Toward a relativistic microscopic substantiation of thermodynamics: the equilibration mechanism

A Yu Zakharov¹ and V V Zubkov²

¹Yaroslav-the-Wise Novgorod State University, Veliky Novgorod, Russian Federation
²Department of General Physics, Tver State University, Tver, Russian Federation

E-mail: Anatoly.Zakharov@novsu.ru, victor.v.zubkov@gmail.com

Abstract. The microscopic deterministic mechanism of the irreversible equilibration process in a relativistic classical system of interacting particles has been established.

1. Introduction
In the paper [1], the kinetic equation and the law of change in the total energy of particles were obtained. We have shown that the energy of a system of particles interacting via the scalar field changes irreversibly. The purpose of this work is to determine the microscopic relativistic mechanisms of thermodynamic equilibration processes.

2. Evolution of a system of particles in the first approximation with respect to the retardation time
To describe the dynamics of a system of interacting particles, we introduce a microscopic distribution function

\[ f_A(r, p, t) = \sum_A \delta^3(r-r_{AA}(t))\delta^3(p-p_{AA}(t)). \]  (1)

where \( r_{AA}(t) \) and \( p_{AA}(t) \) are the instantaneous position and momentum of the \( \alpha \)-th particle of type \( A \), respectively.

In the absence of external fields the exact relativistic kinetic equation has the following form [1]:

\[ \left( \frac{\partial}{\partial t} + \frac{cp}{\sqrt{p^2+m_A^2c^2}} \frac{\partial}{\partial r} + F(r, p, t) \frac{\partial}{\partial p} \right) f_A(r, p, t) = \frac{2}{m_Ac^2} \left( \frac{\partial\phi(r, t)}{\partial t} + \frac{cp}{\sqrt{p^2+m_A^2c^2}} \frac{\partial\phi(r, t)}{\partial r} \right) f_A(r, p, t), \]  (2)

where

\[ F(r, p, t) = -\frac{m_Ac}{\sqrt{p^2+m_A^2c^2}} \left[ \frac{\partial}{\partial r} + \frac{p}{m_Ac^2} \left( \frac{\partial}{\partial r} + \sqrt{p^2+m_A^2c^2} \frac{\partial}{\partial ct} \right) \right] \phi(r, t), \]  (3)

\[ \phi(r, t) = \int \hat{U}(r-r')f_A(r', p', t - \frac{|r-r'|}{c})d^3r'd^3p', \]  (4)
$U(r - r')$ is the potential energy determined for the particles at rest, $\frac{|r-r'|}{c}$ is the retardation of interactions between points $r$ and $r'$.

In the first approximation in the time retardation, we have

$$f \left( r', p', t = \frac{|r-r'|}{c} \right) \approx f(r', p', t) - \frac{|r-r'|}{c} \frac{\partial}{\partial t} f(r', p', t).$$

(5)

Taking into account (5), leaving in the expansion the terms of order not higher than $c^{-1}$, the kinetic equation (11) can be represented as:

$$\frac{\partial f_A(x, p, t)}{\partial t} + \frac{p}{m_A} \frac{\partial f_A(x, p, t)}{\partial x} = \frac{1}{c} \int \int \frac{dU(r-r')}{d^3 r} f_A(r', p', t) d^3 r' d^3 p'$$

$$- \int \int \left( U(r - r') \frac{r-r'}{|r-r'|} + \frac{\partial U(r-r')}{d^3 r} |r-r'| \right) d^3 r' d^3 p'.$$

(6)

Since in the case of an arbitrary potential $U(r)$ the quantity

$$W(r) = \left( U(r) \frac{r}{|r|} + \frac{\partial U(r)}{d^3 r} |r| \right) \neq 0,$$

(7)

then already in the first order in retardation the equation (6) is irreversible.

There is the only exception: the Coulomb potential $U_{\text{Coul}}(r) \sim r^{-1}$, for which $W_{\text{Coul}}(r) \equiv 0$ and irreversibility manifests itself only when higher order terms are taken into account. The same holds for the Lorentz force: irreversibility is manifested starting from the third-order terms $c^{-3}$. This fact has far-reaching consequences.

