Derivation of the fundamental equations of continuum thermodynamics from statistical mechanics*

*This study emerged from a report on a work of Irving and Kirkwood [1] that was presented by the author in a seminar at Indiana University in summer 1954. The seminar was organized by Professor Clifford Truesdell whose inspiration is gratefully acknowledged by the author.

Introduction. Assuming a classical statistical system of point particles the fundamental equations of continuum thermomechanics (continuity equation, equation of motion, and energy equation) shall be derived exactly. The macroscopic state functions (density, velocity, stress, energy density, heat flux) are interpreted as expected values.

The systems can represent any continua (gases, liquids, solids). It is not assumed that the particles are identical. Also, the nature of the interacting forces can be different for different pairs of particles. Therefore it is not necessary that the particles are molecules in the sense of chemistry. The theory is also valid when the continuum is viewed as the system of its atoms (or even elementary particles). It appears to us physically justified to assume that atoms (or at least the elementary particles) are formed of points and rotational and internal degrees of freedom can be neglected. Hence, for the general theory there is no difference between a mixture and a chemical compound. The difference is solely due to the nature of the mutual potentials. The failure of classical mechanics in the atomistic realm and the influence of quantum mechanical effects, however, are not taken into account in our considerations.

In section 2 we will formulate the problem precisely and summarize the results. By introducing appropriate abbreviations in section 1 the considerable difficulties in assignment will be eased. In section 3 the sufficient conditions will be formulated under which the following investigations are valid. Sections 4 and 5 contain the derivation

†Translation†† of the paper

Die Herleitung der Grundgleichungen der Thermomechanik der Kontinua aus der Statistischen Mechanik, Indiana Univ. Math. J., 4:627–646, 1955.‡

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of the expected values of the state functions. In sections 6 and 7 we will prove the
validity of the fundamental equations, first for the case that no external forces are
present. In section 8 we will discuss the influence of external forces. Our investiga-
tions are crucially based on two mathematical Lemmas, formulated and proved in
section 9.

The problem being treated here was tackled by Irving and Kirkwood [1]. This work
differs from [1] in the following points:

1) The proofs satisfy all requirements of mathematical rigor and, additionally,
should be easier than the ones in [1].

2) For the stress tensor and the heat flux we give closed integral expressions. In
[1] these quantities are presented as infinite series which only makes sense if the
probability density as a function of the spatial variable is analytical everywhere.

3) The interpretation of stress tensor and heat flux as expected values will be
carried out in detail. This is only attempted in [1].

4) The assumption that all particles are identical is not made.

5) The external forces do not have to have a potential and may—apart from space
and time—depend also on the velocities of the particles.

6) The use of δ functions has been avoided. In [1] they only serve technical issues.

1 Definitions and assignments

a. Vectors and tensors. Vectors and points (point vectors) are described by lower
case letters in bold font, tensors of higher order are described by capital letters in bold
font. The product of two tensors (dyad) will be represented by the symbol ⊗, the
inner product of two vectors or of a vector and a tensor will be represented by a dot
“·”, and \( \nabla_x \cdot F(x) \) represents the differential (gradient) of the tensor \( F(x) \). \( \nabla_x \cdot F(x) \)
represents the differential (divergence) of \( F(x) \).

b. Probability density. We consider a system of point particles. The \( j^{th} \) par-
ticle is \( (j) \), its mass is \( m_j \). A state of this system is characterized by the par-
ticle locations \( x_1, \ldots, x_N \) and velocities \( \xi_1, \ldots, \xi_N \), i.e. indicated by a “point”
\( (x_1, \ldots, x_N; \xi_1, \ldots, \xi_N) = (x_i; \xi_i) \) of 6N-dimensional phase space \( \Omega \). This phase
space is the product of 2N three dimensional Euclidean vector spaces\(^1\). The proba-
bility density of the states in \( \Omega \) at time \( t \) is denoted by

\[
W = W(x_1, \ldots, x_N; \xi_1, \ldots, \xi_N; t) = W(x_i; \xi_i; t).
\]

c. Potential energy. We assume that the force exerted by \( (j) \) on \( (k) \), \( k_{jk} \), depends
only on the locations \( x_j \) and \( x_k \). By invariance it follows that \( k_{jk} \) must be a central
force whose contribution is dependent only on the distance \( r_{jk} = |x_j - x_k| \). Newton’s

\(^1\)The \( x_i \) and \( \xi_i \) vary in the entire, infinite three dimensional space and not only in a subregion of
it.
third law says that $k_{jk} = -k_{kj}$. The particle pair $(j),(k)$ therefore corresponds to a function,

$$(1.1) \quad V_{jk}(r) = V_{kj}(r),$$

such that $V_{jk}(r_{jk})$ yields the potential energy of the pair. Furthermore,

$$\begin{align*}
(1.2) \quad k_{jk} &= -\nabla_{x_j} V_{jk}(r_{jk}) = -V'_{jk}(r_{jk}) \frac{x_j - x_k}{r_{jk}} \\
&= -k_{kj} = -\nabla_{x_k} V_{jk}(r_{jk}) = V'_{jk}(r_{jk}) \frac{x_k - x_j}{r_{jk}}.
\end{align*}$$

For the total inner potential energy $U$ of the system this results in

$$(1.3) \quad U = U(x_1, \cdots, x_N) = \sum_{j<k} V_{jk}(r_{jk}) = \frac{1}{2} \sum_{j \neq k} V_{jk}(r_{jk}).$$

Here, one has to sum of all those pairs $(j,k)$ for which $j < k$ or $j \neq k$ is true. It is,

$$(1.4) \quad \nabla_{x_j} U = \sum_{k=1 \atop k \neq j}^N \nabla_{x_j} V_{jk}(r_{jk}) = \sum_{k=1 \atop k \neq j}^N V'_{jk}(r_{jk}) \frac{x_j - x_k}{r_{jk}}.$$

d. External forces. Apart from those forces acting on particle $(j)$ due to other particles we assume that yet another external force $k_j$ is exerted that depends only on location $x_j$ and the velocity $\xi_j$ of the particle at time $t$,

$$k_j = k_j(x_j, \xi_j, t).$$

Restrictively, we require, however, that the functions $k_j$ obey the equation

$$\begin{align*}
(1.5) \quad \sum_{j=1}^N \frac{1}{m_j} \nabla \xi_j \cdot k_j(x_j, \xi_j, t) &= 0
\end{align*}$$

identically. In particular, this condition is met if the $k_j(x_j, \xi_j, t)$ do not depend on $\xi_j$.

