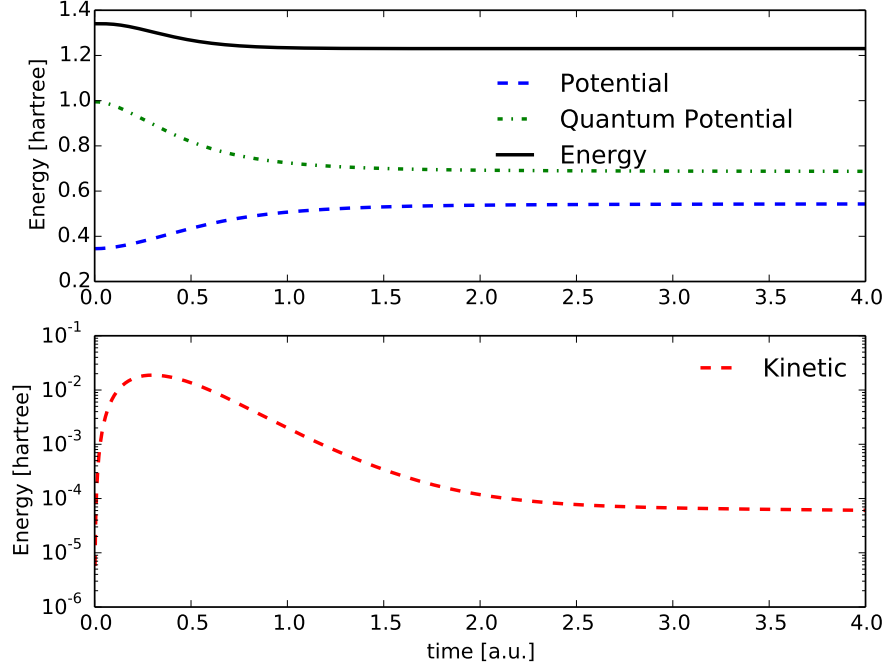


FIG. 2: Energy components with $\gamma = 6$

VII. NUMERICAL IMPLEMENTATION

The implemented code is paralleled by *Message Passing Interface* (MPI), Fig [?] shows the scaling of the computational cost for different number of processors.

