

Molecular dynamics investigations on a quantum system in a thermostat

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Abstract

The model quantum system of fermions in a one dimensional harmonic oscillator potential is investigated by a molecular dynamics method at constant temperature. Although in quantum mechanics the equipartition theorem cannot be used like in the Nosé–Hoover–thermostat it is possible to couple an additional degree of freedom to the system which acts as a thermometer and drives the system towards the desired temperature via complex time steps.

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1 Introduction and summary

Statistical properties of finite systems are of great interest. The aim is to describe the behaviour of systems like atomic clusters or atomic nuclei at finite temperatures and to investigate properties like the specific heat or phase transitions. These statistical properties are given by the partition function which for classical systems in the canonical ensemble reads

$$Z = \int \prod_{i=1}^N d^3x_i d^3p_i \exp \left\{ -\frac{1}{T} H \right\} , \quad (1)$$

where H denotes the Hamilton function, and for quantum systems

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$$Z = \text{tr} \left(\exp \left\{ -\frac{1}{T} \tilde{H} \right\} \right) , \quad (2)$$

where \tilde{H} is the Hamilton operator (Throughout the article operators are underlined by a tilde and $\hbar = c = k_B = 1$). For realistic systems like atomic clusters or nuclei where the Hamilton function or operator contains a (two-body) interaction it is hard or impossible to evaluate the partition function especially for the quantum description.

Equations of motion for the investigated system are often much easier; either they are exactly known and can be integrated at least numerically as it is the case with the classical Hamilton's equation or they can be approximated with standard methods like TDHF or quantum molecular dynamics methods as it is the case on the quantum side. The idea then is to extract the desired thermodynamic quantities from the time evolution of the system. If the system is ergodic, ensemble averages can be replaced by time averages.

During the last decade a huge progress has been made on the classical side of the problem (see for instance [1–4]). To put it into a few words, the basic idea is to exploit the equipartition theorem and use for instance the kinetic energy as a measure of the current temperature. The system is cooled or heated via pseudo-friction coefficients if the present temperature is too high or too low, respectively. The equations of motion are changed in the following way

$$\frac{d}{dt} \vec{x}_k = \frac{\partial H}{\partial \vec{p}_k} , \quad \frac{d}{dt} \vec{p}_k = -\frac{\partial H}{\partial \vec{x}_k} - \vec{p}_k \zeta , \quad k = 1, \dots, N \quad (3)$$

$$\frac{d}{dt} \zeta \propto \left(E_{kin}(N) - \frac{3N}{2} T \right) . \quad (4)$$

The last line, equation (4), shows nicely how the system is driven towards the temperature T via the coupling to the pseudo-friction coefficient ζ . It was shown that the resulting distributions are those of the canonical ensemble (see e.g. the report [4]). In addition ergodicity can be improved by using more pseudo-friction coefficients and different couplings to the original system [3].

In quantum mechanics the problem is much more involved. No useful a priori relation between expectation values of observables and temperature like in the equipartition theorem can be exploited. Attempts have been made to derive a thermal non-linear Schrödinger equation which results in an ergodic wave function [5], but this method needs the relation between mean energy and temperature as an input, which is not known for most systems and therefore itself a matter of investigation. A nontrivial quantum extension of the Nosé-method has been derived in ref. [6] which will be the subject of a forthcoming paper.

The idea of this article is to couple an additional degree of freedom to the original system, which serves as a thermometer. This idea was already successfully applied in nuclear physics in order to determine the caloric curve of nuclei and to investigate the nuclear liquid–gas phase transition [7]. The new aspect in this article is to drive the system via complex time steps towards the desired temperature.

The total system is described by a time–dependent state $|Q(t)\rangle$ consisting of the original system $|system(t)\rangle$ and the thermometer $|thermometer(t)\rangle$

$$|Q(t)\rangle = |system(t)\rangle \otimes |thermometer(t)\rangle . \quad (5)$$

According to the difference between the temperature T_{th} measured by the thermometer and the desired temperature T the total system is evolved by a complex time step $d\tau$.

$$d\tau = dt - id\beta , \quad d\beta \propto (T_{th} - T)/T_{th} , \quad |Q(t)\rangle \rightarrow |Q(t + d\tau)\rangle . \quad (6)$$

As can be inferred from (6) $d\beta > 0$ results in cooling and $d\beta < 0$ in heating of the system.

