WEAKLY NONLOCAL IRREVERSIBLE THERMODYNAMICS -
THE GUYER-KRUMHANSL AND THE CAHN-HILLIARD
EQUATIONS

Abstract. Examples of irreversible thermodynamic theory of nonlocal phenomena are given, based on generalized entropy current. Thermodynamic currents and forces are identified to derive the Guyer-Krumhansl and Cahn-Hilliard equations. In the latter case Gurtin’s rate dependent additional term is received through the thermodynamic approach.

1. Introduction

In the last decades there is a continuous interest in generalized classical continuum theories to include nonlocal phenomena. The best treated and most popular type of nonlocal theories includes higher- and higher order space derivatives (gradients) of the relevant variables into the governing equations. Those investigations are frequently called as gradient or weakly nonlocal continuum theories. However, one cannot include higher order gradients in the governing equations at an arbitrary place, all equations are to be compatible with basic physical principles, first of all with the Second Law of thermodynamics. More properly, we are to construct weakly nonlocal differential equations where the constitutive properties are determined so that solutions of the governing dynamic equations result in nonnegative entropy production.

Weakly nonlocal theories, related thermodynamics, are either supposing a gradient dependent entropy function [1, 2], or are considering a generalized form of the entropy current [3, 4, 5]. However, none of them uses the traditional methods of non-equilibrium thermodynamics, there are no thermodynamic forces and currents identified and no conductivity relations defined. In this paper we will find suitable thermodynamic forces and currents with the help of the generalized entropy current first used by Nyíri [6]. Moreover, we will show that in case of heat conduction the classical Onsagerian method leads to the well-known weakly nonlocal generalization of the heat conduction equation called Guyer-Krumhansl equation. On the other hand, we can get an equation of the Cahn-Hilliard-type as an evolution equation of an extensive variable in the presence of an internal variable of nonlocal type. Several previous ad-hoc assumptions are explained by constitutive relations in the present treatment (e.g. the balance form equation of the heat current).

1.1. Weakly nonlocal extended heat conduction. When treating heat conduction phenomena in solid material, the starting point is the balance equation of internal energy

\[ \partial_t u + \nabla \cdot \mathbf{j}_q = 0. \]

(1)

Here \( u \) is the internal energy density and \( \mathbf{j}_q \) is the heat current density and \( \partial_t \) denotes the partial time derivative. Extended thermodynamics considers the heat current density as an independent variable, introducing it into the basic state
space and a non-equilibrium entropy is defined as a function on this extended state space. With these assumptions one can explain inertial, memory effects getting an appropriate phenomenological model of the wave heat conduction phenomena. The key to receive a well tractable model is to identify suitable thermodynamic currents and forces for a reasonable constitutive theory. This can be achieved by supposing that the non-equilibrium entropy function depends on the currents in a special way, as it was first suggested by Gyarmati [7].

\[
(2) \quad s(u, j_q) = s_0(u) - \frac{1}{2}j_q \cdot m \cdot j_q.
\]

Here \( m \) is the so called matrix of the thermodynamic inductivities. Further on we will assume that \( m \) is constant (as usual). The reciprocal absolute temperature is introduced as the derivative of the entropy function according to the internal energy \( \frac{ds}{du} = \frac{1}{T} \).

A natural physical assumption is that the entropy, being connected to internal energy, does not flow without the heat flow. Therefore, we accept, that the entropy current as a function of our given state variables \((u, j_q)\) has the property \( j_s(u, 0) = 0 \). Using Lagrange mean value theorem and considering this condition, one can get the next functional form

\[
(3) \quad j_s(u, j_q) = B(u, j_q) \cdot j_q,
\]

where the \( B \) called current intensity factor can be supposed to be continuous at a neighborhood of the local equilibrium state \( j_q = 0 \). One can observe that \( B \) is one tensorial order higher than the corresponding current. After a short calculation, a consequence of our assumptions \((1), (2)\) and \( (3)\) is, that the entropy production has the following form

\[
(4) \quad \sigma_s = \partial_t s + \nabla \cdot j_s = (B - \frac{1}{T} I) : \nabla \circ j_q + (\nabla \cdot B - m \cdot \partial_t j_q) \cdot j_q \geq 0.
\]

Here \( I \) is the second order identity tensor, \( : \) and \( \circ \) are the notations of the double contraction and the tensorial product, respectively. The entropy production is nonnegative and equals zero only in thermodynamic equilibrium according to the Second Law.