e. Integrals. The $(6N - 3)$-dimensional subspace of $\Omega$, when discarding the spatial variable $x_j$ belonging to $(j)$, shall be denoted $\Omega_j$. Analogously, we denote the subspace $\Omega_{jk}$ that comes from discarding $x_j$ and $x_k$. Let $F$ be a scalar, vector, or tensor function defined over $\Omega$. Then, the abbreviations,

$$\langle F | x_j = x, x_k = y \rangle, \quad \langle F | x_j = x, x_k = y \rangle,$$

mean that $F$ is the integral over $\Omega_j$ ($\Omega_{jk}$, respectively), where, after performing the integration, the free variable $x_j$ (or the variables $x_j$ and $x_k$, respectively) are to be replaced by $x$ (or by $x$ and $y$), respectively. Generally, we call

$$\int_y f(y) \, dy$$

the volume integral of $f(y)$ over the infinite three-dimensional space of locations $y$. Then, apparently, the relation

$$\begin{align*}
(1.6) \quad \int_y \langle F | x_j = x, x_k = y \rangle \, dy &= \langle F | x_j = x \rangle
\end{align*}$$

is true.
2 Posing the problem

We assume that the probability density, $W(x_i; \xi_i; t)$, is defined for all $(x_i, \xi_i) \in \Omega$ and is continuously differentiable with respect to all variables. Under the restriction that the external forces fulfill the condition (1.5) the principle of the conservation of probability in phase space yields the differential equation in conventional fashion,

\[
\frac{\partial W}{\partial t} = \sum_{i=1}^{N} \left\{-\xi_i \cdot \nabla x_i W + \frac{1}{m_i} (\nabla x_i U - k_i) \cdot \nabla \xi_i W\right\},
\]

which determines the rate of change of $W$.

It is the task of this study to derive the fundamental equations of thermomechanics from (2.1) under the regularity requirements that will be formulated in section 3.

First we will assume the absence of external forces so that (2.1) is simplified to

\[
\frac{\partial W}{\partial t} = \sum_{i=1}^{N} \left\{-\xi_i \cdot \nabla x_i W + \frac{1}{m_i} \nabla x_i U \cdot \nabla \xi_i W\right\}.
\]

The case of $k_i \neq 0$ will be treated in section 8. For $k_i = 0$ the fundamental equations are as follows:

A) Continuity equation

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0.
\]

B) Equation of motion

\[
\rho \left(\frac{\partial u}{\partial t} + u \cdot \nabla u\right) = \nabla \cdot S.
\]

C) Equation of energy

\[
\frac{\partial \epsilon}{\partial t} + \nabla \cdot (q - S \cdot u + \epsilon u) = 0.
\]

These fundamental equations connect the following macroscopic state functions:

\[
\begin{align*}
\rho &= \rho(x, t) = \text{Mass density}, \\
u &= u(x, t) = \text{Velocity}, \\
S &= S(x, t) = \text{Stress tensor}, \\
\epsilon &= \epsilon(x, t) = \text{Energy density}, \\
q &= q(x, t) = \text{Heat flux density}.
\end{align*}
\]

We will prove that these fundamental equations are true if the aforementioned state functions are interpreted as expected values. In sections 4–5 we will show that these expected values are given by the following expressions,

\[
\begin{align*}
\rho &= \sum_j m_j \langle W \mid x_j = x \rangle, \\
\rho u &= \sum_j m_j \langle \xi_j W \mid x_j = x \rangle.
\end{align*}
\]

\footnote{This requirement ensures that phase space is locally volume preserving.}
The stress tensor is symmetric and consists of a kinetic contribution, $S_K$, and an interaction contribution, $S_V$,

$\ \ \ \text{(2.7)} \quad S = S_K + S_V,$

$\ \ \ \text{(2.8)} \quad S_K = - \sum_j m_j (\xi_j - u) \otimes (\xi_j - u) W | x_j = x,$

$\ \ \ \text{(2.9)} \quad S_V = \frac{1}{2} \sum_{j \neq k} \int \left\{ \frac{z \otimes z}{|z|} V'_{jk}(|z|) \int_{\alpha=0}^1 (W | x_j = x + \alpha z, x_k = x - (1 - \alpha) z) d\alpha \right\} dz.$

The energy density splits into the kinetic energy density, $\epsilon_K$, and the interaction energy density, $\epsilon_V$,

$\ \ \ \text{(2.10)} \quad \epsilon = \epsilon_K + \epsilon_V,$

$\ \ \ \text{(2.11)} \quad \epsilon_K = \frac{1}{2} \sum_j m_j (\xi_j^2 W | x_j = x),$ 

$\ \ \ \text{(2.12)} \quad \epsilon_V = \frac{1}{2} \sum_{j \neq k} (V_{jk} (|x_j - x_k|) W | x_j = x).$

The heat flux has three terms, the kinetic contribution, $q_K$, the transport contribution, $q_T$, and the interaction contribution, $q_V$,

$\ \ \ \text{(2.13)} \quad q = q_K + q_T + q_V,$

$\ \ \ \text{(2.14)} \quad q_K = \frac{1}{2} \sum_j m_j (|\xi_j - u|^2 (\xi_j - u) W | x_j = x),$ 

$\ \ \ \text{(2.15)} \quad q_T = \frac{1}{2} \sum_{j \neq k} (\xi_j - u) V_{jk} (|x_j - x_k|) W | x_j = x),$ 

$\ \ \ \text{(2.16)} \quad q_V = -\frac{1}{2} \sum_{j \neq k} \int \left\{ \frac{z}{|z|} z \cdot V'_{jk}(|z|) \right\} \int_{\alpha=0}^1 \left\langle \left( \frac{\xi_j + \xi_k}{2} - u \right) W | x_j = x + \alpha z, x_k = x - (1 - \alpha) z \right\rangle d\alpha \right\} dz.$

3 \textbf{Regularity conditions}

The expectation expressions occurring in (2.5)-(2.16) are improper integrals over $W$ and $V_{jk}$. It is therefore clear that certain regularity conditions must be met for $W$ and $V_{jk}$ if the state functions in (2.5)-(2.16) are well-defined and the functions of $x$ and $t$ are continuously differentiable. Already the condition $\int_\Omega W d\Omega = 1$ requires that $W$ approaches zero sufficiently fast as $|x_j| \to \infty$ and $|\xi_j| \to \infty$.