In the present article the proposed method will be examined with the simple but basic quantum system of N fermions in a common one–dimensional harmonic oscillator potential. The advantage of this system is that all relations of the canonical ensemble are either known analytically or can easily be computed numerically.

In order to equilibrate the system in an ergodic sense a short–range two–body repulsion among the particles is used which does not destroy the implied picture of an ideal quantum gas [8].

The results of time averaging are compared to the canonical ensemble in terms of occupation numbers which in thermodynamic equilibrium characterize the ideal Fermi gas enclosed in a common harmonic oscillator potential completely. It is demonstrated that the system is indeed ergodic, i.e., the time averaged occupations numbers coincide with those obtained in the canonical ensemble.

2 Method and setup

2.1 Model state and equations of motion

In many cases the time-dependent Schrödinger equation cannot be solved. The following time-dependent quantum variational principle (TDVP) [9]

$$\delta \int_{t_1}^{t_2} dt \langle Q(t) | i \frac{d}{dt} - \tilde{H} | Q(t) \rangle = 0 \quad (7)$$

allows to derive approximations to the time-dependent Schrödinger equation on the level of accuracy one needs or can afford. For the variation of the trial state $\langle Q(t) |$ in the complete Hilbert space the TDVP leads to the Schrödinger equation. For trial states given in terms of parameters $Q(t) = \{q_\nu(t) | \nu = 1, 2, \dots\}$ the TDVP leads to Euler-Lagrange equations which in their most general form can be written as

$$\sum_\nu \mathcal{A}_{\mu\nu}(Q) \dot{q}_\nu = - \frac{\partial}{\partial q_\mu} \langle Q(t) | \tilde{H} | Q(t) \rangle \quad (8)$$

$$\mathcal{A}_{\mu\nu}(Q) = \frac{\partial^2 \mathcal{L}_0}{\partial \dot{q}_\mu \partial q_\nu} - \frac{\partial^2 \mathcal{L}_0}{\partial \dot{q}_\nu \partial q_\mu},$$

where $\mathcal{L}_0 = \langle Q(t) | i \frac{d}{dt} | Q(t) \rangle$ and $\mathcal{A}_{\mu\nu}(Q)$ is a skew symmetric matrix. The time evolution of the parameters then defines the time dependence of the many-body state $|Q(t)\rangle$. If for instance $|Q(t)\rangle$ is chosen as a Slater determinant of arbitrary single-particle states one ends up with time-dependent Hartree-Fock [10].

In this investigation the molecular dynamics approach of Fermionic Molecular Dynamics (FMD) [11] is taken where $|Q(t)\rangle$ is a Slater determinant of single-particle Gaussian wave-packets $|q_l(t)\rangle$

$$\langle \vec{x} | q_l(t) \rangle = \exp \left\{ - \frac{(\vec{x} - \vec{b}_l(t))^2}{2 a_l(t)} \right\} \otimes |\uparrow\rangle, \quad \vec{b}_l = \vec{r}_l + i a_l \vec{p}_l. \quad (9)$$

Each single-particle state is parametrized in terms of the time-dependent mean position $\vec{r}_l(t)$, mean momentum $\vec{p}_l(t)$ and the complex width $a_l(t)$. In the notation of (9) the vector \vec{b}_l is composed of \vec{r}_l , \vec{p}_l and a_l . The time dependence of the spin degrees of freedom is not considered, instead it is assumed that all particles are identical fermions with the same spin component $|\uparrow\rangle$. In order to perform complex time steps the complex parameters \vec{b}_l and a_l are used.

The approach of FMD has several advantages, in connection with this investigation it is important to realize that for the one-body Hamiltonian

$$\underline{H} = \sum_l \underline{h}(l), \quad \underline{h}(l) = \frac{\vec{k}^2(l)}{2m} + \frac{1}{2} m\omega^2 \underline{x}^2(l) \quad (10)$$

of the harmonic oscillator the solution of the approximate equations of motion (8) coincides with the exact solution of the Schrödinger equation. For fermions in a harmonic oscillator these equations of motion can be given explicitly [8]

$$\frac{d}{dt} \vec{b}_l = -im\omega^2 a_l \vec{b}_l, \quad \frac{d}{dt} a_l = -im\omega^2 a_l^2 + \frac{i}{m}. \quad (11)$$

Replacing the complex \vec{b}_l in eq. (11) yields

$$\frac{d}{dt} \vec{r}_l = \frac{\vec{p}_l}{m} \quad \text{and} \quad \frac{d}{dt} \vec{p}_l = -m\omega^2 \vec{r}_l. \quad (12)$$

The parameters \vec{r}_l and \vec{p}_l follow the classical trajectories. Nevertheless, the parametrized trial state is the exact solution of the Schrödinger equation. It is also worth to note that for this example the equations of motion of the parameters are the same, regardless whether the many-body state is antisymmetrized, symmetrized or simply a product state.

