THE CLASSICAL LIMIT OF QUANTUM OBSERVABLES IN THE
CONSERVATION LAWS OF FLUID DYNAMICS

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Abstract. In the classical work by Irving and Zwanzig [Irving J.H. and Zwanzig R.W., J. Chem. Phys. 19 (1951), 1173-1180] it has been shown that quantum observables for macroscopic density, momentum and energy satisfy the conservation laws of fluid dynamics. This work derives the corresponding classical molecular dynamics limit by extending Irving and Zwanzig’s result to matrix-valued potentials for a general quantum particle system. The matrix formulation provides the semi-classical limit of the quantum observables in the conservation laws, also in the case where the temperature is large compared to the electron eigenvalue gaps. The classical limit of the quantum observables in the conservation laws is useful in order to determine the constitutive relations for the stress tensor and the heat flux by molecular dynamics simulations. The main new steps to obtain the molecular dynamics limit is to: (i) approximate the dynamics of quantum observables accurately by classical dynamics, by diagonalizing the Hamiltonian using a non-linear eigenvalue problem, (ii) define the local energy density by partitioning a general potential, applying perturbation analysis of the electron eigenvalue problem, (iii) determine the molecular dynamics stress tensor and heat flux in the case of several excited electron states, and (iv) construct the initial particle phase-space density as a local grand canonical quantum ensemble determined by the initial conservation variables.

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1. The purpose of the work and the results

The macroscopic conservation laws for mass, momentum and energy form the basis of continuum fluid mechanics. These conservation laws are formulated in terms of the stress tensor and the heat flux. In order to form a closed system, constitutive relations for the stress tensor and the heat flux are used. Such constitutive relations can be determined approximately from measurements or from molecular dynamics simulations. In both cases one seeks approximations of the stress tensor and the heat flux as functions of the density, momentum and energy and their...
derivatives. The molecular dynamics formulation requires derivation of the stress tensor and the heat flux as functions of the particle dynamics. The derivation of such functional relations is the focus of this work.

The stress tensor and the heat flux were first derived by Irving and Kirkwood, \cite{7}, from molecular dynamics systems based on interaction with scalar pair potentials and has later been modified by Noll, \cite{15}, and Hardy, \cite{6}. These formulations have been used frequently to numerically determine the constitutive relations, cf. \cite{5}. For instance, the work \cite{18} includes comparisons of different methods to numerically determine the stress tensor in molecular dynamics simulations.

Already in 1951 Irving and Zwanzig, \cite{8}, showed that quantum observables for the density, momentum and energy satisfy the conservation laws and derived observables for the stress tensor and the heat flux. Since it is only at the quantum level the particle interaction is determined from fundamental principles their result provides a solid foundation for the basic conservation laws in continuum mechanics. This property that the observables for the density, momentum and energy satisfy the conservation laws does not mean that a closed system of conservation laws is derived, since the derived stress tensor and the heat flux are not determined as constitutive functions of the macroscopic conservation variables. To form a closed system would include the additional step to determine constitutive functions of the conservation variables that approximate the data from molecular dynamics or measurements, which is not studied here.

Irving and Zwanzig used a quantum model with the Hamiltonian given by a sum of kinetic energy and scalar pair potential energy including all particles, i.e. both the nuclei and the electrons. The aim of this work is to extend the derivation by Irving and Zwanzig to a setting with a matrix-valued Hamiltonian consisting of a sum of the kinetic energy of the nuclei (times the identity matrix) and a matrix representing the electron kinetic energy, the electron-electron, electron-nuclei, and nuclei-nuclei interaction. The purpose of having a matrix for the electron part in the Hamiltonian is to replace the time evolution for the electrons by the Schrödinger electron eigenvalue problem. An advantage of including the electron part as a matrix-valued operator is that the classical limit, as the nuclei-electron mass ratio tends to infinity, has been derived rigorously, \cite{17} and \cite{9}, and by knowing the classical limit the system can be simulated by ab initio molecular dynamics for nuclei with the potential generated by the electron eigenvalue problem. For instance, one may ask how the observables of the density, momentum, energy, stress tensor and heat flux are effected by the possibility of excited electron states and how these observables should be computed in molecular dynamics simulations. This question is answered in Theorem 5.1. The classical molecular dynamics limit of quantum observables in \cite{9} is for the setting of constant temperature in the canonical ensemble and shows, for example, how the potential is modified also when the difference of the excited and ground state electron eigenvalue is not large compared to the temperature.

The time evolution of the conserved quantum observables uses the ingenious observation by Irving and Zwanzig that the commutator of the Hamiltonian operator and a quantum observable becomes equal to the Weyl quantization of the Poisson bracket, for an observable that is a polynomial of degree at most two in the momentum coordinate. Combined with the observation that the observables for density, momentum and energy are polynomials of degree at most two in the momentum coordinate the quantum observables therefore satisfy the same conservation laws as in the derivation based on classical particle dynamics by Irving and Kirkwood. In the case of matrix-valued potentials the commutator of the Hamiltonian and the quantum observables for mass, momentum and energy does not reduce to a Poisson bracket since the matrix-valued symbols do not commute in general. The main idea in this work is to show that for a certain diagonalization, based on a non-linear eigenvalue problem, this commutator is reduced to a quantization of a Poisson bracket.

To define the energy observable the works \cite{7, 15, 8, 6} use that the potential energy can be split into a sum of potential energies related to each particle as defined by pair interactions. In the matrix-valued case considered here the splitting is required for the eigenvalues of the matrix
potential which is not a sum of pair potential interactions. Our splitting is instead obtained by using perturbation theory for eigenvalues.

The pair potential theory is also used in the works [7, 15, 8, 6] to reduce forcing terms to divergence of a stress term. Such reduction has been obtained in [1] for general potentials that are invariant with respect to translation and orthogonal transformations by changing to the coordinates depending on all pair distances. This change to the pair distance coordinates is also used here.

The compressible Euler equations have been derived from classical perturbed Newtonian particle dynamics using the relative entropy method in [10]. The classical Newtonian particle dynamics based on short range pair potential interactions is then weakly perturbed in two ways: to avoid unbounded velocities the kinetic energy is modified, for instance as relativistic, and to prove ergodicity with respect to Gibbs distributions the Hamiltonian dynamics is perturbed by a weak noise term that vanishes in the macroscopic hydrodynamic limit. A main accomplishment in [10] is to show that the density solving the Liouville equation that is initially close to a grand canonical Gibbs measure remains close to a grand canonical Gibbs measure at later time, so that the Gibbs measure determines the compressible Euler equations for all time, as long as the solution to the Euler equations remains smooth. The work [10] achieves the mathematically ambitious goal to derive a closed system of conservation laws from microscopic dynamics, which also requires additional assumptions and restricts to a setting with smooth classical solutions to the Euler equations. The Euler equations includes a pressure term that originates from microscopic particle forces. The relative entropy method has also been used to derive the compressible Euler equations, with a certain pressure term, in a scaling limit from a quantum system of fermions under an assumption of ergodicity of the quantum dynamics with respect to the Gibbs measure, see [14]. The objective in our work here is different from [10] and [14], in particular, we derive microscopic expressions for the stress tensor and the heat flux from a general quantum mechanical setting but we do not address the question of deriving a closed system of conservation laws from quantum mechanics.

We formulate the quantum mechanical model and the conservation laws in Section 2. In Sections 3 and 4 we review the derivations of the conservation laws from classical and quantum dynamics, respectively, following the works [7, 15, 6, 8]. These derivations are then modified for obtaining the matrix-valued extension of the quantum dynamics in Section 5, where we state and prove Theorem 5.1 for the classical limit of the quantum observables in the conservation laws. In Section 6 we present an approach for determining an initial density operator that matches the initial conservation variables locally. Following [1] we discuss in Section 7 the question of non-uniqueness of the stress tensor.

2. Problem formulation

2.1. The quantum-mechanical model. We consider derivation of conservation laws from ab initio dynamics for which the starting point is the quantum mechanical model consisting of $N$ nuclei (heavy particles or slow degrees of freedom) and $J$ electrons (light particles or fast degrees of freedom). Each particle has a related position coordinate in $\mathbb{R}^3$ and a discrete spin coordinate. The spin coordinate $\sigma_i$ for each electron take the value $1/2$ or $-1/2$, and similarly the spin coordinate $\bar{\sigma}_i$ for a nucleus can take values in a discrete set $\Sigma_i$, see [12] [2]. The quantum system at time $t$ is then described by a wave function

$$\Phi(x_1, \sigma_1, x_2, \sigma_2, \ldots, x_N, \sigma_N, \bar{x}_1, \bar{\sigma}_1, \bar{x}_2, \bar{\sigma}_2, \ldots, \bar{x}_J, \bar{\sigma}_J, t) \in \mathbb{C},$$

with nucleon position coordinates $x = (x_1, x_2, \ldots, x_N) \in \mathbb{R}^{3N}$ and electron position coordinate $\bar{x} = (\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_N) \in \mathbb{R}^{3J}$, and spin coordinates $\sigma = (\sigma_1, \ldots, \sigma_N) \in \Sigma$ and $\bar{\sigma} = (\bar{\sigma}_1, \ldots, \bar{\sigma}_J) \in \bar{\Sigma} = \{-1/2, 1/2\}^J$. The wave function is required to satisfy the Pauli exclusion principle which implies that it is anti-symmetric with respect to interchanging electron coordinates, namely

$$\Phi(\ldots, \bar{x}_i, \bar{\sigma}_i, \ldots, \bar{x}_j, \bar{\sigma}_j, \ldots, t) = -\Phi(\ldots, \bar{x}_j, \bar{\sigma}_j, \ldots, \bar{x}_i, \bar{\sigma}_i, \ldots, t)$$
and similarly identical fermion nuclei are also anti-symmetric while identical boson nuclei are symmetric with respect its nucleon coordinates, see \[12\, 2\]. We note that

\[
\sum_{\sigma \in \Sigma} \sum_{\sigma' \in \Sigma} \int_{\mathbb{R}^{3(N+1)}} |\Phi(x, \sigma, \bar{x}, \sigma', t)|^2 \, dx \, d\bar{x}
\]

is the probability to find the quantum system in \((x, \sigma, \bar{x}, \sigma')\) at time \(t\). In the absence of magnetic fields, the wave function depends on the spin coordinates only parametrically since the Hamiltonian does not depend on the spin coordinates. To simplify the notation we therefore suppress the spin coordinates of the wave function in the writing below. We assume the atomic units (a.u.) in which the mass and charge of the electron are normalized to be one, and the Planck constant \(\hbar = 1\).