We are looking for constitutive relations for \( B \) and \( \partial_t j_q \) that automatically fulfill the inequality above. The following force-current structure can be chosen

| Force Current | Local | Nonlocal |
|---------------|-------|----------|
| \( \nabla \cdot B - m \cdot \partial_t j_q \) | \( \nabla \circ j_q \) | \( B - \frac{1}{T} I \) |

The linear conductivity relations of Onsager can be written as follows:

\[
(5) \quad j_q = L_{11}(\nabla \cdot B - m \cdot \partial_t j_q) + L_{12} \nabla \circ j_q,
\]

\[
B - \frac{1}{T} I = L_{21}(\nabla \cdot B - m \cdot \partial_t j_q) + L_{22} \nabla \circ j_q.
\]

If the currents are constitutive quantities and depend on the constitutive space, that is a general solution of the dissipation inequality \((1)\). From the equations above \( B \) can be easily eliminated and we can give a general constitutive relation.
purely for \( j_q \)

\[
\begin{align*}
  j_q &= L_{11} \left( \nabla \frac{1}{T} - m \cdot \partial_t j_q \right) + L_{111} \nabla \cdot \left( (L_{22} - L_{111} L_{112}) \nabla \cdot j_q \right) \\
  &+ L_{21} \nabla \cdot \left( \nabla \circ j_q \right) + L_{112} \nabla \circ j_q.
\end{align*}
\]

(6)

This general relation gives the first approximation considering the entropy triggering effects of nonlocalities. The relations (6) and (1) together result in the system of equations to be solved for \( u \) and \( j_q \).

Let us now restrict ourselves to the isotropic case. According to the Curie principle (representation theorems of isotropic tensors) there is no cross coupling in the conductivity equations. In a strictly linear approximation (when \( L \) is constant) we get

\[
m = mI, \quad L_{11} = lI,
\]

where \( m, l \) are a constant scalars and \( L_{22} \) can be written with indices as:

\[
(L_{22})_{ijkl} = l_1 \delta_{ik} \delta_{jl} + l_2 \delta_{il} \delta_{jk} + l_3 \delta_{ij} \delta_{kl}.
\]

Here \( l_1, l_2, l_3 \) and \( l \) are positive constant scalar material parameters to ensure nonnegative entropy production. \( m \) is also positive supposing concave entropy in the extended state space. Therefore the linear approximation of Onsager (5) reduces to

\[
\begin{align*}
  j_q &= l \left( \nabla \cdot B - m \partial_t j_q \right), \\
  B - \frac{1}{T} I &= l_1 (\nabla \circ j_q) + l_2 (\nabla \circ j_q)^* + l_3 \nabla \cdot j_q I,
\end{align*}
\]

(7)

where \( * \) denotes the transpose. Using this expression we can get

\[
lm \partial_t j_q + j_q = l \left( \nabla \frac{1}{T} \right) + l \left( l_1 \Delta j_q + (l_2 + l_3) \nabla \cdot \nabla \cdot j_q \right).
\]

(8)

This is exactly the Guyer-Krumhansl equation for the heat current, introduced to describe the thermal properties of some crystals at low temperatures \[8\]. Originally it was derived with the use of kinetic physics but other derivations are based on two-fluid hydrodynamics \[8\]. In the last decades there were several attempts to get these equations from pure non-equilibrium thermodynamics \[10, 11, 12, 4, 13\]. However, all of these derivations contain several ad-hoc assumptions as supposing a balance-like dynamics for the heat current \( j_q \) and specially simplified constitutive equations. Moreover, the derivations mentioned above do not have the heuristic power of irreversible thermodynamics, therefore the generalization of their assumptions in case of more difficult situations can be very ponderous if not impossible.

