Beyond Classical Thermodynamics: Grain Growth.

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The paper aims to explain why classical thermodynamics is insufficient in macroscopic modeling of solids.

It is my great pleasure to give a talk at the Martin Glicksman Festival. The work which I was going to present here was published recently [1], and I decided to shift the discussion to the motivation of this work, which seems more interesting than the work itself. It is gradually being recognized in various branches of physics that the macroscopic description of solids requires “new thermodynamics” (all references are given in [1] and not repeated here). To explain this point we first outline some basic facts of classical thermodynamics.

Classical thermodynamics. Thermodynamics was developed in practically modern form by Clausius. Clausius thermodynamics naturally yielded the question “Why?”: Why all macroscopic phenomena must obey to the first and the second laws of thermodynamics? The answer was formulated mostly by Boltzmann and consists of two parts:

A. There are two well-separated time scales: the time scale of atomic/molecular motion (fast time) and the time scale of macroprocesses (slow time). Accordingly, there are fast variables and slow variables describing micromotion and macromotion.

B. Equations of macromotion are obtained by elimination of fast variables from the governing equations. The only reason why we observe the first and the second laws of thermodynamics at macrolevel is that the equations of micromotion has the special structure: they are Hamiltonian and ergodic.

If any of these conditions is violated, then, as examples show, we wouldn’t have the thermodynamic laws. Hamiltonian structure of microequations means that there is a
function of coordinates $q$ and momenta $p$ of atoms/molecules and macrovariables $y$, Hamiltonian $H(p,q,y)$, such that dynamics of $p$ and $q$ is governed by the equations

1. \[ \dot{p} = -\frac{\partial H(p,q,y)}{\partial q}, \quad \dot{q} = \frac{\partial H(p,q,y)}{\partial p}. \]

For constant $y$, any trajectory of the system of ordinary differential equations (1) lies on the energy surface $H(p,q,y)=E=\text{const}$ in the $(p,q)$-phase space, $E$ has the meaning of energy. Ergodicity of micromotion means that any “ink spot” on the energy surface (Figure 1a) is spread by trajectories densely over the energy surface (Figure 1b).

\[ \text{Figure 1. Sketch of an energy surface in phase space; an ink spot (a) is spread densely over the energy surface by ergodic phase flow (b).} \]

One had to explain how absolute temperature $T$ and entropy $S$ arise in equations for slow motion. Boltzmann found an explanation of what temperature is. He established the equipartition law: in ergodic Hamiltonian systems the doubled averaged kinetic energies of all degrees of freedom coincide; their common value is $T$. The question on the meaning of entropy, which appears in the formula for heat supply $dQ$, $dQ = TdS$, turned out to be more difficult. Boltzmann suggested that entropy is (up to an additive constant) logarithm of the number $W$ of microstates compatible with the given macrostate

2. \[ S = k \ln W + \text{const}. \]
It remained unclear though what $W$ means for Hamiltonian systems. The final answer was found by J.W. Gibbs and P. Hertz:

3. $S(E, y) = \ln \Gamma(E, y)$,

where $\Gamma(E, y)$ is the volume of phase space bounded by the energy surface $H(p, q, y) = E$.

Remarkably, besides entering the energy balance, entropy possesses the “second face”, discovered by Einstein. Einstein was motivated by seeming model dependence of the Boltzmann equation (2): taking different models of micromotion, one gets different values of $W$, while entropy is determined uniquely from heat measurements. Einstein aimed at writing an equation in which both sides of the equation are experimentally measurable. We explain the Einstein formula in case of the favorite thermodynamic system: gas under piston (Figure 2). In equilibrium piston fluctuates due to collisions with molecules. The gas volume $V$ is a random number and has some probability density $f(V, E)$. Einstein suggested the relation

4. $f(V, E) = \text{const } e^{S(E, V)}$.

Now both sides of the equation can be experimentally measured: $f(V, E)$ is measured by observing the fluctuations of the piston, $S(E, V)$ by measuring the macroscopic properties of the gas.