The quantum mechanical evolution is described by the Schrödinger equation for a wave function \(\Phi : \mathbb{R}^{3N} \times \mathbb{R}^{3J} \times [0, \infty) \to \mathbb{C}\) satisfying

\[
i \partial_t \Phi(x, \bar{x}, t) = \hat{H}(x, \bar{x}, t),
\]

with the Hamiltonian operator

\[
\hat{H} = -\sum_{n=1}^{N} \frac{1}{2M_n} \Delta x^n + \hat{V}(x, \bar{x}),
\]

where \(\hat{V}(x, \bar{x})\) is the electronic operator formed by the electron kinetic energy, electron-electron repulsion, nuclei-nuclei repulsion and electron-nuclei attraction, see \[2\, 11\, 12\].

\[
\hat{V}(x, \bar{x}) = -\frac{1}{2} \Delta x + \hat{v}(x, \bar{x})
\]

\[
\hat{v}(x, \bar{x}) = \sum_{k \neq n} \frac{1}{|x^n - \bar{x}|} + \sum_{n \in \mathcal{E}_n} \frac{Z_n Z_m}{|x^n - x^m|} - \sum_{k \in \mathcal{E}_n} \frac{Z_n}{|x^n - \bar{x}|}.
\]

Here \(Z_n\) is the charge of the nuclei and \(\bar{x}^k \in \mathbb{R}^3\) the coordinate of the electron \(k\).

The summation over all particles in the definition of the potential operator \[2.3\] can be rearranged into a sum over contributions from each nuclei

\[
\hat{V} = \sum_{n=1}^{N} \hat{V}^n,
\]

where \(\hat{V}^n\) is the contribution from the set \(\mathcal{E}_n\) of electrons corresponding to the nucleus \(n\), i.e.,

\[
\hat{V}^n(x, \bar{x}) = -\frac{1}{2} \sum_{k \in \mathcal{E}_n} \Delta x^k + \frac{1}{2} \sum_{\ell \in \mathcal{E}_n, k \neq \ell} \frac{1}{|x^k - \bar{x}|} + \frac{1}{2} \sum_{m \neq n} \frac{Z_n Z_m}{|x^n - x^m|} - \sum_{k \in \mathcal{E}_n} \frac{Z_n}{|x^n - \bar{x}|}.
\]

2.1.1. Electronic operator and the eigenvalue problem. For the sake of simplicity we assume that all nuclei masses are equal, i.e., \(M_n = M \gg 1\); the general case of different masses can be treated by rescaling the nuclei position coordinates. We also change the time scale with \(\tau = M^{-1/2} t\) so that the nuclei dynamics has a limit when \(M \to \infty\). In preparation for the adiabatic approximation we write the wave function of the system as \(\Phi : \mathbb{R}^{3N} \times [0, \infty) \to L^2(\mathbb{R}^{3J})\) and the system Hamiltonian \(\hat{H}\) as

\[
\hat{H} = -\frac{1}{2M} \Delta x + \hat{V}(x),
\]

with the Hermitian operator \(\hat{V}\). We simplify the setting by considering a finite dimensional approximation of the anti-symmetric electronic wave function space (including also the spin coordinates) by applying a projection onto a finite-dimensional subspace of \(L^2(\mathbb{R}^{3J})\) spanned by functions \(\{\phi_1(x), \ldots, \phi_d(x)\}\). Thus \(\hat{V}(x)\) is represented by a Hermitian matrix-valued operator \(V : \mathbb{R}^{3N} \to \mathbb{C}^{d \times d}, \quad V_{ij}(x) = \langle \phi_i, \hat{V}(x), \phi_j \rangle, \quad i, j = 1, \ldots, d\). Here we denote by \(\langle u, v \rangle = \int_{\mathbb{R}^{3J}} u^*(x) v(x) \, dx\) the scalar product on the Hilbert space \(L^2(\mathbb{R}^{3J})\).
We also assume that the eigenvalues \( \lambda_1(x), \lambda_2(x), \ldots, \lambda_d(x) \) of this matrix-valued potential \( V(x) \) defined by the algebraic eigenvalue problem
\[
(2.7) \quad V(x)\Psi_k(x) = \lambda_k(x)\Psi_k(x), \quad \text{for all } x \in \mathbb{R}^{3N}.
\]
satisfy
\[
(2.8) \quad \lambda_1(x) < \lambda_2(x) < \ldots < \lambda_d(x), \\
(2.9) \quad \lambda_1(x) \to \infty \quad \text{as } |x| \to \infty.
\]
The first assumption is in order to have differentiable eigenvectors and the second condition implies that the spectrum of \( \mathcal{H} \) is discrete, see [3].

We note that \( \hat{V} \) is invariant with respect to the affine transformations defined by
\[
(x^1, \ldots, x^N, \bar{x}^1, \ldots, \bar{x}^d) \mapsto (Qx_1 + \alpha, \ldots, Qx_N + \alpha, Q\bar{x}_1 + \alpha, \ldots, Q\bar{x}_J + \alpha),
\]
where \( Q \in O(3) \) is an orthogonal transformation of \( \mathbb{R}^3 \) and \( \alpha \in \mathbb{R}^3 \) a translation, i.e.,
\[
\hat{V}(x, \bar{x}) = \hat{V}(Qx_1 + \alpha, \ldots, Qx_N + \alpha, Q\bar{x}_1 + \alpha, \ldots, Q\bar{x}_J + \alpha).
\]
Therefore also the eigenvalues \( \lambda_k \) and eigenfunctions are invariant with respect to such translations and orthogonal transformations.

The energy related to the particle \( n \) for the eigenvalue \( k \) can be viewed as the difference of \( \lambda_k \) and the \( k \)th-eigenvalue \( \hat{\lambda}_k \) of the perturbed potential operator \( \hat{V} - \hat{V}^n \), where \( \hat{V}^n \) is defined in [2.5]. The difference corresponds to removing the particle \( n \) and its electrons. By the standard perturbation expansion the eigenvalues \( \hat{\lambda}_k \) are to the leading order
\[
\hat{\lambda}_k(x) \approx \langle \Psi_k(x), (\hat{V}(x) - \hat{V}^n(x))\Psi_k(x) \rangle =: \hat{\lambda}_k(x)
\]
and we define \( \lambda_k^n(x) = \lambda_k(x) - \hat{\lambda}_k(x) \), i.e.,
\[
(2.10) \quad \lambda_k^n(x) = \langle \Psi_k(x), \hat{V}^n(x)\Psi_k(x) \rangle.
\]
Property [2.4] implies that for \( k = 1, \ldots, d \) we can write the energy surface \( \lambda_k(x) \) as a sum over contributions from individual nuclei, i.e.,
\[
(2.11) \quad \lambda_k = \sum_{n=1}^N \lambda_k^n.
\]
In the sequel we will consider only one energy surface, often the ground state \( \lambda_1(x) \), and therefore we drop the index \( k \), and use the notation \( \lambda := \lambda_k \) for a given, fixed \( k \).

2.2. The conservation laws. The conservation laws for mass, momentum and energy, based on the density \( \rho : \mathbb{R}^3 \times [0, \infty) \to [0, \infty) \), velocity \( u : \mathbb{R}^3 \times [0, \infty) \to \mathbb{R}^3 \) and energy density \( E : \mathbb{R}^3 \times [0, \infty) \to \mathbb{R} \), take the form
\[
\partial_t \rho(y,t) + \sum_{\ell=1}^3 \partial_{y_\ell} \left( \rho(y,t)u_\ell(y,t) \right) = 0,
\]
\[
(2.12) \quad \partial_t \left( \rho(y,t)u_j(y,t) \right) + \sum_{\ell=1}^3 \partial_{y_\ell} \left( \rho(y,t)u_\ell(y,t)u_j(y,t) - \sigma_{\ell j}(y,t) \right) = 0,
\]
\[
\partial_y E(y,t) + \sum_{\ell=1}^3 \partial_{y_\ell} \left( E(y,t)u_\ell(y,t) + q_\ell(y,t) - \sum_j \sigma_{\ell j}(y,t)u_j(y,t) \right) = 0,
\]
where \( \sigma_{\ell j} : \mathbb{R}^3 \times [0, \infty) \to \mathbb{R} \) is the \( \ell j \)-component of the \( 3 \times 3 \) stress tensor and \( q_\ell : \mathbb{R}^3 \times [0, \infty) \to \mathbb{R} \) is the \( \ell \)-th component of the heat flux. The purpose of this work is to derive these conservation laws from microscopic dynamical systems. First we consider classical systems and then quantum systems.
In this section we consider a system of $N$ classical particles masses $M_n$, position coordinates $x : [0, \infty) \to \mathbb{R}^{3N}$ and momentum coordinates $p : [0, \infty) \to \mathbb{R}^{3N}$ that satisfy the classical equations of motion given by the Hamiltonian

$$H(x,p) = \sum_{k=1}^{N} \frac{1}{2M_k} |p_k|^2 + \lambda(x),$$

where $\lambda : \mathbb{R}^{3N} \to \mathbb{R}$ is a given interaction potential which we relate to the potential energy surface (an eigenvalue $\lambda_k(x)$) in the next section. Thus the evolution of the system is given by the solution of Newtonian dynamics

$$\ddot{x}_k = \frac{1}{M_k} p_k,$$

$$\dot{p}_k = -\nabla \lambda(x_k).$$

We use the notation $x = (x^1, x^2, x^3, \ldots, x^N)$ and $p = (p^1, p^2, p^3, \ldots, p^N)$, where $x^k \in \mathbb{R}^3$ and $p^k \in \mathbb{R}^3$ is the position and momentum, respectively, for the particle $k$ at time $t$, and $M_k$ is the mass of the $k$th-particle. The given potential $\lambda : \mathbb{R}^{3N} \to \mathbb{R}$ is assumed to be invariant with respect to the affine transformations of $\mathbb{R}^3$, i.e. $\lambda(x^1, \ldots, x^N) = \lambda(Qx^1 + \alpha, \ldots, Qx^N + \alpha)$ for any orthogonal $3 \times 3$ matrix $Q$ and any translation $\alpha \in \mathbb{R}^3$. The following theorem will be used to represent the potential $\lambda$ as a function of pairwise distances between particles rather than the positions of each particle:

**Theorem 3.1.** If the two sets of points $\{x^i\}_{i=1}^N$ and $\{y^j\}_{j=1}^N$, where $x^i, y^j \in \mathbb{R}^3$, satisfy $r_{ij} = |x^i - x^j| = |y^i - y^j|$ for $1 \leq i, j \leq N$, then there exist an orthogonal matrix $Q \in \mathbb{R}^{3 \times 3}$ and a translation vector $\alpha \in \mathbb{R}^3$ such that $x^i = Qy^i + \alpha$ for $1 \leq i \leq N$.