In the special case of \( l_1 = l_2 = l_3 = 0 \) we can get the Cattaneo-Vernotte equation for the heat current. In this case the entropy current has its traditional form \( j_s = j_q / T \). Further, we get the Fourier heat conduction equation when \( m = 0 \), in the case of local equilibrium. Assuming the caloric state function in the form \( u = cT \), the weakly nonlocal extended heat conduction equation can be given directly for the temperature as

\[
lmcT + c \partial_t T + l \Delta \frac{1}{T} + lc(l_1 + l_2 + l_3) \Delta \partial_T = 0.
\]

(9)

Let us remark here that several generalizations are known for the classical entropy current expression from the investigations in extended thermodynamics \[3\] to the multifield theories that include finite length localization instabilities in damage mechanics models \[3\]. The treated Nyíri form of the entropy current makes possible to exploit the Second Law in an Onsagerian spirit.
Another important remark is, that the heat current $j_q$ and the intensity factor $B$ are internal variables in thermodynamic sense. If we do not eliminate $B$ from the material equations, then it can be regarded as a current density of the heat current $j_q$, because the dynamic equation for the heat current derived above turns out to have a special balance form (more properly it will be an equation of Ginzburg-Landau type). Supposing that both the entropy and the entropy current depend on $B$, we can continue to introduce internal variables of nonlocal type in the following way: we construct a new current with the help of the given current intensity factor and introduce a new current intensity factor of $B$ in the entropy current. In this way we can get a hierarchical approximation scheme of nonlocal phenomena based on thermodynamic considerations.

2. **Weakly nonlocal extensive variable - the Cahn-Hilliard equation**

Now, another example will be shown that similar structural assumptions of the entropy current can help to build up a current-force system in more general cases, too. Let us consider a continuum with a single scalar extensive variable $a$ (e.g. mass density). Therefore a balance equation is given for $a$

$$\partial_t a + \nabla \cdot j_a = 0.$$  \hfill (10)

However, as we do not consider a simple local equilibrium approximation, we further extend the state space of extended thermodynamics and introduce an internal variable $\xi$ with the tensorial order of the current density. In this case our basic state space is spanned by the variables $(a, j_a, \xi)$. We are to investigate the additional nonlocal terms in the governing equations, therefore, contrary to the previous example, we will neglect the memory effects, so the entropy function will depend only on the extensive quantities

$$s(a, j_a, \xi) = s_0(a).$$  \hfill (11)

The corresponding intensive quantity is denoted by $\Gamma(a) = \frac{ds_0}{da}$. Let us investigate the functional form of the entropy current $j_s(a, j_a, \xi)$. There are some natural physical assumptions that we apply:

- There is no entropy flow in the absence of the flow of $a$ and with zero internal variable:
  $$j_s(a, 0, 0) = 0.$$

- In case of zero internal variable the entropy flow reduces to the classical form:
  $$j_s(a, j_a, 0) = \Gamma j_a.$$

Therefore, according to Lagrange’s mean value theorem and the mentioned natural physical assumptions we may write that

$$j_s(u, 0, \xi) = \Gamma j_a + B \cdot \xi.$$  \hfill (12)

where $B$ is a continuous constitutive function on the state space and its tensorial order is one order higher than the order of $\xi$. Our simplifying assumptions on the entropy and the entropy flow yields the entropy production

$$\sigma_a = \Gamma \partial_t a + \nabla \cdot (\Gamma j_a + B \cdot \xi) = j_a \cdot \nabla \Gamma + B : \nabla \cdot \xi + (\nabla \cdot B) \cdot \xi \geq 0.$$  \hfill (13)