An author’s modest contribution to the field was an addition of derivative to (4):

5. $f(V, E) = \text{const } \frac{\partial}{\partial E} e^{S(E, V)}$.

It turns out that equation (5) is an exact relation that holds for ergodic Hamiltonian systems with any, even small, number of degrees of freedom. Einstein’s formula (4) follows from (5) in the limit of an infinite number of degrees of freedom. Formula (5) clarified a longstanding issue: what is important for classical thermodynamics to be true, a large number of degrees of freedom or the Hamiltonian ergodic structure of the governing equations? It turned out that the relations of classical equilibrium thermodynamics hold for any ergodic Hamiltonian system, and the only
equation that should be modified for low-dimensional systems is Einstein’s formula.

*Why classical thermodynamics is insufficient for solids?* Elimination of fast degrees of freedom for gases and, in many cases, for fluids, results in equations for macroscopic parameters: density, pressure, temperature, velocity, etc. For solids the situation is principally different: after elimination of fast (atomic) degrees of freedom one does not get a macroscopic theory, the description remains on mesoscopic level. For crystals this is dynamics of crystal defects: dislocations, grain boundaries, etc. To get to macrolevel one needs to do one more elimination of “fast” degrees of freedom, in this case “fast” over space. The major new feature is that the system of governing equations is *no longer Hamiltonian*, it is *dissipative*. One important consequence of that is the loss of universality: All ergodic Hamiltonian systems are, to some extent, very similar, they are characterized, in addition to macrovariables by only one additional parameter, energy. Dissipative systems possess attractors, and the variety of attractors is much more diverse. This is why one cannot expect, for example, that there exists a “universal plasticity theory” or a “universal continuum theory of dislocations”.

Now we are going to argue that one more “entropy” appears in the transition from mesoscale to macroscale. In this discussion we focus on the process of grain boundary motion.

*Entropy of microstructure.* Consider a polycrystal, an ensemble of randomly oriented single crystals (Figure 3). If temperature is high enough, the grains grow. We wish to describe this process on the macroscopic level. Classical thermodynamics suggests the following recipe: one has to identify macroscopic parameter/parameters of the system, specify the dependence of grain boundary energy per unit volume $U_m$ on macroparameters and set the equations for evolution of macroparameters in such a way that the thermodynamic entropy grows. Index $m$ stands for microstructure; in the case under consideration microstructure is the grain boundary microstructure.
The simplest macroparameter of the system is the average grain radius $R$. It is
introduced as follows: one computes the average grain volume as the ratio of the volume of the specimen $|V|$ to the number of grains $N$,

$$\bar{v} = \frac{|V|}{N},$$

and $R$ is the radius of the sphere with the volume $\bar{v}$.

From dimension reasoning

6. $U_m = \gamma \frac{X}{R}$,

where $\gamma$ is the grain boundary energy per unit area and $X$ a dimensionless constant. Since

7. $U_m = \frac{1}{2} \gamma (a_1 + \ldots + a_N) |V|^{-1}$,

one can write with $a_1, \ldots, a_N$ being the grain boundary areas,

8. $U_m = \frac{1}{2} \gamma \frac{\bar{a}}{\bar{v}}$,

where $\bar{a}$ is the average grain boundary area,

$$\bar{a} = \frac{a_1 + \ldots + a_N}{N}.$$

Therefore, parameter $X$ is a function of $\bar{a}, \bar{v}$:

$$X = c \frac{\bar{a}}{\bar{v}^{2/3}}$$

Here $c$ is a numerical constant.

According to (7) grain boundary energy per unit volume coincides, up to a constant, with the total area of grain boundaries per unit volume, and in what follows the terms grain boundary energy or total grain boundary area are interchangeable. If one
assumes that all grains are spheres of equal radii, then $X = 1.5$. This is the usual formula accepted in metallurgical literature. However, this is not only just a rough approximation. This approximation eliminates an essential feature of the grain boundary structure: energy of grain boundary structure is a thermodynamic parameter that is independent on the grain size. This follows from (8): for one grain area and volume of the grain can be chosen independently, they are constrained only by the isoperimetric inequality; for an ensemble of grains there is an additional constraint, the tessellation condition, but it leaves enough freedom to choose $\bar{a}$ and $\bar{\nu}$ independently.