**Proof.** Let $\bar{x}^i := x^i - x^1, \bar{y}^i := y^i - y^1$, for $1 \leq i \leq N$. If $\bar{x}^i = \bar{y}^i = 0$, for all $1 \leq i \leq N$, then clearly the claim in the theorem is true. If not, let $i_1$ be an index such that $\bar{x}^{i_1} \neq 0$ (which also implies that $\bar{y}^{i_1} \neq 0$). Let $Q_1, Q_2 \in \mathbb{R}^{3 \times 3}$ be two orthogonal matrices such that $Q_1 \bar{x}^{i_1}$ and $Q_2 \bar{y}^{i_1}$ both lie on the first positive coordinate axis. Then clearly $Q_1 \bar{x}^{i_1} = Q_2 \bar{y}^{i_1}$.

Define $\bar{\bar{x}}^i := Q_1 \bar{x}^i$ and $\bar{\bar{y}}^i := Q_2 \bar{y}^i$ for all $1 \leq i \leq N$. If all $\bar{\bar{x}}^i$ and $\bar{\bar{y}}^i$ lie on the first coordinate axis then $\bar{\bar{x}}^i = \bar{\bar{y}}^i$, for $1 \leq i \leq N$, since every $\bar{\bar{x}}^i$ and $\bar{\bar{y}}^i$ have the same distance to $\bar{\bar{x}}^1$ in the origin, and $\bar{\bar{x}}^1$. Assume now that there exists an index $i_2$ such that $\bar{\bar{x}}^{i_2}$ does not lie on the first coordinate axis. Since $\bar{\bar{x}}^{i_2}$ and $\bar{\bar{y}}^{i_2}$ have the same distance to $\bar{\bar{x}}^1$ and $\bar{\bar{x}}^{i_1}$, also $\bar{\bar{y}}^{i_2}$ does not lie on the first coordinate axis. Let $Q_3, Q_4 \in \mathbb{R}^{3 \times 3}$ be two orthogonal matrices that are rotations around the first coordinate axis such that $Q_3 \bar{\bar{x}}^{i_2}$ and $Q_4 \bar{\bar{y}}^{i_2}$ are both in the “positive xy-plane”, i.e. given as $(a, b, 0)$ for $b > 0$. This makes $Q_3 \bar{\bar{x}}^{i_2} = Q_4 \bar{\bar{y}}^{i_2}$ since the points are on the same distance to $\bar{\bar{x}}^{i_1}$ and $\bar{\bar{x}}^{i_1}$. Define $\bar{\bar{\bar{x}}}^i := Q_3 \bar{\bar{x}}^i$ and $\bar{\bar{\bar{y}}}^i := Q_4 \bar{\bar{y}}^i$ for all $1 \leq i \leq N$. Since the points $\bar{\bar{\bar{x}}}^i$ and $\bar{\bar{\bar{y}}}^i$ have the same distance to the points $\bar{\bar{x}}^1$, $\bar{\bar{x}}^{i_1}$, and $\bar{\bar{x}}^{i_2}$, that all lie in the plane spanned by the first two coordinate directions, but not all of them on a straight line, we must either have that $\bar{\bar{\bar{x}}}^i = \bar{\bar{\bar{y}}}^i$ or $\bar{\bar{\bar{x}}}^i = \bar{\bar{\bar{y}}}^i$, for the reflection in the xy-plane $Q = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$. There cannot be two points $\bar{\bar{\bar{x}}}^i$ and $\bar{\bar{\bar{y}}}^i$ that do not lie in the xy-plane and satisfy $\bar{\bar{\bar{x}}}^i = \bar{\bar{\bar{y}}}^i$ and $\bar{\bar{\bar{x}}}^i = Q \bar{\bar{\bar{y}}}^i$, since then $\bar{\bar{\bar{x}}}^i$ and $\bar{\bar{\bar{y}}}^i$ would be on different distance from $\bar{\bar{\bar{x}}}^i = \bar{\bar{\bar{y}}}^i$.

Hence either $\bar{\bar{\bar{x}}}^i = \bar{\bar{\bar{y}}}^i$ for all $1 \leq i \leq N$, or $\bar{\bar{\bar{x}}}^i = Q \bar{\bar{\bar{y}}}^i$ for all $1 \leq i \leq N$. Since $\bar{\bar{\bar{x}}}^i$ are obtained from $x^i$ by the same set of translations and multiplications by orthogonal matrices for all $1 \leq i \leq N$, and likewise for $\bar{\bar{\bar{y}}}^i$, the proof is complete.

To handle conservation of total momentum we will use Newtons third law for pair interactions and we follow the construction in [1] to determine pair interactions in a general potential that is invariant with respect to translations and orthogonal transformations in $\mathbb{R}^3$: knowing all $N(N-1)/2$ pair distances $r := (r_{12}, r_{13}, \ldots, r_{N-1N}) := (|x^1 - x^2|, |x^1 - x^3|, \ldots, |x^{N-1} - x^N|)$
determines $x$ up to a translation and orthogonal transformation in $\mathbb{R}^3$ and since $\lambda(x)$ remains the same for such translations and orthogonal transformations the potential is determined by all pair distances, i.e.

$$\lambda(x) =: \tilde{\lambda}(r(x)).$$

We will use the partial derivatives $\partial_{r;i,k} \lambda(r_{12}, r_{13}, \ldots, r_{N-1,N})$. Not all $r \in \mathbb{R}^{N(N-1)/2}$ correspond to particle positions $x \in \mathbb{R}^{3N}$ and there are $N(N-1)/2$ partial derivatives $\partial_{r;i,k} \lambda(r)$ while the gradient $\nabla \lambda(x)$ only has $3N$ components. Therefore the partial derivatives $\partial_{r;i,k} \lambda(r)$ are not uniquely defined by $\nabla \lambda(x)$. Section 4 shows how to determine $\partial_{r;i,k} \lambda(r)$.

To define the observables for density, momentum and energy and their dependence on the space coordinate $y \in \mathbb{R}^3$ we use a non negative smooth symmetric mollifier $\eta : \mathbb{R}^3 \to \mathbb{R}$, $\eta \in C^\infty(\mathbb{R}^3)$, with compact support, satisfying

$$\int_{\mathbb{R}^3} \eta(y)dy = 1,$$

$$\eta(y) \geq 0, \quad \eta(y) = \eta(-y), \quad \text{for all } y \in \mathbb{R}^3,$$

$$\eta(y) = 0, \quad \text{for } |y| > \epsilon.$$

The macroscopic density $\rho : \mathbb{R}^3 \times [0, \infty) \to \mathbb{R}$ is defined by the particle system as

$$\rho(y, t) = \int_{\mathbb{R}^{6N}} \sum_n M_n \eta(y - x^n_t) f(x_0, p_0) dx_0 dp_0,$$

where $x^n_t$ is a function of the initial condition $(x_0, p_0)$, and $f : \mathbb{R}^{6N} \to [0, \infty)$ is a given initial particle distribution function, described in Section 6. Irving and Kirkwood, [7], use this definition with $\eta$ equal to a point mass and a general initial distribution $f$. Noll, [15], formulates the integration with respect to point masses in terms of the one-point and two-point density correlations functions instead and provides precise conditions for the validity of the derivation. Hardy, [8], uses the mollifier $\eta$ but not the integration over the initial particle distribution.

3.1. The conservation of mass. Let $z_0 = (x_0, p_0)$ denote the phase-space coordinate in $\mathbb{R}^{6N}$ and $x \cdot y = \sum_{i=1}^3 x^iy^i$ the Euclidean scalar product in $\mathbb{R}^3$. Differentiation of the density implies

$$\partial_t \rho(y, t) = - \int_{\mathbb{R}^{6N}} \sum_{n=1}^N M_n \dot{x}^n_t \cdot \nabla \eta(y - x^n_t) f(z_0) dz_0$$

$$= - \int_{\mathbb{R}^{6N}} \sum_{n=1}^N p^n_t \cdot \nabla \eta(y - x^n_t) f(z_0) dz_0$$

and by defining the velocity $u : \mathbb{R}^3 \times [0, \infty) \to \mathbb{R}^3$ as

$$\rho(y, t)u(y, t) := \int_{\mathbb{R}^{6N}} \sum_{n=1}^N \eta(y - x^n_t) p^n_t f(z_0) dz_0$$

we obtain the conservation law for the mass

$$\partial_t \rho(y, t) + \sum_{k=1}^3 \partial_{y_k} \left( \rho(y, t) u_k(y, t) \right) = 0.$$

3.2. The conservation of momentum. Differentiation of the momentum yields

$$\partial_t (\rho(y, t) u(y, t)) = - \int_{\mathbb{R}^{6N}} \sum_{n=1}^N M_n^{-1} p^n_t \cdot \nabla \eta(y - x^n_t) p^n_t f(z_0) dz_0$$

$$- \int_{\mathbb{R}^{6N}} \sum_{n=1}^N \eta(y - x^n_t) \nabla x^i \lambda(x_t) f(z_0) dz_0.$$
In order to write the second term as a divergence term we follow Noll’s, \[15\], and Hardy’s method, \[6\], based on identifying gradients with respect to pair distances and converting the difference in \(\eta\) at the the corresponding point to a gradient term: the combination of the pair distance derivative, using the definition of \(\tilde{\lambda}\) in (3.2),

\[
\sum_{n=1}^{N} \eta(y - x^n) \nabla_{x^n} \lambda = \sum_{n} \sum_{j<k} \eta(y - x^n) \partial_{y^n} \tilde{\lambda}(r) \nabla_{x^n}(|x^j - x^k|)
\]

(3.4)

\[
= \sum_{n<k} (\eta(y - x^n) - \eta(y - x^k)) \partial_{x^n} \tilde{\lambda}(r) \nabla_{x^n}(|x^n - x^k|)
\]

and the difference at the corresponding points

\[
\eta(y - x^n) - \eta(y - x^k) = \int_{0}^{1} \frac{d}{ds} \eta(y - sx^n - (1 - s)x^k) ds
\]