The following three conditions are sufficient for the validity of the results in this work: A) There is a number $\delta > 0$ such that the function 

$G(x_i; \xi_i; t) = W(x_i; x_i; t) \prod_{j=1}^N |x_j|^{3+\delta} \prod_{k=1}^N |\xi_k|^{3+\delta},$
as well as its derivatives are restricted by a constant solely dependent on $t$.

B) The functions $V_{jk}(r)$ are defined for all $r$, continuously differentiable and, together with their derivatives, are finite.

C) The functions $k_{jk}(x, \xi, t)$ are defined for all values of $x, \xi, t$, continuously differentiable, and with the constants $A(t)$ and $B(t)$, solely dependent on time, and satisfy have,

$$|k_{jk}| < A(t)|\xi| + B(t), \quad |\nabla_\xi k_{jk}| < A(t)|\xi| + B(t).$$

These conditions are sufficient for the convergence of all the improper integrals, interchanging the order of integration, and for differentiation and integration etc.

Furthermore, condition A ensures the validity of the following Lemma, which is proved by partial integration:

Suppose that $F(x; \xi_i)$ is a continuously differentiable function defined in $\Omega$ which, with the constants $A$ and $B$, satisfies the inequalities,

$$|F| < A \prod_{k=1}^{N} |\xi_k|^3 + B, \quad |\nabla_{x_j} F| < A \prod_{k=1}^{N} |\xi_k|^3 + B, \quad |\nabla_{\xi_j} F| < A \prod_{k=1}^{N} |\xi_k|^3 + B.$$ 

Then, these formulas are valid:

$$\int F \nabla_{x_j} W = - \int W \nabla_{x_j} F, \quad \int F \nabla_{\xi_j} W = - \int W \nabla_{\xi_j} F,$$

where one integrates over a subspace of $\Omega$ that contains the space of $x_j$ or $\xi_j$, respectively, as another subspace (omitting the volume elements). In particular, if $F$ is independent of $x_j$ or $\xi_j$, one has,

$$\int F \nabla_{x_j} W = 0 \quad \text{or} \quad \int F \nabla_{\xi_j} W = 0,$$

respectively.

Note I. The equation (2.1) is a linear partial differential equation of first order for $W$. According to generally known rules $W(x; \xi; t)$ is therefore uniquely determined for all $t$ if the initial density, $W(x; \xi; 0) = W_0(x; \xi)$ is prescribed. Therefore it would be desirable to apply regularity conditions only to $W_0(x; \xi)$ and not to $W(x; \xi; t)$, and then prove A as a property of $W$. The author, however, did not yet succeed in this.

Note II. If $W$ is not differentiable for all $(x_j; \xi_j) \in \Omega$ and $t$ the equation (2.1) generally loses its meaning. The statistical mechanics, however, is meaningful if $W$ is only integrable over $\Omega$. It is possible to generalize our investigations to this case. The condition A can then be replaced by the requirement that $W \prod_{k=1}^{N} |\xi_k|^3$ be integrable for all $t$ over $\Omega$. Then, the expressions (2.3)–(2.16) remain meaningful. The state functions, however, being functions of $x$ and $t$ are no longer continuously differentiable for all values of $x$ and $t$ such that the fundamental equations in the form (2.2)–(2.4) in general, have no meaning. They must be replaced by the laws of conservation of mass, momenta, and energy in finite form.

To carry out this sort of generalization demands considerable formal work. But this can be avoided by understanding all the present differentiations in the sense of the
theory of distributions by L. Schwartz [2]. Then, (2.1) is completely equivalent
with the principle of conservation of probability. The fundamental equations (2.2)–
(2.4) are generally valid in the sense of the theory of distributions and also when
the probability density $W$ does not even exist. In this latter case $W$ and the state
functions are to be viewed as measures. The fundamental equations are valid in
the conventional sense only for those values of $x$ and $t$ for which the state functions
represent continuously differentiable functions. One can readily derive the transition
conditions at the discontinuity surfaces (collision and acceleration waves) once (2.2)–
(2.4) are understood in the sense of distributions.

4 Expected values of the state functions

The value of a physical quantity, $F$, for the particle $(j)$ shall be given by a function,
$f_j(x_i; \xi_i)$, defined in $\Omega$. According to the rules of probability calculus and according
to section 1e one has

$$ (4.1) \quad \mathcal{E}_j(F) \, dx = \langle f_j \, W \mid x_j = x \rangle dx $$

as the expected value of $F$ for $(j)$ under the condition that $(j)$ is in the volume element
$dx$ at $x$. Hence, the density $\mathcal{E}(F)$ of the expected value of $F$ for all particles at the
position $x$ is

$$ (4.2) \quad \mathcal{E}(F) = \sum_j \mathcal{E}_j(F) = \sum_j \langle f_j W \mid x_j = x \rangle. $$

The expected value of $F$ for $(j)$ under the condition that $(j)$ is in the volume element
$dx$ at $x$ and $(k)$ in the volume element $dy$ at $y$ is given by

$$ (4.3) \quad \mathcal{E}_{jk}(F) \, dx \, dy = \langle f_j \, W \mid x_j = x, x_k = y \rangle \, dx \, dy. $$

a. Density and velocity. It follows immediately from (4.2) that (2.5) and (2.6) repre-
sent the expected values for mass and momentum densities.

b. Stress tensor. Let $J$ be a region of three-dimensional space with a continuously
differentiable boundary, $\mathcal{F}$. We call $A$ the exterior of $J$ with $n_x$ being the normal
unit vector at $x \in \mathcal{F}$ pointing outwards, and with $d\mathcal{F}_x$ the associated surface element
(see Fig. 1).