2.2 Time averaging

The time averaging of an operator \underline{B} is done by taking the trace with the statistical operator $\underline{R}_{\text{erg}}$ [8]

$$\underline{R}_{\text{erg}} := \lim_{t_2 \rightarrow \infty} \frac{1}{(t_2 - t_1)} \int_{t_1}^{t_2} dt |Q(t)\rangle \langle Q(t)| \quad (13)$$

which yields

$$\overline{\langle \underline{B} \rangle} := \text{Tr}(\underline{R}_{\text{erg}} \underline{B}) = \lim_{t_2 \rightarrow \infty} \frac{1}{(t_2 - t_1)} \int_{t_1}^{t_2} dt \langle Q(t) | \underline{B} | Q(t) \rangle. \quad (14)$$

In general the statistical operator $\underline{R}_{\text{erg}}$ is a functional of the initial state $|Q(t_1)\rangle$, the Hamilton operator \underline{H} and the equations of motion. If the ergodic assumption is fulfilled, the statistical operator should only depend on $\langle \underline{H} \rangle$.

2.3 Thermometer and coupling

In order to determine the temperature of the system it is coupled to a thermometer. A thermometer is a device for which thermodynamic relations, like those of kinetic energy and temperature in the classical case, are known. Here the thermometer is realized in terms of distinguishable particles in another harmonic oscillator potential.

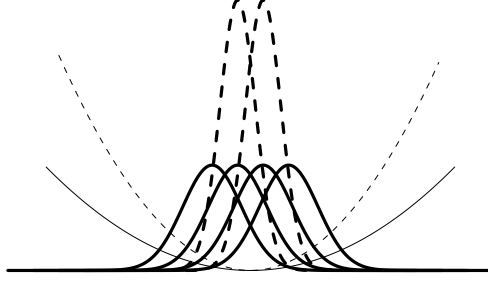


Fig. 1. Arrangement of fermion wave-packets in their oscillator potential (solid lines) and thermometer wave-packets in their oscillator (dashed lines).

Figure 1 sketches the setup. The fermion system consists of four Gaussian wave-packets (thick solid line) enclosed in their harmonic oscillator potential (thin solid line). The two thermometer wave-packets (thick dashed lines) reside in the other harmonic oscillator (thin dashed line). The complete system is represented by the state $|Q(t)\rangle$

$$\begin{aligned}
 |Q(t)\rangle &= |Q_f(t)\rangle \otimes |Q_{th}(t)\rangle \\
 |Q_f(t)\rangle &= \underline{A}(|q_{f1}(t)\rangle \otimes |q_{f2}(t)\rangle \otimes |q_{f3}(t)\rangle \otimes |q_{f4}(t)\rangle) \\
 |Q_{th}(t)\rangle &= |q_{th1}(t)\rangle \otimes |q_{th2}(t)\rangle
 \end{aligned} \tag{15}$$

where $|Q_f(t)\rangle$ describes the fermions (\underline{A} being the antisymmetrization operator) and $|Q_{th}(t)\rangle$, which is a product state, the thermometer wave-packets. The time evolution according to (8) is driven by the Hamilton operator

$$\begin{aligned}
 \underline{H} &= \underline{H}_f + \underline{H}_{th} + \underline{V}_{f,f} + \underline{V}_{f,th} \\
 \underline{H}_f &= \sum_{i=1}^{N_f} \left(\frac{\tilde{k}_i^2}{2m_f} + \frac{1}{2} m_f \omega_f^2 x_i^2 \right), \quad \underline{H}_{th} = \sum_{i=1}^{N_{th}} \left(\frac{\tilde{k}_i^2}{2m_{th}} + \frac{1}{2} m_{th} \omega_{th}^2 x_i^2 \right),
 \end{aligned} \tag{16}$$

where \underline{H}_f is the Hamilton operator of the fermion subsystem, \underline{H}_{th} the Hamilton operator of the thermometer subsystem,

$$V_{f,f} = \sum_{i < j} V_0 \exp \left\{ -\frac{(\underline{x}_i - \underline{x}_j)^2}{r_0^2} \right\} \quad (17)$$

$$\omega_f = 8 \text{ MeV} , \quad r_0 = \frac{0.01}{\sqrt{m_f \omega_f}} , \quad V_0 = (10^4 \dots 10^5) \omega_f ,$$