(3.5)

\[
= \int_{0}^{1} (x^k - x^n) \cdot \nabla \eta(y - sx^n - (1 - s)x^k) ds
\]

\[
= - \text{div}_y \int_{0}^{1} \eta(y - sx^n - (1 - s)x^k) (x^n - x^k) ds
\]

shows that

\[
\sum_{n} \eta(y - x^n) \nabla_{x^n} \lambda = - \text{div}_y \left( \sum_{n<k} \int_{0}^{1} \eta(y - sx^n - (1 - s)x^k) (x^n - x^k) ds \right)
\]

\[
\times \partial_{x^n} \tilde{\lambda}(r) \nabla_{x^n} |x^n - x^k|.
\]

We conclude that the following conservation law for the momentum holds

\[
\partial_t (\rho(y, t) u_j(y, t)) = - \sum_{\ell=1}^{3} \partial_{y_\ell} \int_{\mathbb{R}^6 N} \sum_{n=1}^{N} M_n^{-1} \eta(y - x^n_\ell) p^n_j(t)p^n_k(t) f(z_0) dz_0
\]

(3.6)

\[
+ \sum_{\ell=1}^{3} \partial_{y_\ell} \int_{\mathbb{R}^6 N} \sum_{n<k} \int_{0}^{1} \eta(y - sx^n_\ell - (1 - s)x^k_\ell) (x^n_\ell(t) - x^k_\ell(t)) ds
\]

\[
\times \partial_{x^n_\ell} \tilde{\lambda} \partial_{x^k_\ell} (|x^n_\ell(t) - x^k_\ell(t)|) f(z_0) dz_0.
\]

To write the conservation law for momentum in the form (2.12) we follow the steps in \[15\]. Let

\[
v^n_\ell := \frac{p^n_\ell}{M_n} - u(y, t)
\]

where by (3.3)

\[
u(y, t) = \frac{\int_{\mathbb{R}^6 N} \sum_{n=1}^{N} \eta(y - x^n_\ell) p^n_\ell f(z_0) dz_0}{\int_{\mathbb{R}^6 N} \sum_{n=1}^{N} M_n \eta(y - x^n_\ell) f(z_0) dz_0}.
\]

Definition (3.3) implies

\[
\int_{\mathbb{R}^6 N} \sum_{n=1}^{N} M_n \eta(y - x^n_\ell) v^n_\ell f(z_0) dz_0 = 0
\]
so that the first integral in (3.6) satisfies
\[ \int_{\mathbb{R}^N} \sum_{n=1}^{N} M_n^{-1} \eta(y - x^n_t) p^n_m(t) p^n_l(t) f(z_0) \, dz_0 \]
\[ = \int_{\mathbb{R}^N} \sum_{n=1}^{N} M_n \eta(y - x^n_t) \left( v^n_j(t) v^n_l(t) + u_j(t) v^n_l(t) + v^n_j(t) u_l(t) + u_j(t) u_l(t) \right) f(z_0) \, dz_0 \]
\[ = \int_{\mathbb{R}^N} \sum_{n=1}^{N} M_n \eta(y - x^n_t) \left( v^n_j(t) v^n_l(t) + u_j(t) u_l(t) \right) f(z_0) \, dz_0. \]

The conservation law for the momentum can therefore be formulated as
\[ \partial_t (\rho(y, t) u_j(y, t)) + \sum_{\ell=1}^{3} \partial_{y_\ell} (\rho(y, t) u_j(y, t) u_\ell(y, t) - \sigma_{ij}(y, t)) = 0, \]
where
\[ \sigma_{ij}(y, t) := \int_{\mathbb{R}^N} \tilde{\sigma}_{ij}(x, p; y, t) f(x_0, p_0) \, dx_0 \, dp_0, \]
\[ \tilde{\sigma}_{ij}(x, p; y, t) := -\sum_{n=1}^{N} M_n \eta(y - x^n) v^n_j v^n_l \]
\[ + \sum_{n < k} \int_0^1 \eta(y - sx^n - (1-s)x^k)(x^n - x^k) \, ds \]
\[ \times \partial_{n}\lambda \partial_{k}\eta(|x^n - x^k|), \]
(formula 3.7)
defines the stress tensor using \( v^n = M_n^{-1} p^n - u(y, t). \)

3.3. The conservation of energy. In order to define the energy density we need to define the potential energy related to each particle. In the case of pair potentials this is straightforward by summing the pair potentials including the particle, as in [7] [15] [6]. Since we have a more general potential, which does not have to be a sum of pair potentials, this step requires a new construction: here we use the potential energy \( \lambda^n \), related to particle \( n \), introduced in (2.10) and (2.11).

We define the energy density \( E : \mathbb{R}^3 \times [0, \infty) \to \mathbb{R} \) by
\[ E(y, t) = \int_{\mathbb{R}^N} \sum_{n} \eta(y - x^n_t) \left( \frac{|p^n|^2}{2M_n} + \lambda^n(x_t) \right) f(x_0, p_0) \, dx_0 \, dp_0 \]
and differentiate it to obtain
\[ \partial_t E_t(y, t) = -\int_{\mathbb{R}^N} \sum_{n} M_n^{-1} p^n_l \cdot \nabla \eta(y - x^n_t) \left( \frac{|p^n|^2}{2M_n} + \lambda^n(x_t) \right) f(x_0, p_0) \, dx_0 \, dp_0 \]
\[ - \int_{\mathbb{R}^N} \sum_{n} M_n^{-1} \eta(y - x^n_t) p^n_l \cdot \nabla x^n \lambda(x_t) f(x_0, p_0) \, dx_0 \, dp_0 \]
\[ + \int_{\mathbb{R}^N} \sum_{n,m} M_n^{-1} \eta(y - x^n_t) p^n_m \cdot \nabla x^m \lambda^n(x_t) f(x_0, p_0) \, dx_0 \, dp_0. \]

We have
\[ \sum_{n} M_n^{-1} \eta(y - x^n_t) p^n_l \cdot \nabla x^n \lambda(x_t) = \sum_{n,m} M_n^{-1} \eta(y - x^n_t) p^n_m \cdot \nabla x^n \lambda^m(x_t) \]
\[ = \sum_{n,m} M_n^{-1} \eta(y - x^n_t) p^n_m \cdot \nabla x^n \lambda^m(x_t), \]
so the right hand side in (3.8) becomes

\[ \partial_t E(y,t) = -3 \sum_{\ell=1}^{3} \partial_{y_\ell} \int_{\mathbb{R}^6N} \sum_{n} M_n^{-1} p_n^\ell(t) \eta(y-x_t^n) \left( \frac{|p_n^n|^2}{2M_n} + \lambda^n(x_t) \right) f(x_0,p_0) dx_0 dp_0 + \int_{\mathbb{R}^6N} \sum_{n,m} (\eta(y-x_t^n) - \eta(y-x_t^m)) (M_m^{-1} p_m^\ell) \cdot \nabla x_m \lambda^n(x_t) f(x_0,p_0) dx_0 dp_0. \]

By using (3.5) we obtain the conservation law for the energy

\[ \partial_t E(y,t) = -3 \sum_{\ell=1}^{3} \partial_{y_\ell} \int_{\mathbb{R}^6N} \sum_{n} M_n^{-1} p_n^\ell(t) \eta(y-x_t^n) \left( \frac{|p_n^n|^2}{2M_n} + \lambda^n(x_t) \right) f(x_0,p_0) dx_0 dp_0 \]

(3.9)

By using (3.5) we obtain the conservation law for the energy

\[ \partial_t E(y,t) = -3 \sum_{\ell=1}^{3} \partial_{y_\ell} \int_{\mathbb{R}^6N} \sum_{n,m} \int_0^1 \eta(y-x_t^n + s(x_t^m - x_t^n)) ds \eta(x_t^n(t) - x_t^m(t)) \times (M_m^{-1} p_m^\ell) \cdot \nabla x_m \lambda^n(x_t) f(x_0,p_0) dx_0 dp_0. \]

In order to write the energy conservation in the standard form (2.12) we use

\[ \sum_{n=1}^{N} \eta(y-x^n)(u_n^\ell + v_n^\ell) \left( \frac{|p_n^n|^2}{2M_n} + \lambda^n(x) \right) = \sum_{n=1}^{N} \eta(y-x^n) u_n^\ell \left( \frac{|p_n^n|^2}{2M_n} + \lambda^n(x) \right) + \sum_{n=1}^{N} \eta(y-x^n) v_n^\ell \left( \frac{|p_n^n|^2}{2M_n} + \lambda^n(x) \right) + \sum_{n=1}^{N} \eta(y-x^n) M_n v_n^\ell u \cdot v_n. \]

The first term in the right hand side becomes \( E(y,t)u_\ell(y,t) \) under the integration in (3.9), and the last term is part of \( \sum_j \sigma_{\ell j}(y,t) u_j(y,t) \). The term including the factor \( v_n^\ell |u|^2 \) vanishes upon integration over the initial distribution due to the definition (3.3) and the second term is included in the heat flux. The conservation of energy can therefore be written

\[ \partial_t E(y,t) + 3 \sum_{\ell=1}^{3} \partial_{y_\ell} (E(y,t)u_\ell(y,t) + q_\ell(y,t)) - \sum_{j} \sigma_{\ell j}(y,t) u_j(y,t) = 0 \]

where the heat flux is defined as

(3.10)

\[ q_\ell(y,t) := \int_{\mathbb{R}^6N} \tilde{q}_\ell(x_t,p_t; y,t) f(x_0,p_0) dx_0 dp_0, \]

\[ \tilde{q}_\ell(x,p;y,t) := \sum_n v_n^\ell \eta(y-x^n) \left( \frac{M_n |v_n|^2}{2} + \lambda^n(x) \right) + \sum_{n,m} \int_0^1 \eta(y-x^n + s(x^m - x^n)) ds (x_t^n - x_t^m) \times \left( \frac{p_m^n}{M_m} \cdot \nabla x_m \lambda^n(x) - \sum_j u_j(y,t) \partial_{x^{n,m}} \lambda(x(r^{12}, \ldots, r^{N-1N})) \partial_{x^{n}} |x^n - x^m| \right) . \]
4. The conservation laws derived from quantum mechanics

Irving and Zwanzig [8] derived the conservation laws when the particle system is modeled by the Schrödinger equation for a wave function $\Phi : \mathbb{R}^{3(N+J)} \times [0, \infty) \rightarrow \mathbb{C}$ satisfying

$$i \partial_t \Phi(\tilde{x}, t) = \hat{H}_0 \Phi(\tilde{x}, t),$$

with the Hamiltonian

$$\hat{H}_0 = - \sum_{n=1}^{N+J} \frac{1}{2M_n} \Delta \tilde{x}^n + \nu(\tilde{x}) ,$$

based on the particle masses $M_n$, e.g. as defined in (2.3). The wave function $\Phi$ is in an appropriate subset of $L^2(\mathbb{R}^{3(N+J)})$ taking anti-symmetry of electron coordinates into account. Irving and Zwanzig used the Schrödinger equation for a wave function $\Phi$:

$$\partial_t \Phi(t) = \hat{H}_0 \Phi(t),$$

for any $\phi \in L^2(d\tilde{x})$. For instance, quantization of the Hamiltonian symbol

$$A = \sum_{n=1}^{N+J} \frac{|\tilde{p}_n|^2}{2M_n} + \nu(\tilde{x})$$

yields the operator $\hat{H}_0$.