Let us introduce the notion of the moment of the potential:

$$U_{\text{mom}}(r - r') = U(r - r') |r - r'|.$$

(8)

Then we have

$$\left( U(r - r') \frac{r-r'}{|r-r'|} + \frac{\partial U(r-r')}{d^3 r} |r-r'| \right) = \frac{\partial}{d^3 r} U_{\text{mom}}(r - r'),$$

(9)

and the rate of change in the total energy of the system of particles in the first approximation in the retardation time can be represented in the form

$$\frac{d}{dt} \sum a \frac{m_a c^2}{\sqrt{1-(v_a/c)^2}}$$

$$= - \int \int d^3 r d^3 p f_A(r, p, t) \frac{p}{m_A} \int \int \frac{dU(r-r')}{d^3 r} f_A(r', p', t) d^3 r' d^3 p'$$

$$+ \int \int d^3 r d^3 p f_A(r, p, t) \frac{p}{m_A} \int \int \frac{dU_{\text{mom}}(r-r')}{d^3 r} \frac{\partial f_A(r', p', t)}{d^3 r} d^3 r' d^3 p'.$$

(10)

Here we took into account that in the first approximation in $c^{-1}$ the total energy of the particles can be written as

$$\sum a \frac{m_a c^2}{\sqrt{1-(v_a/c)^2}} \approx \sum a \left( m_a c^2 + \frac{m_a v_a^2}{2} \right).$$

(11)

The first term on the right-hand side of the equation (10) is the derivative of the potential interaction energy of resting point particles (or the potential energy of a system of interacting particles in the non-relativistic approximation). Indeed
Thus, the equation (10) can be written in the form

\[
\begin{align*}
\frac{d}{dt} \left( \sum_{a} \sum_{b} U_{ab}(r_a(t) - r_b(t)) \right) &= \frac{d}{dt} U(t).
\end{align*}
\]

Hence it follows that the first relativistic correction in the equation (13) describes the change in the non-relativistic energy of a system of interacting particles.

Consider now the second term on the right-hand side of the formula (10). For this, we take into account the following identities

\[
\begin{align*}
\int d^3p \frac{P_{r}}{m_A} f_A(r, p, t) &= \sum_{a} \frac{P_{r_a}}{m_A} \delta(r - r_a(t)) = j(r, t), \\
\int \frac{\partial f_A(r, p', t)}{\partial t} d^3p' &= \frac{\partial}{\partial t} \int f_A(r', p', t) d^3p' \\
&= \frac{\partial}{\partial t} n(r', t) = -\text{div } j(r', t),
\end{align*}
\]

where \(j(r, t)\) is the vector of the particle flux density.

As a result, the second term in (10) takes the form

\[
\begin{align*}
\int d^3r d^3p f_A(r, p, t) \frac{P_{r}}{m_A} \int \frac{\partial u_{\text{mom}}(r-r')}{\partial r} \frac{1}{c} \frac{\partial f_A(r', p', t)}{\partial t} d^3r' d^3p' &= -\frac{1}{c} \int d^3r j(r, t) \int \frac{\partial u_{\text{mom}}(r-r')}{\partial r} \text{div } j(r', t) d^3r' \\
&= \frac{1}{c} \int d^3r j_A(r, t) \int \frac{\partial^2 u_{\text{mom}}(r-r')}{\partial x_a \partial x_{\beta}} j_\beta(r', t) d^3r'.
\end{align*}
\]

Using the representation of the moment of potential in the form of the Fourier integral

\[
U_{\text{mom}}(r - r') = \frac{1}{(2\pi)^3} \int d^3k \bar{U}_{\text{mom}}(k) \exp(-ik(r - r')).
\]

we find

\[
\frac{\partial^2 u_{\text{mom}}(r-r')}{\partial x_a \partial x_{\beta}} = \frac{1}{(2\pi)^3} \int d^3k \bar{U}_{\text{mom}}(k) k_\alpha k_\beta \exp(-ik(r - r')).
\]

Consequently, the second term on the right-hand side of the formula (10) has the following form
As a result, the rate of change in the particle energy in the first approximation in the retardation of interactions has the following form:

\[
\frac{1}{(2\pi)^3} \int d^3k \, \mathcal{U}_{\text{mom}}(k) k_a k_b \\
\times \int d^3r \, j_{a}(r, t) \exp(-ikr) \int d^3r' \, j_{b}(r', t) \exp(ikr')
\]

\[
= \frac{1}{(2\pi)^3} \int d^3k \, |k| \mathcal{U}(k, t)|^2 \mathcal{U}_{\text{mom}}(k).
\]

Thus, the evolution of the nonrelativistic energy of a system of interacting particles in the first approximation in the retardation of interactions is determined by the Fourier transform of the moment of the interparticle potential. Let us express \( \hat{U}_{\text{mom}}(k) \) in terms of the Fourier transforms of the interatomic potential and the function \( \mathcal{V}(r) \):

\[
\hat{U}_{\text{mom}}(k) = \frac{8\pi}{|k|^2}
\]