Let us consider now the strictly linear approximation with constant coefficients in case of isotropic materials only. Now the choice of the currents and forces is
straightforward. There are two coupled terms in the linear laws

\[ j_a = l_{11} \nabla \Gamma + l_{12} \nabla \cdot B, \]
\[ \xi = l_{21} \nabla \Gamma + l_{22} \nabla \cdot B, \]
\[ B = l_1 (\nabla \circ \xi) + l_2 (\nabla \circ \xi)^* + l_3 \nabla \cdot \xi I. \]

(12) \hspace{2cm} (13) \hspace{2cm} (14)

Here the matrix of the conductivity coefficients is positive definite to ensure nonnegative entropy production. We can eliminate \( \xi \) from the first two equations:

\[ \xi = l_{22}^{-1} j_a + (l_{21} - l_{22} l_{12}^{-1} l_{11}) \nabla \Gamma. \]

(15)

Eliminating \( B \) and \( \xi \) from the first equation, we get the following equality

\[ j_a = l_{11} \nabla (\Gamma - \alpha \Delta \Gamma) + l_1 l_{22} \Delta j_a + l_{22} (l_2 + l_3) \nabla \circ \nabla \cdot j_a, \]

where \( \alpha = (l_1 + l_2 + l_3) (l_{11} l_{22} - l_{12} l_{21}) \) is positive.

So we eliminated the internal variable and received (10) and (15) as dynamic equations to be solved.

Putting (15) into the balance (10) we finally obtain

\[ \partial_t a + l_{11} \Delta (\Gamma - \alpha \Delta \Gamma) - l_{22} (l_1 + l_2 + l_3) \Delta \partial_t a = 0. \]

(16)

This equation is astonishingly similar to the Cahn-Hilliard equation, but there are some essential differences.

- The last extra term does not appear in the traditional equation. Gurtin received a similar additional term with the help of microforce balance (a strong additional assumption) in the special case when the variable \( a \) is the mass density \( [15] \). Supposing that \( l_{22} = 0 \), this additional term vanishes. Let us remark that this rate dependent term appears in the linear Onsagerian conductivity equations at the same thermodynamic approximation level as all the others.

- Under the second Laplace operator there is the intensive variable \( \Gamma \), instead of the extensive \( a \), contrary to the original Cahn-Hilliard equation.

- All of the material parameters in (16) are positive, as a consequence of the Second Law, a nonnegative entropy production. In the original equation the signs of the coefficients are fixed according to stability considerations that are not connected to the entropy balance.

- The nonlinearities and anisotropies show a different structure than in the original equation.

- In most of the previous derivations of the Cahn-Hilliard equation, a “generalized chemical potential” appeared by analogy, and was inserted without any further ado into the mass balance. Here in our derivation we received a real generalization of the diffusion current in the same sense and with the same method as in the original irreversible thermodynamic approach.

3. Discussion

In this letter only some basic examples are treated. A more general theory of weakly nonlocal irreversible thermodynamics can be created according to the methods discussed above. It makes possible to incorporate and investigate several other classical nonlocal equations (phase field, Kardar-Parisi-Zhang, etc.) into the well established structure of non-equilibrium thermodynamics and investigate them form the point of view of structural compatibility. The present treatment has several serious advantages if compared to other approaches. First of all the
compatibility of those equations with the Second Law of thermodynamics can be investigated. These researches can deepen our understanding of the connection between the Second Law and the stability of materials in a static and also in a dynamic sense [16].

As we have already mentioned, one of the main advantages of the above scheme is the use of the force-current relations of Onsager, which makes easy to generate approximatively constitutive functions that are compatible with the Second Law. It is straightforward to go beyond the linear approximation and consider higher order terms in the series. Furthermore, with this scheme we can be sure that the amendment of the Second Law suggested by Muschik and Ehrentraut [17] is fulfilled, that is the positivity of the entropy production is ensured by purely constitutive assumptions.