The Schrödinger equation implies the evolution $\Phi(\cdot, t) = e^{-it\hat{H}_0} \Phi(\cdot, 0)$ and consequently an observable at time $t$ defined by $\langle \Phi(\cdot, t), \hat{A} \Phi(\cdot, t) \rangle$ satisfies

$$\langle \Phi(\cdot, t), \hat{A} \Phi(\cdot, t) \rangle = \langle \Phi(\cdot, 0), e^{it\hat{H}_0} \hat{A} e^{-it\hat{H}_0} \Phi(\cdot, 0) \rangle$$

using the $L^2(d\tilde{x})$ scalar product $\langle v, w \rangle := \int_{\mathbb{R}^{3(N+J)}} v(\tilde{x}) w(\tilde{x}) d\tilde{x}$. By defining the evolution of observables as

$$\hat{A}_t := e^{it\hat{H}_0} \hat{A} e^{-it\hat{H}_0}$$

differentiation implies the Heisenberg-von Neumann equation

$$\partial_t \hat{A}_t = i[\hat{H}_0, \hat{A}_t],$$

where $[\hat{B}, \hat{C}] = \hat{B}\hat{C} - \hat{C}\hat{B}$ is the commutator. We also obtain

$$\partial_t \hat{A} = i e^{it\hat{H}_0} [\hat{H}_0, \hat{A}] e^{-it\hat{H}_0}$$

and $\hat{A}_0 = \hat{A}$. Let $\hat{f}$ be a density operator. Section 6 presents a precise definition of a density operator related to the given initial data of the macroscopic density, momentum and energy. The Irving and Zwanzig quantum density observable is then defined by the $L^2(\mathbb{R}^{3(N+J)})$ trace

$$\rho(y, t) = \text{Tr} (\hat{\rho}_t \hat{f})$$

where the density observable is the quantization of the density symbol

$$\hat{\rho}_0 = \left( \sum_n M_n \eta(y - \tilde{x}^n) \right).$$

The quantum momentum and energy observables are analogously defined as

$$\hat{p}_0 = \left( \sum_n \eta(y - \tilde{x}^n) \tilde{p}^n \right),$$

$$\hat{E}_0 = \left( \sum_n \eta(y - \tilde{x}^n) \left( \frac{\tilde{p}_n^2}{2M_n} + \nu^n(\tilde{x}) \right) \right).$$
where \( \nu = \sum_n \nu^n \) is a partition with the potential energy related to each particle, analogous to (2.5). Irving and Zwanzig observed the following crucial property, proved at the end of the section.

**Lemma 4.1.** For any twice differentiable scalar symbol that is a polynomial of degree two in the momentum variable

\[
\hat{A}(\hat{x}, \hat{p}) := a_0(\hat{x}) + \sum_{n=1}^{N+J} a_n(\hat{x}) \cdot \hat{p}^n + \sum_{m,n=1}^{N+J} a_{n,m}(\hat{x}) \hat{p}^n \cdot \hat{p}^m \in \mathbb{C}
\]

there holds

\[
i [\hat{H}_0, \hat{A}(\hat{\xi}, \nu)] = (\nabla_{\hat{p}} H_0(\hat{x}, \hat{p}) \cdot \nabla_{\hat{x}} \hat{A}(\hat{x}, \hat{p}) - \nabla_{\hat{x}} H_0(\hat{x}, \hat{p}) \cdot \nabla_{\hat{p}} \hat{A}(\hat{x}, \hat{p}))^\wedge
\]

\[
=: \{ H_0(\hat{x}, \hat{p}), \hat{A}(\hat{x}, \hat{p}) \}^\wedge,
\]

where \( a_0(\hat{x}) \in \mathbb{R}, a_n(\hat{x}) \in \mathbb{R}^3, a_{n,m}(\hat{x}) \in \mathbb{R}^{3 \times 3} \).

That is, for a symbol that is a polynomial of degree at most two in the momentum variable the quantum evolution of the observable reduces to the classical evolution based on the Poisson bracket. The quantum observables for density, momentum and energy are based precisely on symbols which are degree zero, one and two, respectively, in the momentum variable. Irving and Zwanzig therefore conclude that the quantum observables satisfy analogous conservation laws as those for classical particle dynamics, namely: differentiation of the density and using (4.2), Lemma 4.1 and the definition of \( \hat{p} \) imply the conservation of mass

\[
\partial_t \rho(y, t) = \text{Tr} \left( \partial_t \hat{p}_J \right)
= \text{Tr} \left( e^{it \hat{H}_0} i [\hat{H}_0, \hat{\rho}_0] e^{-it \hat{H}_0} \hat{f} \right)
\]

\[
= \text{Tr} \left( e^{it \hat{H}_0} \{ \hat{H}_0, \hat{\rho}_0 \} e^{-it \hat{H}_0} \hat{f} \right)
= -\text{Tr} \left( e^{it \hat{H}_0} \text{div}_y \hat{p}_0 e^{-it \hat{H}_0} \hat{f} \right)
= -\text{div} \left( \text{Tr} \left( \hat{p}_J \hat{f} \right) \right),
\]

and similarly differentiation of the momentum and energy establish the conservation laws for the momentum

\[
\partial_t \text{Tr} \left( \hat{p}_J \hat{f} \right) = -3 \sum_{\ell=1}^3 \partial_{y_\ell} \text{Tr} \left( \left( \sum_{n=1}^{N} M_n^{-1} \eta(y - \hat{x}^n) \hat{p}^n \hat{p}_\ell \right)
+ \sum_{n} \sum_{m} \int_0^1 \eta(y - s\hat{x}^n + (1-s)\hat{x}_\ell^m) (\hat{x}_\ell^m - \hat{x}_\ell^m) ds \times \partial_{x_{nm}} \nu \left( \hat{x}_\ell^{r, \ldots, n^{N+J-1N+J}} \right) \nabla_{\hat{x}^{n}} (\hat{x}^{n} - \hat{x}_\ell^m) \hat{f} \right)
\]

and the energy

\[
\partial_t \text{Tr} \left( \hat{E}_J \hat{f} \right) = -3 \sum_{\ell=1}^3 \partial_{y_\ell} \text{Tr} \left( \left( \sum_{n=1}^{N} M_n^{-1} \hat{p}_\ell^n \eta(y - \hat{x}^n) \right) \frac{|\hat{p}_\ell^n|^2}{2M_n} + \nu^n(\hat{x}) \right)
+ \sum_{n,m} \int_0^1 \eta(y - \hat{x}^m + s(\hat{x}^m - \hat{x}_\ell^m)) ds (\hat{x}_\ell^m - \hat{x}_\ell^m) (M^{-1}_m \hat{p}_\ell^m \cdot \nabla_{\hat{x}_\ell^m} \nu^n(\hat{x})) \hat{f} \right).
\]

**Proof of Lemma 4.1.** We have the composition rule \( \hat{A}\hat{B} = \hat{C} \) where

\[
C = e^{\frac{1}{i} \left( \nabla_{\hat{x}} \cdot \nabla_{\hat{p}} - \nabla_{\hat{x}} \cdot \nabla_{\hat{p}} \right)} A(\hat{x}, \hat{p}) B(\hat{x}', \hat{p}') \bigg|_{\hat{p} = \hat{p}'} =: \hat{A}\# \hat{B},
\]

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see [19]. Therefore
\[ [\hat{H}_0, \hat{A}] = \langle H_0 \# \hat{A} \rangle - \langle \hat{A} \# H_0 \rangle \]
and
\[ \langle \nabla_{\hat{x}} \cdot \nabla_{\hat{p}} - \nabla_{\hat{x}'} \cdot \nabla_{\hat{p}} \rangle (H_0(\hat{x}, \hat{p})\hat{A}(\hat{x}', \hat{p}') - \hat{A}(\hat{x}, \hat{p})H_0(\hat{x}', \hat{p}')) = \nabla \nu(\hat{x}) \cdot \nabla_{\hat{p}} \hat{A}(\hat{x}', \hat{p}') - M^{-1} \hat{p} \cdot \nabla_{\hat{x}} \hat{A}(\hat{x}', \hat{p}') \\
- \nabla_{\hat{x}} \hat{A}(\hat{x}, \hat{p}) \cdot M^{-1} \hat{p}' + \nabla \nu(\hat{x}') \cdot \nabla_{\hat{p}} \hat{A}(\hat{x}, \hat{p}) = \nabla \nu(\hat{x}) \cdot \nabla_{\hat{p}} \hat{A}(\hat{x}', \hat{p}') + \nabla \nu(\hat{x}') \cdot \nabla_{\hat{p}} \hat{A}(\hat{x}, \hat{p}) \\
- M^{-1} \hat{p} \cdot \nabla_{\hat{x}} \hat{A}(\hat{x}', \hat{p}') - M^{-1} \hat{p}' \cdot \nabla_{\hat{x}} \hat{A}(\hat{x}, \hat{p}) = : I(\hat{x}, \hat{x}', \hat{p}, \hat{p}'). \]

Evaluation at the point \((\hat{x}', \hat{p}') = (\hat{x}, \hat{p})\) yields
\[ \frac{i^2}{2} \langle \nabla_{\hat{x}'} \cdot \nabla_{\hat{p}} - \nabla_{\hat{x}} \cdot \nabla_{\hat{p}} \rangle (H_0(\hat{x}, \hat{p})\hat{A}(\hat{x}', \hat{p}') - \hat{A}(\hat{x}, \hat{p})H_0(\hat{x}', \hat{p}')) \bigg|_{\hat{x} = \hat{x}'} = \{ H_0, \hat{A} \}. \]

The differentiation to the second order becomes
\[ \langle \nabla_{\hat{x}} \cdot \nabla_{\hat{p}} - \nabla_{\hat{x}'} \cdot \nabla_{\hat{p}} \rangle I(\hat{x}, \hat{x}', \hat{p}, \hat{p}') = \sum_{m,n} \partial_{\hat{x}_m} \partial_{\hat{x}_n} \nu(\hat{x}) \partial_{\hat{p}_m} \partial_{\hat{p}_n} \hat{A}(\hat{x}', \hat{p}') \\
- \sum_{m,n} \partial_{\hat{x}_m} \partial_{\hat{x}_n} \nu(\hat{x}') \partial_{\hat{p}_m} \partial_{\hat{p}_n} \hat{A}(\hat{x}, \hat{p}) \\
- \sum_{n} M^{-1}_n \partial_{\hat{x}_n}^2 \hat{A}(\hat{x}, \hat{p}) \\
+ \sum_{n} M^{-1}_n \partial_{\hat{p}_n}^2 \hat{A}(\hat{x}', \hat{p}') := \Pi(\hat{x}, \hat{x}', \hat{p}, \hat{p}'), \]
so that \(\Pi(\hat{x}, \hat{x}', \hat{p}, \hat{p}) = 0\).