$V_{f,f}$ the short-range repulsion between all fermions needed to equilibrate the fermion subsystem and $V_{f,th}$ the momentum dependent short-range repulsion between fermions and thermometer wave packets, which is given in terms of its matrix elements in the appendix.

There are several conditions that need to meet in order to let the method work. The original system better has to be ergodic by itself and the coupling of the thermometer must lead to thermal equilibrium between the system and the thermometer. These conditions depend on the interaction which is needed to equilibrate the system. Some experience [8,7] and physical reasoning show that such interactions should be short ranged, repulsive and possibly momentum dependent. In addition the time evolution has to run over many typical cycles of the system so that enough collisions happen. I also found that the thermometer works best if $\omega_{th} > \omega_f$ so that the thermometer has a smaller heat capacity and that the mass $m_{th} < m_f$ so that the thermometer wave packets cross the region of the fermions. I chose $\omega_{th} = \pi \omega_f$ and $m_{th} = m_f / \pi^2$.

If the system is ergodic the total energy of the thermometer subsystem determines the temperature T_{th}

$$T_{th} = \omega_{th} \left[\ln \left(\frac{E_{th} + N_{th} \frac{\omega_{th}}{2}}{E_{th} - N_{th} \frac{\omega_{th}}{2}} \right) \right]^{-1} . \quad (18)$$

3 Results

3.1 Canonical ensemble of fermions in a harmonic oscillator

Since all results of the time averaging are compared to the canonical ensemble, the canonical ensemble is shortly explained for N fermions in a common one-dimensional harmonic oscillator potential \underline{H}_f . The statistical operator is given by

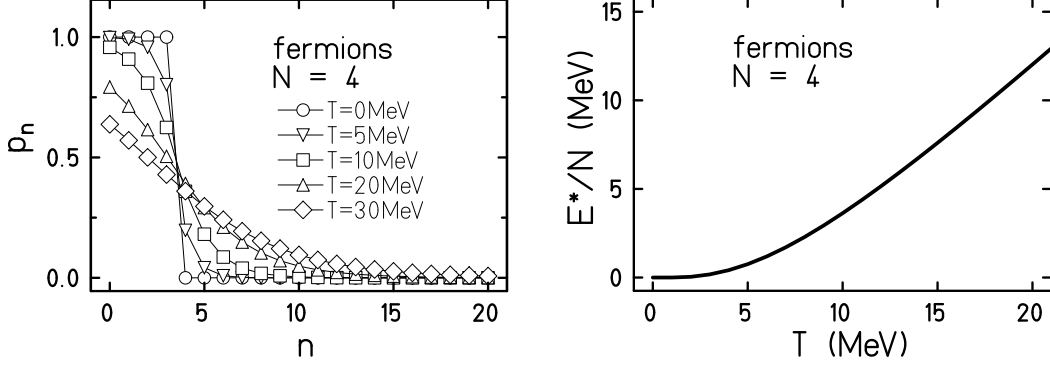


Fig. 2. Canonical ensemble for four fermions: Occupation numbers p_n of the oscillator eigenstates for five temperatures (l.h.s.) and excitation energy as a function of temperature (r.h.s.).

$$\tilde{R}(T) = \frac{1}{Z(T)} \exp \left\{ -\frac{\tilde{H}_f}{T} \right\} \quad (19)$$

$$\tilde{H}_f = \sum_{l=1}^N \tilde{h}(l), \quad \tilde{h}(l) = \omega_f \sum_{n=0}^{\infty} \left(n + \frac{1}{2} \right) \tilde{c}_n^+ \tilde{c}_n,$$

then the statistical mean of an operator \tilde{B} is calculated as

$$\langle \langle \tilde{B} \rangle \rangle_T := \text{Tr} (\tilde{R}(T) \tilde{B}) \quad (20)$$

In eq. (20) the subscript T indicates that the average in the canonical ensemble is taken at a constant temperature T .