As generally known, the stress tensor is characterized by the fact that for any part
$J$ of the considered body, the force, $k$, exerted by $A$ on $J$ can be represented in the form

$$ (4.4) \quad k = \int_{\mathcal{F}} S(x) \cdot n_x \, d\mathcal{F}_x. $$

One readily sees that according to (2.8),

$$ (4.5) \quad k_K = \int_{\mathcal{F}} S_K \cdot n_x \, d\mathcal{F}_x $$

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3Translator’s footnote: The image was cropped from a pdf of the original paper. Note the differences in font styles in the figure and in the text.
gives the expected value of the “kinetic” force that corresponds to the momentum per unit time transported from \(A\) to \(J\). Therefore \(J\) has to be thought of moving along with the average velocity \(u\). The kinetic contribution \(2.8\) corresponds to what is normally called “viscous tension”, in the kinetic theory of mono atomic gases.

Figure 1:

Now, let us assume that the particle \((j)\) is at the position \(x_j = v \in J\) and that the particle \((k)\) be at the position \(x_k = w \in A\). Then, according to \(1.2\), \((k)\) exerts the following force on \((j)\),

\[
\mathbf{k}_{jk}(v, w) = -\nabla_v V_{jk}(|v - w|) \frac{v - w}{|v - w|}.
\]

According to \(4.3\), the expected value of the force, exerted by \((k)\) in \(A\) on \((j)\) in \(J\), is therefore given by

\[
\int_{v \in J} \int_{w \in A} \sum_{j \neq k} \mathbf{k}_{jk}(v, w) \langle W | x_j = v, x_k = w \rangle \, dv \, dw.
\]

After summation over \(j\) and \(k\) we obtain from the expected value \(k_V\) of the total force that is exerted by the particles in \(A\) on those in \(J\). With \(4.6\) this yields

\[
k_V = -\int_{v \in J} \int_{w \in A} \sum_{j \neq k} \left\{ \frac{v - w}{|v - w|} V'_{jk}(|v - w|) \langle W | x_j = v, x_k = w \rangle \right\} \, dw \, dv.
\]

As one can readily see, the integrand fulfills the conditions \(A, B\) and \(C\) of section 9. According to Lemma II, \(9.4\) and with \(2.9\) it therefore follows that

\[
k_V = \int_{\mathcal{F}} \mathbf{S}_V \cdot \mathbf{n}_x \, d\mathcal{F}_x.
\]

The force \(k\) exerted by \(A\) on \(J\) is composed from the kinetic force \(k_K\) \(4.5\) and the interaction force \(k_V\) \(4.7\). Because of \(2.7\) we therefore have,

\[
k = k_K + k_V = \int_{\mathcal{F}} (\mathbf{S}_K + \mathbf{S}_V) \cdot \mathbf{n}_x \, d\mathcal{F}_x = \int_{\mathcal{F}} \mathbf{S} \cdot \mathbf{n}_x \, d\mathcal{F}_x.
\]
This equation satisfies (4.4) and so the expected value of the stress tensor is indeed given by (2.7)–(2.9).

c. Energy density. Let us think of the kinetic energy, $\frac{1}{2}m_j\xi_j^2$, of particle $(j)$ as being localized at the position $x_j$ of this particle. Then, according to (4.2) the expected value, $\epsilon_K(x)$, of the kinetic energy density at position $x$ is given by (2.11).

The localization of the potential energy demands a certain arbitrariness as it is assigned to particle pairs, and not—as for the kinetic energy—to individual particles. We assume that the potential energy corresponding to the pair $(j), (k)$, $V_{jk}(|x_j - x_k|)$, is distributed equally at the positions $x_j$ and $x_k$. Then, at position $x_j$, the total potential energy is,

\[(4.8) \quad V_j = V_j(x_1, \cdots, x_N) = V_j(x_i) = \frac{1}{2} \sum_{k=1}^{N} V_{jk}(r_{jk}), \quad r_{jk} = |x_j - x_k|.\]

Then, according to (4.2), (2.12) yields the expected value, $\epsilon_V(x)$, of the density localized according to (4.8).

d. Heat flux (density). The heat flux, $q = q(x)$, is characterized by the fact that for any part $J$ of the body, the energy transferred per unit time from $J$ to $A$, can be represented in the form,

\[(4.9) \quad Q = \int_F q(x) \cdot n_x \, dF_x,\]

(see Fig.1).

One is readily convinced that with (2.14) the expected value of the kinetic energy flowing per unit time from $J$ to $A$ is represented by the expression

\[(4.10) \quad Q_K = \int_F q_K \cdot n_x \, dF_x.\]

Therefore, $q_K$, given by (2.14), is indeed the kinetic contribution of the heat flux. This is well known from the kinetic theory of mono-atomic gases.

Let us consider the expression,

\[(4.11) \quad q_T^* = q_T + \epsilon_V u = \frac{1}{2} \sum_{j \neq k} \langle \xi_j V_{jk}(|x_j - x_k|)W | x_j = x \rangle,\]

and compare to (2.12) and (2.15). According to (4.8) we have

\[(4.12) \quad q_T^* = \sum_j \langle \xi_j V_j W | x_j = x \rangle.\]

The expression $\xi_j V_j(x_j)$ indicates the flow of potential energy, localized according to (4.8) at $x_j$. Therefore, with (4.12) and because of (4.2), we have

\[Q_T^* = \int_F q_T^* \cdot n_x \, dF_x\]

as the potential energy that must be transferred per time unit through $F$. However, $J$ has to be seen as fixed in time. In order to obtain the potential energy $Q_T$
that is transported per time unit via the moving surface $\mathcal{F}$ one has to subtract the macroscopic convection contribution,

$$Q_T^0 = \int_{\mathcal{F}} \epsilon_V u \cdot n_x \, d\mathcal{F}_x.$$  

So, because of (4.11) one finds

(4.13) $$Q_T = Q_T^* - Q_T^0 = \int_{\mathcal{F}} q_T \cdot n_x \, d\mathcal{F}_x.$$  

Therefore, the $q_T$ given in (2.15) is indeed the contribution of the heat flux that stems from the transport of the potential energy.