One can say that the heuristic power of the Onsagerian approach can be a disadvantage if contrasted with the more general exploitations of the entropy inequality. However, an application of the more exact Liu procedure shows that our assumptions on the entropy current are not only correct, but essentially one cannot construct more general constitutive relations. These problems and some other example applications are to be treated in a forthcoming paper [18].

Finally we remark, that there are not well established methods to derive weakly nonlocal equations in kinetic physics (see e.g. [19, 11]). According to the present investigations, the role of the entropy current can be essential to develop a powerful approximation scheme, like the moment series expansion in case of memory effects.

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References

[1] F. Falk. Chan-Hilliard theory and irreversible thermodynamics. *Journal of Non-Equilibrium Thermodynamics*, 17:53–65, 1992.
[2] O. Penrose and P. C. Fife. Thermodynamically consistent models of phase-field type for the kinetics of phase transitions. *Physica D*, 43:44–62, 1990.
[3] I. Müller and T. Ruggeri. *Extended Thermodynamics*, volume 37 of *Springer Tracts in Natural Philosophy*. Springer Verlag, New York-etc., 2nd edition, 1996.
[4] G. Lebon, D. Jou, J. Casas-Vázquez, and W. Muschik. Heat conduction at low temperature: A non-linear generalization of the Guyer-Krumhansl equation. *Periodica Polytechnica Chemical Engineering*, 41(2):185–196, 1997. Lecture held on ‘Minisymposium on Non-Linear Thermodynamics and Reciprocal Relations’, September 22-26, Balatonvilágos, Hungary.
[5] P. M. Mariano and G. Augusti. Multifield description of microcracked continua: A local model. *Mathematics and Mechanics of Solids*, 3:183–200, 1998.
[6] B. Nyíri. On the entropy current. *Journal of Non-Equilibrium Thermodynamics*, 16:179–186, 1991.
[7] I. Gyarmati. The wave approach of thermodynamics and some problems of non-linear theories. *Journal of Non-Equilibrium Thermodynamics*, 2:233–260, 1977.
[8] R. A. Guyer and J. A. Krumhansl. Solution of the linearized phonon Boltzmann equation. *Physical Review*, 148(2):766–778, 1966.
[9] C. P. Enz. Two-fluid hydrodynamics description of ordered systems. *Reviews of Modern Physics*, 46(4):705–753, 1974.
[10] G. Lebon and P. C. Dauby. Heat transport in dielectric crystals at low temperature: A variational formulation based on Extended Irreversible Thermodynamics. *Physical Review A*, 42(8):4710–4715, 1990.
[11] R. E. Nettleton. Reciprocity and consistency in non-local Extended Thermodynamics. *Open Systems and Information Dynamics*, 2(1):41–47, 1993.
[12] G. Lebon and M. Grmela. Weakly nonlocal heat conduction in rigid solids. Physics Letters A, 214:184–188, 1996.
[13] G. Lebon, D. Jou, J. Casas-Vázquez, and W. Muschik. Weakly nonlocal and nonlinear heat transport in rigid solids. Journal of Non-Equilibrium Thermodynamics, 23:176–191, 1998.
[14] J. Verhás. On the entropy current. Journal of Non-Equilibrium Thermodynamics, 8:201–206, 1983.
[15] M. G. Gurtin. Generalized Ginzburg-Landau and Cahn-Hilliard equations based on a microforce balance. Physica D, 92:178–192, 1996.
[16] T. Matolesi. On the mathematical structure of thermodynamics. Journal of Mathematical Physics, 41(4):2021–2042, 2000.
[17] W. Muschik and H. Ehrentraut. An amendment to the Second Law. Journal of Non-Equilibrium Thermodynamics, 21:175–192, 1996.
[18] P. Ván. Weakly nonlocal non-equilibrium thermodynamics. to be submitted to Physica D, 2001.
[19] R. L. Liboff. Kinetic Theory (Classical, Quantum, and Relativistic Descriptions). Prentice Hall, Englewood Cliffs, New Jersey, 1990.

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