By the definition of (8), the Fourier transform of the moment of a potential is the convolution of the functions \( \hat{U}(k) \) and \( \hat{V}(k) \):

\[
\hat{U}_{\text{mom}}(k) = -\frac{1}{\pi^2} \int d^3q \frac{\hat{U}(q)}{|k-q|^2}.
\]

Substitute this expression into the formula (20) and find

\[
\frac{d}{dt} \left( \sum_a \frac{m_a v_a^2(t)}{2} + \frac{1}{2} \sum_a \sum_b U_{ab}(r_a(t) - r_b(t)) \right)
\]

\[
= \frac{4}{(2\pi)^3} \int d^3k \, |k| \mathcal{U}(k, t)|^2 \int d^3q \frac{\hat{U}(q)}{|k-q|^2}.
\]

Thus, the function \( \hat{U}_{\text{mom}}(k) \) (22) is non-positive for all \( k \). Therefore, we have:

### 3. The stability criterion of interatomic potentials and the zero law of thermodynamics

Inter-atomic interactions in condensed matter physics are described, as a rule, using various model potentials. An extensive literature is devoted to the problem of finding inter-atomic potentials [3–6]. We will not limit our consideration to the choice of a specific form of model inter-atomic potentials. Let us take into account the only significant limitation on the explicit form of inter-atomic interactions. This limitation is due to the requirement for the existence of a thermodynamic limit, according to which the logarithm of the partition function of the system must be an extensive function. Inter-atomic potentials satisfying this requirement are called stable or non-catastrophic. The criterion for the stability of interatomic potentials was established in the works of Dobrushin, Fisher and Ruelle [7, 8]. In terms of the Fourier transform of potentials for the case of two-body inter-atomic potentials, this criterion has the form [9]:

\[
\hat{U}(q) \geq 0.
\]
Energy constancy is possible if and only if
\[
\frac{d}{dt}\left(\sum_a m_a v_a^2(t) + \frac{1}{2} \sum_a \sum_b U(r_a(t) - r_b(t))\right) = -\frac{4}{(2\pi)^3 c} \int d^3k |\tilde{j}(k, t)|^2 \int d^3q \frac{\tilde{v}(q)}{|q-k|^3} \leq 0.
\]
(25)

for all \(k\), i.e. all particles are at rest.

4. Discussion and future directions

The main results of this work are as follows.

It has been established that for the class of interatomic potentials stable according to Dobrushin-Fischer-Ruelle, the system of interacting particles, regardless of its initial state, in the absence of external fields, irreversibly passes into a state with minimum energy.

The relativity theory and the principle of causality lead to the following conclusions.

a. The non-existence of instantaneous interactions between particles is the reason that the thermodynamic behavior of systems.

b. A consistent microscopic explanation and substantiation of the zero principle of thermodynamics within the framework of classical nonrelativistic mechanics is impossible.

c. In the absence of external influences, the energy of a system of particles, the interaction potential between which at rest satisfies the Dobrushin-Ruelle-Fischer stability criterion, monotonically decreases over time and tends to a minimum. All particles are at rest in this state.

d. The energy excess of the initial state over the final state of the system is carried away by the field through which the particles interact.

What is the state of thermodynamic equilibrium of real systems?

Within the framework of the concept developed in this work, a more thorough analysis of the notion of an isolated system of particles is required. This is due to the fact that the concept of the potential energy of a system of interacting particles, which depends on the instantaneous simultaneous coordinates of these particles, does not exist within the framework of the relativistic theory. Therefore, the field through which the particles interact begins to play a decisive role. In fact, the field is an additional and very specific component of the system.

Within the framework of classical thermodynamics, an isolated system is a system of interacting particles that does not exchange either matter or energy with the surrounding world. In the relativistic theory, the issue of exchange with the outside world is considered separately for particles and for the field.

In this regard, we will consider two options for placing a particle system in a box.

- The walls are impenetrable for particles, but are transparent for the electromagnetic field. In this case, the escaping field carries away the excess of energy, and the system of particles inside the box comes to the ground state, in which all particles are at rest in accordance with the equation (26).

- The walls are impenetrable to both particles and the field. Then all the particles of the system are under the influence of the “external” field reflected by the walls of the box. In this case, one can expect that the system of particles passes into a stationary state of dynamic equilibrium with the field, by analogy with the simple model [10].

Since the interactions between atoms are of an electromagnetic nature and all real systems are always immersed in an alternating intrinsic and external electromagnetic field, the exchange of energy between macroscopic bodies to a large extent occurs not directly, but through a universal mediator – the electromagnetic field. The retardation of interactions transmitted by an electromagnetic field is a universal mechanism that implements the laws of thermodynamics.
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