Finally, let us consider

$$q_V^* = q_V - S_V \cdot u$$  

(4.14)

$$= -\frac{1}{2} \sum_{j \neq k} \int \mathbb{I}_{\mathbb{R}^3} \frac{z}{|z|} z \cdot V'_{jk}(|z|)$$  

$$\cdot \int_{|x|}^{1} \left\langle \frac{\xi_j + \xi_k}{2} \right\rangle \left\langle \frac{\xi_j + \xi_k}{2} \right\rangle W | x_j = x + \alpha z, x_k = x - (1 - \alpha) z \rangle \, d\alpha \right\rangle \, d\mathcal{F}_x,$$  

(compare to (2.9) and (2.16)). In section 5 we will show that

(4.15) $$Q_V^* = \int_{\mathcal{F}} q_V^* \cdot n_x \, d\mathcal{F}_x$$  

represents the expected value of the potential energy, transferred per unit time from $J$ to $A$, which stems from particles in $A$ performing work on particles in $J$. Here, $J$ can be viewed as fixed in time. In order to obtain the interaction energy $Q_V$, transferred from $A$ to the moving $J$, one has to subtract from $Q_V^*$ the macroscopic interaction work performed by $J$ on $A$ per unit time,

$$Q_V^0 = -\int_{\mathcal{F}} (S_V \cdot u) \cdot n_x \, d\mathcal{F}_x.$$  

So, according to (4.14) one finds that

(4.16) $$Q_V = Q_V^* - Q_V^0 = \int_{\mathcal{F}} (q_V^* + S_V \cdot u) \cdot n_x \, d\mathcal{F}_x = \int_{\mathcal{F}} q_V \cdot n_x \, d\mathcal{F}_x.$$  

Consequently, (2.16) indeed gives the interaction contribution to the heat flux.

$Q = Q_K + Q_T + Q_V$ is the total energy per unit time transferred from the moving $J$ to $A$, and (4.9) is satisfied because of (4.10), (4.13), (4.15), and (2.13). It has therefore been shown that the expected value of the heat flux is indeed given by (2.13)-(2.16).

5 Interaction contribution to the heat flux

We wish to prove the validity of equation (4.15), replacing expression (4.14) by $q_V^*$. To this end we investigate the mechanical system $S$ composed solely from particles
\[ \psi(x_i \in J; t) = \sum_{x_j \in J} \sum_{x_k \in A} V_{jk}(|x_j - x_k(t)|). \]

Here, \( x_j \in J \) is to be viewed as the independent variable while \( x_k(t) \) are those functions that describe the trajectories of the particles \( x_k \in A \). The internal energy of the system \( S \) is \( E_I \). Then, the total energy \( E \) with respect to the external potential (5.1) is given by

\[ E = E_I + \psi(x_i \in J; t). \]

According to the energy law in particle mechanics,

\[ \dot{E} = \frac{\partial}{\partial t} \psi(x_i \in J; t) \]

along with (5.1)

\[ \dot{E} = \sum_{x_j \in J} \sum_{x_k \in A} V'_{jk}(r_{jk}) \frac{x_j - x_k(t)}{|x_j - x_k(t)|} \cdot (-\dot{x}_k(t)) \]

and because of \( \dot{x}_k = \xi_k \),

\[ \dot{E} = - \sum_{x_j \in J} \sum_{x_k \in A} V'_{jk}(r_{jk}) \frac{x_j - x_k}{r_{jk}} \cdot \xi_k, \quad r_{jk} = |x_j - x_k|. \]

The energy, \( E \), however, does not equal that energy that is localized in \( J \) according to (4.8). The energy \( E^* \) localized in \( J \) according to that statement is composed from the internal energy \( E_I \) and half of the potential energy that corresponds to all those particle pairs \((j), (k)\) for which \( x_j \in J \) and \( x_k \in A \). Therefore, we have:

\[ E^* = E_I + \frac{1}{2} \sum_{x_j \in J} \sum_{x_k \in A} V_{jk}(r_{jk}). \]

From this, (5.1) and (5.2) results

\[ E^* = E - \frac{1}{2} \sum_{x_j \in J} \sum_{x_k \in A} V_{jk}(r_{jk}). \]

Differentiation with respect to \( t \) yields

\[ \dot{E}^* = \dot{E} - \frac{1}{2} \sum_{x_j \in J} \sum_{x_k \in A} V'_{jk}(r_{jk}) \frac{x_j - x_k}{r_{jk}} \cdot (\xi_j - \xi_k), \]

where \( \dot{x}_j \) and \( \dot{x}_k \) have been replaced by \( \xi_j \) and \( \xi_k \), respectively. Insertion of (5.3) into (5.5) results in

\[ \dot{E}^* = - \sum_{x_j \in J} \sum_{x_k \in A} V'_{jk}(r_{jk}) \frac{x_j - x_k}{r_{jk}} \cdot \frac{\xi_j + \xi_k}{2}. \]
This expression indicates how much the energy, localized by statement (4.8) in $\mathcal{J}$, varies per unit time and due to the interaction between the particles. The energy flux contribution directed from $\mathcal{J}$ to $\mathcal{A}$ is therefore given by $-\dot{E}^\ast$. According to (4.3), the expected value of this contribution has the form,

$$Q^\ast_V = \int_{v \in \mathcal{J}} \int_{w \in \mathcal{A}} \sum_{j \neq k} V'_{jk}(|v - w|) \frac{v - w}{|v - w|} \cdot \left( \xi_j + \frac{\xi_k}{2} W \big| x_j = v, x_k = w \right) dvdw.$$

The integrand fulfills the conditions $A, B, C$ in section 9. With (4.14) this results according to Lemma II, (9.4) in

$$Q^\ast_V = \int_{\mathcal{J}} q^\ast_V \cdot n_x dF_x.$$

Q.E.D.