Differentiation to the third order implies
\[ \langle \nabla_{\hat{x}} \cdot \nabla_{\hat{p}} - \nabla_{\hat{x}'} \cdot \nabla_{\hat{p}} \rangle \Pi(\hat{x}, \hat{x}', \hat{p}, \hat{p}') = 0 \]
which together with the Taylor expansion of the exponential proves the lemma. \(\square\)

5. The Classical Limit of the Quantum Conservation Laws

The aim here is to consider the quantum evolution where the electron part is considered operator valued and the Weyl quantization is only in the nuclei part. For simplicity all nuclei masses are assumed to be equal, \(M_n = M\). We consider the case \(M \gg 1\). We also change the time scale so that the nuclei dynamics has a limit, when \(M \to \infty\), as follows: the wave function in (1.1) can be written as \(\Phi : \mathbb{R}^{3N} \times [0, \infty) \to L^2(\mathbb{R}^J)\) and it solves the Schrödinger equation
\[ \frac{i}{M^{1/2}} \partial_t \Phi(x, \tau) = \hat{H} \Phi(x, \tau), \]
with the change of the time scale \(\tau = M^{-1/2}t\). The classical limit obtained as \(M \to \infty\) is well behaved in this time scale, in the sense that the nuclei move a distance of order one in time one, as we shall see in Theorem 5.1. The Hamiltonian is
\[ \hat{H} = -\frac{1}{2M} \Delta_x + V(x) \]
with the Hermitian \(L^2(\mathbb{R}^J)\) operator \(V(x)\), as in (2.2). The corresponding Heisenberg - von Neumann equation takes the form
\[ \partial_t \hat{A}_\tau = iM^{1/2} [\hat{H}, A_\tau] \]
where the symbol \(A_\tau(x, p)\) maps \(L^2(\mathbb{R}^J)\) to \(L^2(\mathbb{R}^J)\). This form of operator valued symbols are suitable for studying the \(M \to \infty\) limit of the observables we have in the conservation laws, since the corresponding Weyl quantizations are based on highly oscillatory Fourier integral operators that only use the nuclei coordinates. We simplify the setting by considering discretized versions
of \( L^2(\mathbb{R}^{3J}) \) so that instead \( V(x) \) is a Hermitian matrix that maps \( \mathbb{C}^d \) to \( \mathbb{C}^d \) for a finite \( d \), as described in Section 2.1.1. We also assume that its eigenvalues \( \lambda_1(x), \lambda_2(x), \ldots, \lambda_d(x) \) defined by (2.7) satisfy (2.8) and (2.9). The Weyl quantization takes the form

\[
\hat{A} \phi(x) = \left( \frac{M^{1/2}}{2\pi} \right)^{3N} \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3N}} e^{iM^{1/2}(x-y) \cdot p} A(x, y) dp \phi(y) dy.
\]

Although this form of matrix valued symbols \( H \) and \( A \) is useful to obtain the semi-classical limit as \( M \to \infty \), matrix valued symbols introduce a complication: the important property in Lemma 4.1 that the commutator with respect to the conservation observables reduces to the quantization of the Poisson bracket does not hold for matrix valued symbols, since these matrices do not commute in general unless the symbols are diagonal. A main tool to determine the classical limit is therefore to diagonalize \( H \) and the observables \( A \) in the conservation laws, based on the composition operator \# as follows.

The symbol \( C \) for the product of two Weyl operators \( \hat{A} \hat{B} = \hat{C} \) is determined by

\[
C(z, p) = e^{2M^{1/2}(\nabla_x \cdot \nabla_{p'} - \nabla_x \cdot \nabla_{p''})} A(z, p) B(z', p') \bigg|_{z = z', p = p'} =: (A \# B)(z, p),
\]

see [19]. Assume now that \( \Psi : \mathbb{R}^{3N} \to \mathbb{C}^d \) and \( \Psi(x) \) is any unitary matrix with the Hermitian transpose \( \Psi^*(x) \) and define \( \hat{\tilde{A}} : \mathbb{R}^{3N} \to \mathbb{C}^{d^2} \) by

\[
\hat{\tilde{A}}_r = \hat{\Psi}(x) \hat{A}_r \hat{\Psi}^*(x)
\]

so that

\[
\hat{\tilde{A}}_r = \hat{\Psi}^*(x) \hat{A}_r \hat{\Psi}(x).
\]

Then

\[
[\hat{H}, \hat{\tilde{A}}_r] = \hat{\Psi} \left[ \hat{\Psi}^* \hat{H} \hat{\Psi}, \hat{\tilde{A}}_r \right] \hat{\Psi}^*
\]

and consequently

\[
\partial_r \hat{\tilde{A}}_r = iM^{1/2} [\hat{\Psi}^* \hat{H} \hat{\Psi}, \hat{\tilde{A}}_r].
\]

The composition rule (5.1) yields \( \hat{\Psi}^* \hat{H} \hat{\Psi} = (\hat{\Psi}^* \# \hat{H} \# \hat{\Psi}) \). The next step is to determine \( \Psi \) so that

\[
\hat{H} := \hat{\Psi}^* \# \hat{H} \# \hat{\Psi}
\]

is diagonal. Having \( \hat{H} \) diagonal implies that \( \hat{\tilde{H}} \) is diagonal and then \( \hat{A} \) remains diagonal if it initially is diagonal, since then

\[
\frac{d}{d\tau} \hat{\tilde{A}}_{jk}(\tau) = iM^{1/2} \left( \hat{H}_{jj} \hat{\tilde{A}}_{jk}(\tau) - \hat{\tilde{A}}_{jk}(\tau) \hat{H}_{kk} \right) = 0, \quad \text{for } j \neq k.
\]

The composition rule (5.1) with

\[
H(x, p) = \frac{|p|^2}{2} I + V(x)
\]

implies that

\[
\hat{H} = \hat{\Psi}^* \# \hat{H} \# \hat{\Psi}
\]

\[
= \frac{|p|^2}{2} I + \Psi^* V \Psi + \frac{1}{4M} \nabla \Psi^* \cdot \nabla \Psi
\]

\[
= \Psi^* \left( \frac{|p|^2}{2} I + V + \frac{1}{4M} \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^* \right) \Psi,
\]

as verified in [9, Lemma 3.1]. Therefore the aim is to choose the unitary matrix \( \Psi \) so that it is a solution to the non linear eigenvalue problem

\[
(V + \frac{1}{4M} \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^*) \Psi = \Phi \hat{\Lambda}
\]
where $\Lambda$ is diagonal, that is

$$\bar{H}(x, p) = \frac{|p|^2}{2} I + \Lambda(x). \quad \text{(5.3)}$$

A solution, $\Psi$, to this non-linear eigenvalue problem is an $O(M^{-1})$ perturbation of the eigenvectors to $V(x)$ provided the eigenvalues do not cross and $M$ is sufficiently large. The next section shows as in [9] that (5.2) has a unique solution, if also the potential $V$ is real analytic.

We also need a partition of the eigenvalues $\Lambda = \sum_{n=1}^{N} \Lambda^n$ related to the potential energy for each particle similar to (2.10) now including also the small non-linear part. In fact also the non-linear part has a natural composition into particle contributions, now based on the sensitivity of the eigenvectors with respect to position $x_n$. We have

$$V + \frac{1}{4M} \Psi \nabla \Psi \cdot \nabla \Psi = \sum_{n=1}^{N} (V^n + \frac{1}{4M} \Psi \nabla x_n \Psi \cdot \nabla x_n \Psi \Psi)$$

and define for $n = 1, \ldots, N$

$$\bar{\lambda}^n_k := \langle \Psi_k, (V^n + \frac{1}{4M} \Psi \nabla x_n \Psi \cdot \nabla x_n \Psi \Psi) \Psi_k \rangle, \quad k = 1, \ldots, d,$$

$$\bar{\Lambda}^n = \text{diag} (\bar{\lambda}^n_1, \ldots, \bar{\lambda}^n_d), \quad \text{(5.4)}$$

which implies

$$\bar{\Lambda} = \sum_{n=1}^{N} \bar{\Lambda}^n, \quad \bar{\lambda} = \sum_{n=1}^{N} \bar{\lambda}^n.$$

We will use the observables defining density, momentum and energy as follows. Let

$$\bar{\rho}_0(x, y) = \sum_{n=1}^{N} \eta(y - x^n) I$$

and as before its time evolution is determined by the Heisenberg-von Neumann equation

$$\partial_t \hat{\rho}_{\tau} = iM^{1/2}[\hat{\bar{H}}, \hat{\rho}_{\tau}],$$

with the solution

$$\hat{\rho}_{\tau} = e^{i\tau M^{1/2} \hat{\bar{H}}} \hat{\rho}_0 e^{-i\tau M^{1/2} \hat{\bar{H}}},$$

which shows that the time evolution also can be written as

$$\bar{\partial}_t \hat{\rho}_\tau = iM^{1/2} e^{i\tau M^{1/2} \hat{\bar{H}}} [\hat{\bar{H}}, \hat{\rho}_0] e^{-i\tau M^{1/2} \hat{\bar{H}}}. \quad \text{(5.5)}$$

The momentum and energy density symbols are defined as

$$\bar{\rho}_0 = \sum_{n=1}^{N} \eta(y - x^n) p^n I, \quad \bar{\rho}_0 = \sum_{n=1}^{N} \eta(y - x^n) (|p^n|^2 I + \bar{\Lambda}^n(x)).$$