The most prominent physical quantities which will be investigated in the following are the mean energy, which can be represented in closed form as

$$\langle \langle \tilde{H}_f \rangle \rangle_T = E_0(N) + \sum_{k=1}^N k \frac{\omega_f}{2} \left[\coth \left(k \frac{\omega_f}{2T} \right) - 1 \right] \quad (21)$$

$$E_0(N) = N^2 \frac{\omega_f}{2}$$

and the mean occupation probabilities p_n

$$p_n = \langle \langle \tilde{c}_n^+ \tilde{c}_n \rangle \rangle_T, \quad (22)$$

where \tilde{c}_n^+ denotes the creation operator of a fermion in the single-particle energy-eigenstate $|n\rangle$. The occupation probabilities are displayed in fig. 2 on the l.h.s. for various temperatures, the r.h.s. shows the dependence of the mean excitation energy on the temperature.

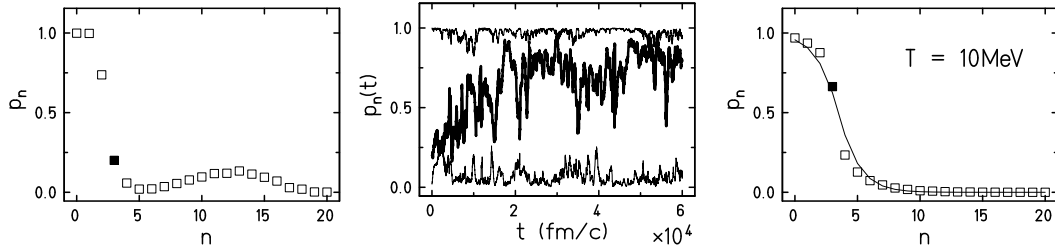


Fig. 3. Occupation probabilities p_n ; l.h.s.: distribution at $t = 0$; middle: time evolution $p_n(t)$ for $n = 0$ — top line, $n = 3$ — middle, $n = 6$ — bottom line; r.h.s.: time averaged distribution (symbols), the line shows the canonical result.

3.2 Time evolution in the thermostat

The deterministic time evolution of the system is followed over about 400 cycles ($\equiv 60000$ fm/c) of the fermion system. Initially the four-fermion system is far from equilibrium which can be inferred from fig. 3 (l.h.s.) where the occupation probabilities of an initial state $|Q_f(t=0)\rangle$ are displayed.

Due to the interaction between all wave packets and due to the heating or cooling according to the present temperature the occupation numbers are reshuffled with time. This is seen in fig. 3 (middle) where the time evolution of the momentary occupation numbers $p_n(t)$ is presented for $n = 0$, $n = 3$ and $n = 6$. The picture reminds of deterministic chaos. The result of time averaging is shown on the r.h.s. of fig. 3 (symbols) where the dependence obtained in the canonical ensemble is given by the solid line (see also fig. 2). How the system evolves from non-equilibrium towards equilibrium can be visualized nicely by the occupation number of state 3 which in all three figures is given in bold.

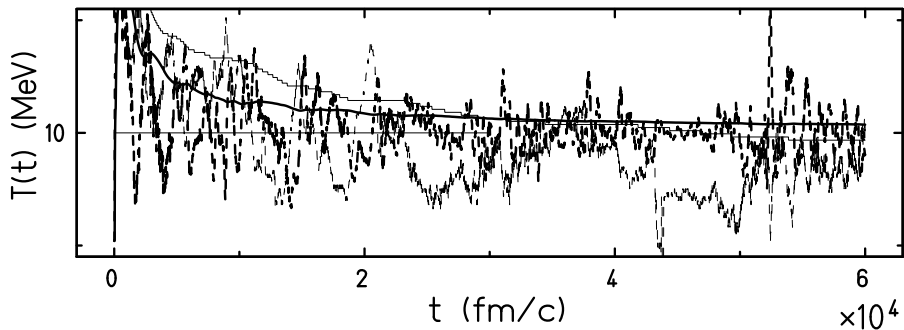


Fig. 4. Time evolution of actual temperatures (dashed lines) and time averaged temperatures (solid lines) for the thermometer system (thick lines) and for the fermion system (thin lines).