### 6 Continuity equation and equation of motion

The proof of the continuity equation (2.2) is very easy. Multiply (2.1a) with $m_j$, integrate over $\Omega_j$, replace $x_j$ by $x$ and sum over $j$. Because of (3.2) various terms cancel. Eventually, one obtains equation (2.2) with (2.5) and (2.6).

We multiply (2.1a) with $m_j \xi_j$, integrate over $\Omega_j$, replace the free variable $x_j$ by $x$ and finally sum over $j$, then, taking (3.2) and (2.6) into account, we obtain the equation

$$\frac{\partial}{\partial t} (\rho u) = v_1 + v_2,$$

where

$$v_1 = - \sum_j m_j \langle \xi_j (\xi_j \cdot \nabla_{x_j} W) | x_j = x \rangle,$$

$$v_2 = \sum_j \langle (\nabla_{x_j} U \cdot \nabla \xi_j W) \xi_j | x_j = x \rangle.$$

Exchanging integration and differentiation with respect to $x_j$ in (6.2) yields,

$$v_1 = \nabla_x \cdot \left\{ - \sum_j m_j \langle (\xi_j \otimes \xi_j) W | x_j = x \rangle \right\}.$$

Since,

$$(\xi_j \otimes \xi_j) = (\xi_j - u) \otimes (\xi_j - u) + u \otimes \xi_j + \xi_j \otimes u - u \otimes u,$$

and taking (2.5), (2.6), and (2.8) into account, it follows that

$$v_1 = \nabla_x \cdot \{ S_K - u \otimes \rho u \} = \nabla_x \cdot S_K - u \nabla_x \cdot (\rho u) - \rho u \cdot \nabla_x u.$$
Inserting (3.1) in (6.3) yields

$$v_2 = - \sum_j \langle \nabla_{x_j} U W \mid x_j = x \rangle.$$  

If we replace $\nabla_{x_j} U$ by expression (1.4) we find

$$v_2 = - \sum_{j \neq k} \left\langle V'_{jk}(r_{jk}) \frac{x_j - x_k}{r_{jk}} W \mid x_j = x \right\rangle, \quad r_{jk} = |x_j - x_k|.$$  

With (1.6),

$$v_2 = - \int_y \left\{ \frac{x - y}{r} \sum_{j \neq k} V'_{jk}(r) \langle W \mid x_j = x, x_k = y \rangle \right\} d\mathbf{y}, \quad r = |x - y|.$$  

One can easily see that the integrand fulfills the conditions $A, B, C$ in section 9. In particular, the validity of (9.1) is found if the summation indices $j$ and $k$ are exchanged in (6.5). According to Lemma I, (9.2) follows with (2.9),

$$v_2 = \nabla_x \cdot S_V.$$  

We insert this and (6.4) into (6.1), and obtain,

$$\frac{\partial}{\partial t} (\rho u) = u \frac{\partial \rho}{\partial t} + \rho \frac{\partial u}{\partial t} = -u \nabla_x \cdot (\rho u) - \rho u \cdot \nabla_x u + \nabla_x \cdot (S_K + S_V).$$  

Bearing in mind the continuity equation (2.2) the equation of motion (2.3) indeed follows.

### 7 Energy equation

We multiply (2.1a) with $(1/2m_j \xi_j^2 + V_j)$ (see (4.8), integrate over $\Omega_j$, subsequently replace $x_j$ by $x$ and sum over $j$. Because of (3.2) various terms cancel. Eventually, with (2.10)-(2.12) we obtain

$$\frac{\partial \epsilon}{\partial t} = q_1 + q_2 + q_3,$$

where

$$q_1 = -\frac{1}{2} \sum_j m_j \langle \xi_j^2 \xi_j \cdot \nabla_{x_j} W \mid x_j = x \rangle,$$

$$q_2 = - \sum_j \sum_l \langle V_j \xi_l \cdot \nabla_{x_j} W \mid x_j = x \rangle,$$

$$q_3 = -\frac{1}{2} \sum_j \langle \xi_j^2 \nabla_{x_j} U \cdot \nabla_{\xi_j} W \mid x_j = x \rangle.$$
Exchanging integration and differentiation with respect to $x_j$ in (7.2) yields

$$q_1 = -\nabla_x \cdot \left\{ \frac{1}{2} \sum_j m_j (\xi^2_j W | x_j = x) \right\}.$$  

Because

$$\xi^2_j \xi_j = (\xi_j - \mathbf{u})^2 (\xi_j - \mathbf{u}) + 2 [(\xi_j - \mathbf{u}) \otimes (\xi_j - \mathbf{u})] \cdot \mathbf{u} + \mathbf{u} \xi^2_j + \mathbf{u}^2 (\xi_j - \mathbf{u}),$$

and taking (2.5), (2.6), (2.8), (2.11) and (2.14) into account, it follows that

(7.5) \hspace{1cm} q_1 = -\nabla_x \cdot (q_K - \mathbf{u} \cdot S_K + \mathbf{u} \epsilon_K).$

Inserting (4.8) into (7.3) and bearing (3.2) in mind, we obtain

(7.6) \hspace{1cm} q_2 = -\frac{1}{2} \sum_{j \neq k} \left\{ (V_{jk}(r_{jk}) \xi_j \cdot \nabla_{x_j} W | x_j = x) \right.  
\left. + (V_{jk}(r_{jk}) \xi_k \cdot \nabla_{x_k} W | x_j = x) \right\}$

According to the product rule,

$$V_{jk}(r_{jk}) \nabla_{x_j} W = \nabla_{x_j} [V_{jk}(r_{jk})W] - \nabla_{x_j} V_{jk}(r_{jk})W.$$  

If one inserts this into the first term on the right hand side of (7.6) and rearranges the second term according to equation (3.1) this yields

(7.7) \hspace{1cm} q_2 = -\frac{1}{2} \sum_{j \neq k} \left\{-\nabla_x (\xi_j V_{jk}(r_{jk})W | x_j = x) \right.  
\left. + (\xi_j \cdot \nabla_{x_j} V_{jk}(r_{jk})W | x_j = x) + (\xi_k \cdot \nabla_{x_k} V_{jk}(r_{jk})W | x_j = x) \right\}.$$