The diagonal form of $\bar{H}$ combined with the property that the symbols $\bar{\rho}_0, \bar{\rho}_0$ and $\bar{E}_0$ and $\bar{H}$ are polynomials of degree at most two as functions of the momentum coordinate imply by Lemma 4.11 the reduction of the corresponding quantum commutators to classical Poisson brackets. Therefore, we have as in (4.3)

$$iM^{1/2} [\hat{\bar{H}}, \hat{\rho}_0] = -\text{div}_y \hat{\rho}_0,$$
and by (5.34)

\begin{equation}
(5.6) \quad \frac{\partial}{\partial \tau} \hat{\rho}_\tau = - \text{div}_y \hat{p}_\tau.
\end{equation}

Let $\hat{f}$ be a given density operator in $[L^2(\mathbb{R}^{3N})]^d$, as described precisely in Section 6. The conservation law for the mass becomes

\begin{equation}
(5.7) \quad \frac{\partial}{\partial \tau} \text{Tr} (\hat{\varphi} \hat{\rho}_\tau \hat{\varphi}^* \hat{f}) = - \text{div} \left( \text{Tr} (\hat{\varphi} \hat{p}_\tau \hat{\varphi}^* \hat{f}) \right).
\end{equation}

Theorem 5.1. Assume that $\hat{f}$ be a given density operator in $[L^2(\mathbb{R}^{3N})]^d$, as described precisely in Section 6. The conservation law for the momentum becomes

\begin{equation}
(5.8) \quad \frac{\partial}{\partial \tau} \hat{\varphi} \hat{p}_\tau \hat{\varphi}^* \hat{f} = - \text{div} \left( \text{Tr} (\hat{\varphi} \hat{\varphi}^* \hat{f}) \right),
\end{equation}

and the conservation law for the energy becomes

\begin{equation}
(5.9) \quad \frac{\partial}{\partial \tau} \text{Tr} (\hat{\varphi} \hat{p}_\tau \hat{\varphi}^* \hat{f}) = - \text{div} \left( \text{Tr} (\hat{\varphi} \hat{\varphi}^* \hat{f}) \right).
\end{equation}

In Section 6 we will motivate an initial density $\hat{f} = \hat{\varphi} \hat{\varphi}^* \hat{f}$ as a local grand canonical Gibbs density, where $\hat{f}$ is diagonal, with the local temperature and chemical potential determined by the macroscopic density and energy. That is, $\hat{f}$ is diagonalized be the same transformation as $\hat{H}$. These traces can be then written as

\begin{equation}
\text{Tr} (\hat{\varphi} \hat{\varphi}^* \hat{f}) = \text{Tr} (\hat{\varphi} \hat{\varphi}^* \hat{f} \hat{\varphi} \hat{\varphi}^* \hat{f}) = \text{Tr} (\hat{\varphi} \hat{\varphi}^* \hat{f} \hat{\varphi} \hat{\varphi}^* \hat{f}) = \text{Tr} (\hat{\varphi} \hat{\varphi}^* \hat{f})
\end{equation}

where $\hat{f}$ is diagonal and equal to $\hat{\varphi} \hat{\varphi}^* \hat{f}$, $\hat{S}$ and $\hat{Q}$, respectively.

The work [12] proves the following theorem which provides the classical limit of the quantum observables in the conservation laws. The proof is based on Weyl’s law, see [17, 9] namely that quantum observables has the classical representation

\begin{equation}
(5.11) \quad \frac{\text{Tr} (\hat{\varphi} \hat{\varphi}^* \hat{f})}{\text{Tr} (\hat{\varphi} \hat{\varphi}^* \hat{f})} = \sum_{j=1}^d \int_{\mathbb{R}^{2N}} \overline{A}_{jj} (0, z) \overline{f}_{jj} (z) dz
\end{equation}

for any $\overline{A}_{jj} (0, \cdot) \in L^2(\mathbb{R}^{2N})$ and $\overline{f}_{jj} \in L^2(\mathbb{R}^{2N}) \cap L^1(\mathbb{R}^{2N})$.
eigenvalues, and that there is a constant $C$ such that
\[
\max_i \sum_{\vert \alpha \vert \leq 3} \Vert \partial_x^\alpha \partial_x \lambda_j \Vert_{L^\infty(\mathbb{R}^N)} \leq C, \\
\sum_{\vert \alpha \vert \leq 3} \Vert \partial_x^\alpha \tilde{A}_{jj}(0, \cdot) \Vert_{L^2(\mathbb{R}^{2N})} \leq C, \\
\Vert \tilde{f} \Vert_{L^2(\mathbb{R}^{2N})} \leq C,
\]
hold, then there is a constant $c$, depending on $C$, such that the canonical ensemble average satisfies
\[
\left| \frac{\text{Tr} (\hat{A}_x \hat{f})}{\text{Tr} (\hat{f})} - \sum_{j=1}^d \int_{\mathbb{R}^{2N}} \frac{\tilde{A}_{jj}(0, z_j^0(z_0)) \tilde{f}_{jj}(z_0) \delta}{\sum_{k=1}^d \int_{\mathbb{R}^{2N}} f_{kk}(z)dz} \right| \leq cM^{-1},
\]
as $M \to \infty$, where $z_j^0 = (x_j, p_j)$ is the solution to the Hamiltonian system
\[
\begin{align*}
\dot{x}_j &= p_j \\
\dot{p}_j &= -\nabla \lambda_j(x_j), \quad \tau > 0,
\end{align*}
\]
(5.12)
based on the Hamiltonian $H_{jj}(z) = |p|^2/2 + \lambda_j(x)$, with initial data $(x_0, p_0) = z_0$.

We note that the classical limit can be written
\[
\sum_{j=1}^d \int_{\mathbb{R}^{2N}} \tilde{A}_{jj}(0, z_j^0(z_0)) \tilde{f}_{jj}(z_0) \delta \sum_{k=1}^d \int_{\mathbb{R}^{2N}} f_{kk}(z)dz \\
= \sum_{j=1}^d \int_{\mathbb{R}^{2N}} q_j^* \tilde{A}_{jj}(0, z_j^0(z_0)) \tilde{f}_{jj}(z_0) \delta \sum_{k=1}^d \int_{\mathbb{R}^{2N}} f_{kk}(z)dz,
\]
where the probability, $q_j^*$, to be in electron state $j$ is
\[
q_j^* := \frac{\int_{\mathbb{R}^{2N}} \tilde{f}_{jj}(z)dz}{\sum_{k=1}^d \int_{\mathbb{R}^{2N}} f_{kk}(z)dz}, \quad j = 1, \ldots, d.
\]
(5.13)

In conclusion, the quantum observables (5.7), (5.9) and (5.10) for macroscopic density, momentum and energy, based only on nuclei position and momentum coordinates and the electron eigenvalues, satisfy the conservation laws with well defined observables. These observables have a classical limit, as $M \to \infty$, provided $\lambda_j$ and $\tilde{\lambda}_j$ are sufficiently regular. In comparison, the Irving and Zwanzig quantum formulation also solves the conservation laws exactly, but the classical limit is not directly available.

The diagonal terms in the flux terms $\tilde{S}$ and $\tilde{Q}$ are the same as in the classical dynamics (4.6) and (3.9). Therefore Theorem 5.1 applied to the conservation laws (5.6) and (5.8), for the quantum observables using the splitting $p_j^N = v_j^N + u(y, \tau)$ for the fluxes $\tilde{S}$ and $\tilde{Q}$, implies that the canonical form of the conservation laws holds:
\[
\begin{align*}
\partial_\tau \rho(y, t) + \sum_{\ell=1}^3 \partial_{y_\ell} \left( \rho(y, t) u_\ell(y, \tau) \right) &= 0, \\
\partial_\tau \rho(y, \tau) u_j(y, \tau) + \sum_{\ell=1}^3 \partial_{y_\ell} \left( \rho(y, \tau) u_j(y, \tau) u_\ell(y, \tau) - \sigma_{\ell j}(y, \tau) \right) &= 0, \\
\partial_\tau E(y, \tau) + \sum_{\ell=1}^3 \partial_{y_\ell} \left( E(y, \tau) u_j(y, \tau) + q_\ell(y, \tau) - \sum_j \sigma_{\ell j}(y, \tau) u_j(y, \tau) \right) &= 0,
\end{align*}
\]
(5.14)
where
\[
\rho(y, \tau) = \sum_j q_j^* \int_{\mathbb{R}^N} \bar{\rho}_{jj}(z^j, y) \bar{f}_j(z_0) d z_0 ,
\]
\[
u(y, \tau) = \sum_j q_j^* \int_{\mathbb{R}^N} \bar{\nu}_{jj}(z^j, y) \bar{f}_j(z_0) d z_0 / \rho(y, \tau) ,
\]
\[
E(y, \tau) = \sum_j q_j^* \int_{\mathbb{R}^N} \bar{E}_{jj}(z^j, y) \bar{f}_j(z_0) d z_0 ,
\]
\[
\sigma(y, \tau) = \sum_j q_j^* \int_{\mathbb{R}^N} \bar{\sigma}(z^j; y, \tau) \bar{f}_j(z_0) d z_0 ,
\]
\[
q(y, \tau) = \sum_j q_j^* \int_{\mathbb{R}^N} \bar{q}(z^j; y, \tau) \bar{f}_j(z_0) d z_0 ,
\]
and \( \bar{\sigma}(z^j; y, \tau) \) and \( \bar{q}(z^j; y, \tau) \) are defined in (3.7) and (3.10), respectively, now using \( \lambda = \bar{\lambda}_j \), and
\[
\bar{\rho}_0 = \sum_n \eta(y - x^n)1 ,
\]
\[
\bar{\nu}_0 = \sum_n \eta(y - x^n)p^n1 ,
\]
\[
\bar{E}_0 = \sum_n \eta(y - x^n)\left( \frac{|p^n|^2}{2}1 + \bar{\Lambda}^n(x) \right) .
\]

Theorem 5.1 proves in particular that the observables are determined by a weighted average with the probability \( q_j^* \) to be in state \( j \). Using this probability model, the conservation laws 5.11 are consistent with the derivation of the conservation laws from the classical dynamics in Section 4.

5.1. Solution of the nonlinear eigenvalue problem. This section presents a version of the standard regular perturbation analysis of matrix eigenvalue problems, cf. [10], which shows that the nonlinear eigenvalue problem (5.2) can be written as a nonlinear system of first order partial differential equations solved by Cauchy-Kovalevsky’s theorem.