Since the relation between temperature and mean energy is known for the fermion system (see eq. 21), it can be checked how well the fermion temperature is reflected by the thermometer. Figure 4 shows four temperatures,

two for the thermometer (thick lines) and two for the fermion system (thin lines). The solid lines are related to the time averaged energies of the fermion and thermometer subsystems, respectively, where the averaging is performed from the beginning until the current time. The dashed lines show the momentary temperatures. One sees that the fermion system is quite excited initially whereas the thermometer starts being cold. One also realizes that the momentary temperatures fluctuate strongly, which is not astonishing since both subsystems are very small. Taking $1/\sqrt{N}$ as a rough estimate for relative fluctuations it becomes clear that for instance in the fermion subsystem ($N = 4$) fluctuations of 50% of the mean value are quite normal.

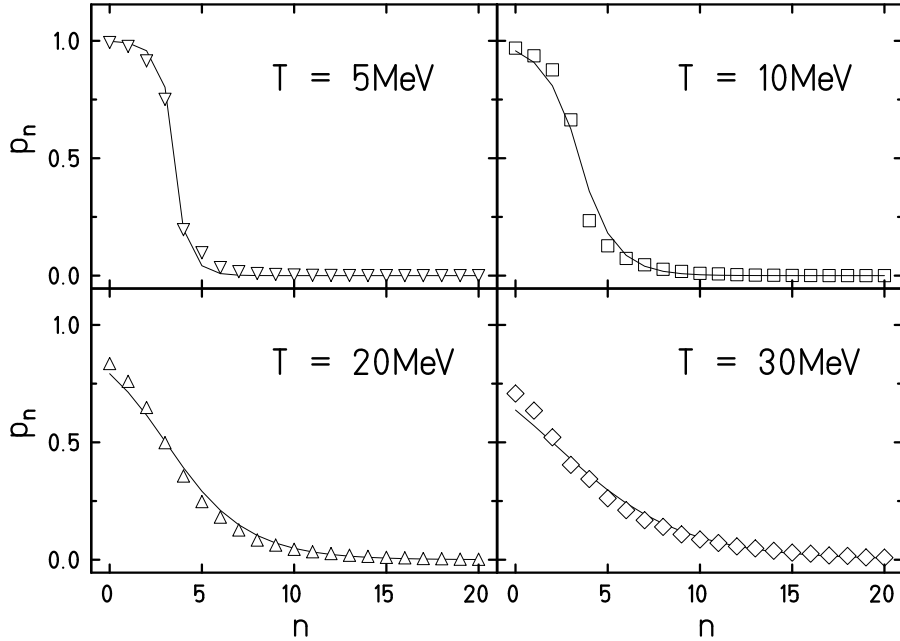


Fig. 5. Time averaged occupation numbers (symbols) compared with those of the canonical ensemble (solid lines).

The simulation explained in detail for $T = 10$ MeV is repeated for other temperatures. The resulting occupation probabilities are displayed in fig. 5. It is impressive that the time averaged occupation numbers match those of the canonical ensemble for a wide range of temperatures almost exactly,

$$\overline{\langle \xi_n^+ \xi_n \rangle} \approx \langle \langle \xi_n^+ \xi_n \rangle \rangle \Big|_T \quad \forall n, \quad (23)$$

meaning that the system is ergodic, i.e., that time averages approach ensemble averages of the canonical ensemble.

Nevertheless, the proposed method has also limitations. The necessary interaction of all constituents prevents accurate investigations close to the ground state, because the system is always excited due to the interaction. For a quantum system close to the ground state this leads already to a large temperature

deviation (see fig. 3). Methods to circumvent this problems are under investigation.

A Interaction of fermions and thermometer wave packets

The interaction between fermions (index k) and thermometer wave packets (index l) is modeled via the following expression

$$\langle Q | \tilde{V}_{f,th} | Q \rangle = \sum_{k,l} \frac{V_0}{R_{kl}} (p_k - p_l)^2 \exp \left\{ -\frac{(r_k - r_l)^2}{R_{kl}^2} \right\}$$

$$R_{kl}^2 = r_0^2 + 0.2 \left(\frac{|a_k|^2}{a_{kR}} + \frac{|a_l|^2}{a_{lR}} \right), \quad r_0 = \frac{0.01}{\sqrt{m_f \omega_f}}, \quad V_0 = (10^{-1} \text{ fm}^3 \dots 1 \text{ fm}^3) \omega_f .$$

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