Equation (3.1), applied to (7.4), yields

(7.8) \hspace{1cm} q_3 = -\sum_j (\xi_j \cdot \nabla_{x_j} UW | x_j = x) = -\sum_{j \neq k} (\xi_j \cdot \nabla_{x_j} V_{jk}(r_{jk})W | x_j = x),$

where (1.4) has been employed. Via addition of (7.7) and (7.3) and by insertion of (1.2) we obtain

(7.9) \hspace{1cm} q_2 + q_3 = -\nabla_x \cdot q^*_T - q_0,$

where $q^*_T$ is given by (4.11) and where

$$q_0 = \frac{1}{2} \sum_{j \neq k} \left\langle V_{jk}(r_{jk}) \frac{x_j - x_k}{r_{jk}} \cdot (\xi_j + \xi_k) W | x_j = x \right\rangle.$$

Because of (1.6), we can write $q_0$ in the form of

$$q_0 = \int_y \left\{ \frac{x - y}{r} \cdot \sum_{j \neq k} V'_{jk}(r) \cdot \left\langle \frac{\xi_j + \xi_k}{2} W | x_j = x, x_k = y \right\rangle \right\} dy, \quad r = |x - y|.$$
In the same way as for (6.5) one easily sees also here that the conditions $A, B, C$ in section 9 are fulfilled for this integrand. Therefore it follows from Lemma I, (9.2) that
\[ q_0 = -\nabla_x \cdot q_V^* \]
is true where $q_V^*$ is given by (4.14). Inserting this into (7.9) it follows with (7.5), (7.1), (4.11), and (4.14) that
\[ \frac{\partial \varepsilon}{\partial t} = -\nabla_x \cdot \{q_K - u \cdot S_K + u \varepsilon_K + q_T^* + q_V^*\} \]
\[ = -\nabla_x \cdot \{q_K + q_T + q_V - u \cdot (S_K + S_V) + u(\varepsilon_K + \varepsilon_V)\}, \]
i.e. the energy equation (2.4).

8 External forces

When the external forces $k_j$ are different from zero and provided that (1.5) is fulfilled, the following situation emerges:

a. The Continuity Equation (2.2) remains valid.

b. According to
\[ f = f(x, t) = \sum_j (k_j W | x_j = x) \]
the Equation of Motion (2.3) transforms into
\[ \rho \left( \frac{\partial u}{\partial t} + u \cdot \nabla_x u \right) = \nabla_x \cdot S + f \]
Here, $f(x, t)$ represents the expected value of the external force density, according to (4.2).

c. With
\[ A = A(x, t) = \sum_j (\xi_j \cdot k_j W | x_j = x) \]
the Energy Equation (2.4) becomes
\[ \frac{\partial \varepsilon}{\partial t} + \nabla_x \cdot (q - S \cdot u + \varepsilon u) = A. \]
Here, and according to (4.2), $A(x, t)$ corresponds to the expected value of the work performed by the external forces per unit volume and unit time.
To prove a we bear in mind that the equation (2.1) is obtained by adding the term,
\[ -\sum_{i=1}^N \frac{1}{m_i} k_i \cdot \nabla \xi_i W, \]
to the right hand side of (2.1a). According to the explanations in section 6 one has to add to the right hand side of (2.2) the term

\[- \sum_j \sum_l \frac{m_j}{m_l} (k_l \cdot \nabla \xi_l W \mid x_j = x).\]

Rearranging with the help of (3.1), we obtain

\[\sum_j m_j \left\langle \left( \sum_l \frac{1}{m_l} \nabla \xi_l \cdot k_l \right) W \mid x_j = x \right\rangle = 0.\]

This, however, entirely disappears according to (1.5), whereby we have proved claim \(a\). Completely analogous calculations prove claims \(b\) and \(c\).

From (8.1) and (8.3) one can see that the functional form \(f(x, t)\) and \(A(x, t)\) do not only depend on the external forces \(k_j\) but also on \(W\), i.e. the respective microscopic state of the system. In certain cases knowledge about certain macroscopic averages over \(W\) suffice for the determination of \(f\) and \(A\). We will treat two of such cases: A) Electrical and gravitational fields. If the external forces stem from an electric field of strength \(e_j(x, t)\), we have

\[(8.5) \quad k_j(x, \xi, t) = e_j e(x, t),\]

where \(e_j\) is the charge of particle \((j)\). For the expected value of the charge density \(\lambda\) and the electric current density \(i\), we obtain according to (4.2)

\[(8.6) \quad \lambda = \lambda(x, t) = \sum_j e_j \langle W \mid x_j = x \rangle,\]

\[(8.7) \quad i = i(x, t) = \sum_j e_j \langle \xi_j W \mid x_j = x \rangle.\]

With (8.5)–(8.7), (8.1) and (8.3) yield:

\[(8.8) \quad f = \lambda e, \quad A = i \cdot e.\]

For the case of a gravitational field, \(g(x, t)\), we have to set \(e_j = m_j\) and obtain, because of (2.5) and (2.6),

\[(8.9) \quad f = \rho e, \quad A = \rho u \cdot g.\]

B) Magnetic field. In this case

\[(8.10) \quad k_j(x, \xi, t) = e_j \xi \times b(x, t),\]

where \(b\) is the magnetic field strength. Because of

\[\nabla \xi \cdot k_j(x, \xi, t) = e_j (\text{rot} \xi \xi) \cdot b = 0\]

case (1.5) is fulfilled. For a restricted/limited \(b(x, t)\), the \(k_j\) satisfies the regularity condition \(c\) in section 3. Inserting (8.10) in (8.1) and (8.3), and with (8.7) borne in mind, we obtain

\[(8.11) \quad f = b \times i, \quad A = 0.\]
9 Two Lemmas

Let \( f(v, w) \) be a scalar vector- or tensor function of the two vector variables \( v \) and \( w \) that satisfy the following conditions:

A) \( f(v, w) \) is defined for all \( v \) and \( w \) and continuously differentiable.

B) There exists a \( \delta > 0 \) such that the function,
\[
g(v, w) = f(v, w)|v|^{3+\delta}|w|^{3+\delta},
\]
as well as its derivatives are bounded.