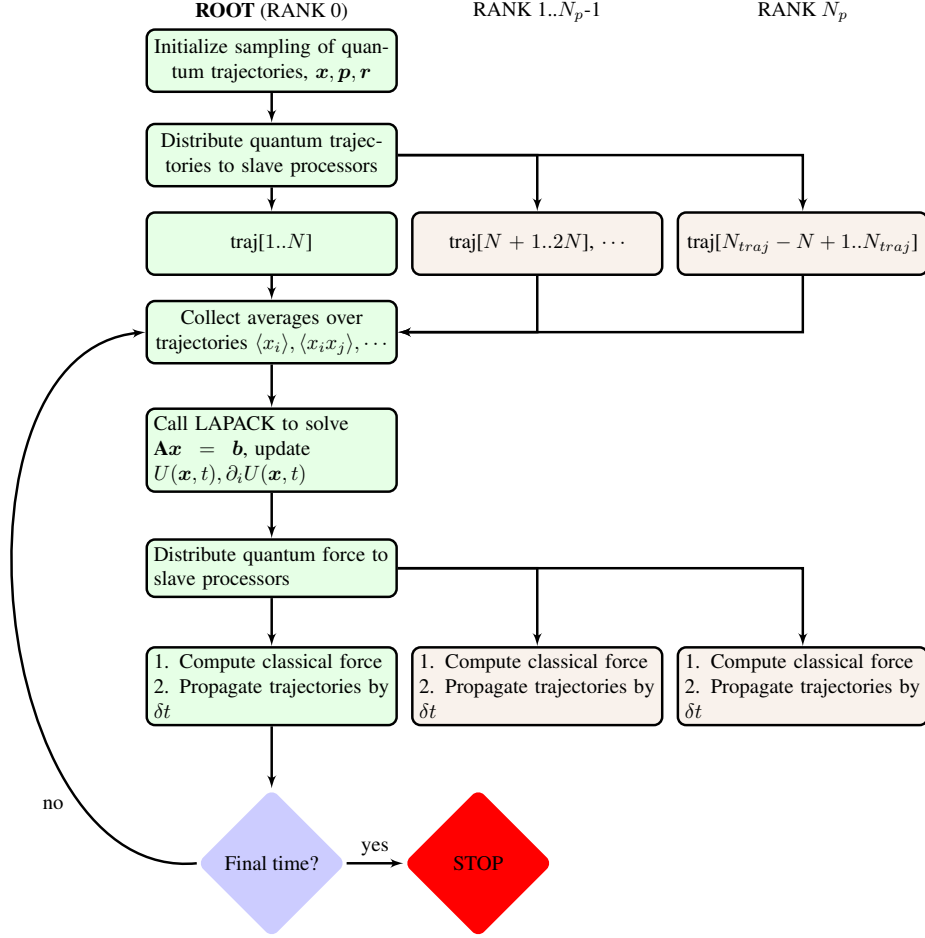


FIG. 3: Flowchart of parallelization, quantum trajectories are distributed among processors such that the computing of classical force is paralleled

VIII. RESULTS

IX. DYNAMIC PROPERTIES

- using electronic structure (for example, DFT, DFTB may not work) theory to get potential energy, to see if many-body interactions are important
- tbd

X. RADIAL DISTRIBUTION FUNCTION

To have a theoretical measure of the inter-atom distance distribution at ground state for atomic solids accounting for quantum effects, it seems appropriate to define a radial distribution function

$$g(r) = \frac{1}{4\pi\rho N r^2} \frac{\langle \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) | \sum_{i,j \neq i}^N \delta(r - |\mathbf{r}_{ij}|) | \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) \rangle}{\langle \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) | \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) \rangle} \quad (36)$$

$$= \frac{1}{4\pi\rho N r^2} \sum_{i,j < i}^N \frac{\langle \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) | \delta(r - |\mathbf{r}_{ij}|) | \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) \rangle}{\langle \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) | \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) \rangle} \quad (37)$$

for wavefunction with exchange symmetry, i.e. particles are indistinguishable

$$g(r) = \frac{N}{\rho} \frac{\langle \delta(r - |\mathbf{r}_{12}|) \rangle}{4\pi r^2} \quad (38)$$

$$= \frac{N}{4\pi\rho r^2} \int d\mathbf{r}_1 d\mathbf{r}_2 \delta(r - |\mathbf{r}_{12}|) \rho(\mathbf{r}_1, \mathbf{r}_2) \quad (39)$$

where $\rho(\mathbf{r}_1, \mathbf{r}_2)$ is the joint probability.

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \int d\mathbf{r}_3 \dots d\mathbf{r}_N \rho(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (40)$$

We would like to see if the form would give right solution at two limiting cases.

The first limiting case is a perfect solid, every atom has a fixed position in space, \mathbf{R}_i .

$$g(r) = \sum_{i,j \neq i} \delta(r - |\mathbf{R}_{ij}|) \quad (41)$$

the pair distribution function will be peaks at all the possible distance, which is what we expect to see.

Another case is non-interacting limit and the ground state density can be approximated with a uniform distribution $\rho(\mathbf{r}_1, \mathbf{r}_2) = (\frac{1}{V})^2$, the system should behave like ideal gas. The PDF will be

$$g(r) = \frac{N}{\rho} \left(\frac{1}{V}\right)^2 \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\delta(r - |\mathbf{r}_{12}|)}{4\pi r^2} \quad (42)$$

$$= \frac{N}{\rho V} \quad (43)$$

$$= 1 \text{ (ideal gas)} \quad (44)$$

$$(45)$$

System in reality should be in the intermediate of this two limiting cases, for small vibrations in the equilibrium position ($|\delta\mathbf{r}| \ll |\mathbf{r}|$), a spreading of the infinity peak is likely to show up. For numerical difficulty, we would use a Gaussian function to replace the δ function, or draw a histogram for different intervals, by counting trajectories with r_{12} fitting that range.

$$\delta(x) = \lim_{\alpha \rightarrow \infty} \sqrt{\frac{2\alpha}{\pi}} e^{-\alpha x^2} \quad (46)$$

try new density $\rho = 0.005231$ *a.u.* to compute pair distribution function. change the long-range potential fitting to fit the density.