Define for small \( \epsilon \in \mathbb{R} \) the matrix \( \bar{V}(\epsilon) := \bar{V} + \epsilon B \) where \( \bar{V} \) and \( B \) are real symmetric \( d \times d \) matrices, depending on a parameter \( x \in \mathbb{R}^N \) and on another parameter \( M \in \mathbb{R} \). Assume also the matrices \( \bar{V} \) and \( B \) are real analytic as a function of \( x \). Differentiate, with respect to \( \epsilon \), the eigenvalue problem
\[
\bar{V}(\epsilon)\psi_k(\epsilon) = \lambda_k(\epsilon)\psi_k(\epsilon) ,
\]
with the eigenvalues \( \lambda_k(\epsilon) \in \mathbb{R} \) and the corresponding normalized real valued eigenvectors \( \psi_k(\epsilon) \in \mathbb{R}^d, k = 1, \ldots, d \), to obtain
\[
(\bar{V}(\epsilon) - \lambda_k(\epsilon))\psi_k'(\epsilon) = -(\bar{V}'(\epsilon) - \lambda_k'(\epsilon))\psi_k(\epsilon) .
\]
The scalar product with \( \psi_\ell(\epsilon) \) implies the bounded derivatives
\[
\psi_\ell^* \psi_k'(\epsilon) = \frac{\psi_\ell^*(\epsilon)B\psi_k(\epsilon)}{\lambda_\ell(\epsilon) - \lambda_k(\epsilon)} \quad \ell \neq k ,
\]
\[
\lambda_k'(\epsilon) = \psi_k(\epsilon)^*B\psi_k(\epsilon) .
\]
The remaining component in the \( \psi_k(\epsilon) \) direction becomes zero by the normalization
\[
0 = \frac{d}{d\epsilon} (\psi_k(\epsilon)^*\psi_k(\epsilon)) = 2\text{Re}\left( \frac{d\psi_k(\epsilon)}{d\epsilon} \right)^*\psi_k(\epsilon) = 2(\frac{d\psi_k(\epsilon)}{d\epsilon})^*\psi_k(\epsilon) .
\]
In particular, the non linear eigenvalue problem \((5.17)\) has \(B(x) = \Psi(x)\nabla\Psi^*(x) \cdot \nabla\Psi(x)\Psi^*(x)\) so that it can be written as the system of partial differential equations

\[
\begin{align*}
\psi^\ell(x, \epsilon) & \frac{\partial}{\partial \epsilon} \psi^k(x, \epsilon) = \frac{(\nabla\Psi^*(x, \epsilon) \cdot \nabla\Psi(x, \epsilon))_{kk}}{\lambda_k(x, \epsilon) - \lambda_k(x, \epsilon)} , \quad \ell \neq k , \quad 0 < \epsilon < \frac{1}{4M} , \\
\psi^\ell(x, \epsilon) & \frac{\partial}{\partial \epsilon} \psi^k(x, \epsilon) = 0 , \\
\frac{\partial}{\partial \epsilon} \lambda_k(x, \epsilon) & = (\nabla\Psi^*(x, \epsilon) \cdot \nabla\Psi(x, \epsilon))_{kk} ,
\end{align*}
\tag{5.17}
\]

with the initial data

\[
\begin{align*}
\Psi(x, 0) & = \bar{\Psi}(x) , \\
\lambda_k(x, 0) & = \bar{\lambda}_k(x) .
\end{align*}
\]

where \(\bar{\lambda}_1(x), \ldots, \bar{\lambda}_d(x)\) and \((\bar{\Psi}(x))\) are the eigenvalues and the matrix of eigenvectors of \(\hat{V}(x)\). There is a solution to \((5.17)\) for large \(M\) in the case that \(V\) is real analytic and the eigenvalues \(\bar{\lambda}_k\) are distinct for all \(x\): since then also \(\bar{\lambda}\) and \(\bar{\Psi}\) are real analytic and Cauchy-Kovalesky’s theorem, see [4], yields a local solution to the nonlinear system of partial differential equations \((5.17)\).

6. The initial particle density

Assume we know the initial data \((\rho(\cdot, 0), \rho u(\cdot, 0), E(\cdot, 0))\) for the macroscopic conservation laws, although in practise this data can be hard to determine, e.g. for the flow in a river. Current molecular dynamics simulations can only use a small fraction of the number of particles in a real system. Therefore we need an initial particle density that is related to a larger ensemble. We seek a density that has the property that the marginal distribution of a subsystem weakly coupled to a larger heat bath system is the same as the whole system. Under certain assumptions stated in [9] the classical Gibbs density is the only density with this property. Given the local values of the macroscopic conserved variables the goal here is therefore to determine a local grand canonical Gibbs density

\[
\bar{f}_j(x, p; y) \sim e^{-\mathcal{H}(x, p, j; y)/T(y)}
\]

where

\[
\mathcal{H}(x, p, j; y) := \sum_{n=1}^{N} \eta(y - x^n)(\hat{H}^n(x, p, j) - M_n\mu(y)) ,
\]

based on local values of the temperature \(T(y)\) and the chemical potential \(\mu(y)\), such that

\[
\begin{pmatrix}
\rho(y, 0) \\
\rho u(y, 0) \\
E(y, 0)
\end{pmatrix} = (\text{Tr}(\hat{f}))^{-1}\text{Tr}\left(\begin{pmatrix}
\bar{\rho}_0 \\
\bar{\rho}_0 \\
\bar{E}_0
\end{pmatrix} \hat{f}\right) .
\tag{6.2}
\]

Weyl’s law given by the quantum-classical representation \((5.11)\) combined with \((6.2)\) show that the equation

\[
\rho u(y, 0) = \frac{\int_{\mathbb{R}^d} \sum_{n=1}^{N} \eta(y - x^n)p^n \sum_{j=1}^{d} \bar{f}_j(x, p)dxdp}{\int_{\mathbb{R}^d} \sum_{j=1}^{d} \bar{f}_j(x, p)dxdp}
\]

defines the initial velocity \(u(y, 0)\). It remains to verify if varying \(T(y)\) and \(\mu(y)\) yield large enough sets to match the initial data for \(\rho\) and \(E\).

If \(|\mu(y)| \gg 1\) we roughly get \(\mathcal{H} \sim -\sum_{n=1}^{N} \eta(y - x^n)\mu(y)\). Laplace principle implies that as \(\mu(y) \to -\infty\) the grand canonical density will sample the minimum of the observable \(\sum_{n=1}^{N} \eta(y - x^n)\mu(y)\).
(x^n) and as \( \mu(y) \to \infty \) the microscopic particle density will sample the maximum of \( \sum_{n=1}^{N} \eta(y - x^n) \). Therefore varying \( \mu(y) \) from \( -\infty \) to \( \infty \) will change the local density

\[
\rho(y, 0) = \frac{\int_{\mathbb{R}^{6N}} \eta(y - x^n)M_n \sum_{j=1}^{d} \tilde{f}_j(x, p)dx dp}{\int_{\mathbb{R}^{6N}} \tilde{f}_j(x, p)dx dp}
\]

from nearly vacuum to arbitrary high macroscopic density.

The temperature is related to the microscopic kinetic energy and we have

\[
E(y, 0) = \frac{\int_{\mathbb{R}^{6N}} \sum_{n=1}^{N} \sum_{j=1}^{d} \eta(y - x^n)(|\tilde{p}|^2 + \lambda_n^2(x)) \tilde{f}_j(x, p)dx dp}{\int_{\mathbb{R}^{6N}} \tilde{f}_j(x, p)dx dp}
\]

We see that the factor \( \eta(y - x^n)\frac{|\tilde{p}|^2}{2M_n}e^{-\eta(y-x^n)|p|^2/(T(y)/2M_n)} \) upon integration with respect to \( p^n \) will be proportional to \( T(y) \). The other terms in \( E(y, 0) \) will have upper and lower bounds uniform in \( T \). Therefore by varying the temperature a large open set of macroscopic energies can be attained.

Finally, we note that minimizing the entropy \( \sum_{j=1}^{d} \int_{\mathbb{R}^{6N}} \tilde{f}_j(z) \log \tilde{f}_j(z)dz \) under the constraints that the value of the macroscopic density is \( \rho(y, 0) \) and the macroscopic energy is \( E(y, 0) \) yields the probability density

\[
\tilde{f}_j(z) = ce^{-\sum_{n=1}^{N} \eta(y-x^n)M_n\lambda_0(y)-\sum_{n=1}^{N} \eta(y-x^n)\tilde{H}(z,j)\lambda_1(y)} = ce^{-\tilde{H}(z,j)}/T(y)
\]

for \( c = 1/\sum_{j=1}^{d} \int_{\mathbb{R}^{6N}} e^{-\tilde{H}(z,j)}/T(y)dz \) with the Lagrange multipliers \( \lambda_1(y) = 1/T(y) \) and \( \lambda_0(y) = \mu(y)/T(y) \). The Gibbs density \( \tilde{\lambda} \) is therefore consistent with this constrained minimization.

7. The partial derivatives \( \partial_{\rho,\lambda} \tilde{\lambda}(\tilde{x}) \)

The function \( \tilde{\lambda} \) is defined by \( \tilde{\lambda} \) on the set \( M \subset \mathbb{R}^{N(N-1)/2} \) consisting of all vectors \( r := (r_{12}, r_{13}, \ldots, r_{N-1,N}) \) such that there exist particle positions \( x^i \in \mathbb{R}^3, i = 1, \ldots, N \) and \( r_{ij} = |x^i - x^j| \) for \( 1 \leq i < j \leq N \). The goal here is to define the gradient \( \nabla_r \tilde{\lambda} \) such that the chain rule \( \nabla \tilde{\lambda}(x) = (\partial r/\partial x)^T \nabla_r \tilde{\lambda}(r) \) is valid on \( M \). We therefore need to solve the linear equation \( Av = b \) for \( v = \nabla_r \tilde{\lambda} \), where we have used the notation \( A = (\partial r/\partial x)^T \) and \( b = \nabla \tilde{\lambda} \). Since this is an underdetermined linear system we choose the solution \( v \) that minimizes the \( l^2 \) norm. The stationary point to the Lagrangian \( L(v, y) = |v|^2/2 + y \cdot (Av - b) \), where \( y \) is the Lagrange multiplier, has the solution

\[
v = A^T(AA^T)^{-1}b.
\]

Since generically the matrix \( A \) has full rank, equation (7.1) contains a computable expression for \( v = \nabla_r \tilde{\lambda} \), which can be used in the expression for the stress tensor in (3.7).

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