C) The functional relation
\[
f(v, w) = -f(w, v)
\]
is true.

Under these circumstances the following two Lemmas are valid.

**Lemma I.**

\[
\int_y f(x, y)dy = -\frac{1}{2} \nabla_x \cdot \int_z \{z \otimes \int_{\alpha=0}^{1} f(x + \alpha z, x - (1 - \alpha)z) d\alpha\} dz
\]

**Proof:** The conditions A and B ensure that the absolute convergence of the improper integrals, occurring in the following, as well as the validity of the anticipated exchanges of integration sequences etc. According to (9.1) we have,
\[
\int_y f(x, y)dy = -\int_y f(y, x)dy.
\]

If we introduce the new integration variable \( z = x - y \) into the left, and \( z = y - x \) into the right hand integral, we find
\[
\int_y f(x, y)dy = \int_z f(x, x - z)dz = -\int_z f(x + z, x)dz
\]

(9.3)
\[
= \frac{1}{2} \int_z [f(x, x - z) - f(x + z, x)]dz.
\]

According to the chain rule this gives
\[
\nabla_x f(x + \alpha z, x - (1 - \alpha)z) = \nabla_v f + \nabla_w f
\]
and
\[
\frac{d}{d\alpha} f(x + \alpha z, x - (1 - \alpha)z) = z \cdot (\nabla_v f + \nabla_w f)
\]
where we have to insert on the right hand sides \( v = x + \alpha z \) and \( w = x - (1 - \alpha)z \) as arguments of \( \nabla_v f \) and \( \nabla_w f \). Therefore, we have
\[
z \cdot \nabla_x f(x + \alpha z, x - (1 - \alpha)z) = \frac{d}{d\alpha} f(x + \alpha z, x - (1 - \alpha)z).
\]

Integration of this equation with respect to \( \alpha \) from \( \alpha = 0 \) to \( \alpha = 1 \) yields,
\[
z \cdot \nabla_x \int_{\alpha=0}^{1} f(x + \alpha z, x - (1 - \alpha)z)d\alpha = f(x + z, x) - f(x, x - z).
\]
Insertion into (9.3) yields (9.2). Q. E. D.

**Lemma II.** Let \( J \) be any region in space with piece-wise smooth border surface \( F \). Let \( A \) be the exterior of \( J \) and \( \mathbf{n_x} \) the normal unit vector at point \( x \) on \( F \) pointing outwards (see Fig. 1). Then,

\[
(9.4) \quad \int_{v \in J} \int_{w \in A} f(v,w) \, dw \, dv = -\frac{1}{2} \int_F \int_z \int_{\alpha=0}^1 f(x + \alpha z, x - (1 - \alpha)z)(z \cdot \mathbf{n_x}) \, d\alpha \, dz \, dF_x.
\]

**Proof:** First, one sees immediately that because of the antisymmetry of \( f(v,w) \) (9.1)

\[
\int_{v \in J} \int_{w \in J} f(v,w) \, dv \, dw = 0.
\]

Therefore, we have

\[
(9.5) \quad \int_{v \in J} \int_{w \in A} f(v,w) \, dv \, dw = \int_{v \in J} \int_{w} f(v,w) \, dw \, dv.
\]

Now, according to Lemma I,

\[
(9.6) \quad \int_{w} f(v,w) \, dw = \nabla_v \cdot g(v),
\]

where

\[
(9.7) \quad g(v) = -\frac{1}{2} \int_z \left\{ z \otimes \int_{\alpha=0}^1 f(v + \alpha z, v - (1 - \alpha)z) \, d\alpha \right\} \, dz.
\]

According to Gauss' theorem,

\[
\int_{v \in J} \nabla_v \cdot g(v) \, dv = \int_F g(x) \cdot \mathbf{n_x} \, dF_x.
\]

From this and from (9.5)–(9.7) results in the relation (9.4) claimed. Q. E. D.

**References**

[1] J.H. Irving and J.G. Kirkwood. The statistical mechanical theory of transport processes. IV. the equations of hydrodynamics. *J. Chem. Phys.*, 18:817–829, 1950. Available online at [doi:10.1063/1.1747782](https://doi.org/10.1063/1.1747782).

[2] L. Schwartz. *Théorie des distributions*. Paris, 1950.

**Appendix**

The following changes were made to equations in the original manuscript.

1. Equation (1.4): replaced \( \nabla x_j \) with \( \nabla x_j \).
2. Equation (2.14): replaced \((\xi_j - u)(\xi_j - u)^2\) with \(|\xi_j - u|^2(\xi_j - u)\).

3. Section 3: replaced \(G(x_i; \xi_i; t) = W(x_i; x_i; t) \prod_{j=1}^{N} |x_j|^{3+\delta} \prod_{k=1}^{N} |\xi_k|^{6+\delta}\) with

\[
G(x_i; \xi_i; t) = W(x_i; x_i; t) \prod_{j=1}^{N} |x_j|^{3+\delta} \prod_{k=1}^{N} |\xi_k|^{3+\delta}
\]

4. Equation (3.2)_1: replaced \(F \nabla x_j W = 0\) with \(\int F \nabla x_j W = 0\)

5. Equation (7.3): replaced \(\nabla x_2\) with \(\nabla x_j\).

6. Section 8: replaced \(\sum_j m_j \left\langle \left( \sum_l^1 \frac{1}{m_l} \nabla_{\xi_l} \cdot k_l \right) W \mid x_j = x \right\rangle\) with

\[
\sum_j m_j \left\langle \left( \sum_l^1 \frac{1}{m_l} \nabla_{\xi_l} \cdot k_l \right) W \mid x_j = x \right\rangle = 0
\]

7. Proof of Lemma II: replaced \(\int_{v \in J} \int_{w \in A} f(v, w) \, dv \, dw = 0\) with

\[
\int_{v \in J} \int_{w \in J} f(v, w) \, dv \, dw = 0
\]

8. Equation (9.5)_1: replaced \(\int_{v \in J} \int_{w \in A} f(v, w) \, dw \, dv\) with

\[
\int_{v \in J} \int_{w} f(v, w) \, dw \, dv
\]