How rough is the usual approximation $X = 1.5$? Analysis of various 2D structures obtained by sectioning of polycrystals shows that the 2D analogy of parameter $X$, the ratio of grain perimeter to square root of grain area has variations of order $10-20\%$. Undoubtedly, for 3D structures the variations of $X$ and, thus, energy are not less. Is the variation of grain boundary energy of $10\%$ essential? If we plug in numbers for Al with grain size $50 \mu m$ and compare grain boundary energy with energy of dislocation network $U_d$ with dislocation density $10^{12} 1/m^2$, we get

$$U_d \sim \frac{1}{10} U_m.$$ 

This means that for all processes where interaction of grain boundaries with dislocations is important, one has to take into account that grain boundary energy is not a function of the grain size. Treating grain boundary area as independent from grain size becomes even more important in grain boundary dynamics because segregation of solute atoms on grain boundary and formation of a solute atmosphere is controlled by grain boundary area.

At first glance, we come to a situation which is quite different from the usual thermodynamic setting: energy is not a function of macroparameters. There is, however, an analogy with a classical thermodynamic system, a gas. The state of gas is characterized by two parameters, density and temperature, or, equivalently, density $\rho$ and energy per unit mass $U$, i.e. energy in this case is also an independent parameter. For parameters of state $\rho$ and $U$, the properties of the gas are described by the equation of state $S = S(\rho, U)$ where $S$ is the thermodynamic entropy of gas. The relation $S = S(\rho, U)$ is universal, i.e. it holds for any sufficiently slow processes. So, the idea comes that there might be some “entropy of grain boundary structure”, $S_m$ (we call $S_m$ further
entropy of microstructure) such that the properties of the structure are characterized by the equation of state

9. \( S_m = S_m(U_m, R) \),

which holds for sufficiently large class of processes. The analogy between grain boundary structure and gas is superficial but not meaningless as it captures the crux of the matter: the independence of \( U_m \) and \( R \), and the possibility that some measure of “chaos” in the grain boundary structure, \( S_m \), could be a universal function of \( U_m \) and \( R \). Then the questions arise: How to define \( S_m \)? How to find it experimentally? Does equation (9) really hold for all processes? Besides, it would be interesting to check the author’s conjecture, that for isolated thermodynamically stable systems, \( S_m \), in contrast to usual thermodynamic entropy, decays:

\[
\frac{dS_m}{dt} \leq 0.
\]

Of course, all these issues can be convincingly addressed only by experiments. As an ad hoc approach one can study them theoretically by choosing a model for the evolution of the grain boundary structure. For example, as such one can take Hillert theory ignoring for a moment that this theory yields the self-similar grain size distributions deviating from the experimentally observed one. The difficulty is that Hillert equation for time evolution of the grain size distribution admits only a cumbersome numerical investigation. To get around this difficulty, Hillert equation was slightly and physically insignificantly modified [1]. The modified equation can be solved analytically and, besides, yields a better fit to experimental observations.

In Hillert theory as well as in the modified one, it is accepted that averaged grain area and averaged grain volume are linked as that for spheres. Nevertheless, energy of grain boundary area remains independent from the average grain size but for the reason quite different from the above-mentioned: Denote by \( f(t,v) \) the probability density of grain volumes. Averaged grain boundary area and averaged grain size are proportional to integrals of \( f(t,v) \) with different weights,
\[ \int v^2 f(t, v) dv \quad \text{and} \quad \int vf(t, v) dv. \]

Due to that they can change independently in the course of grain boundary evolution. In this special case, as was argued in [1], entropy of the grain boundary structure should be introduced as Boltzmann-Shannon entropy,

10. \( S^* = -\int f(t, v) \ln[f(t, v) v_0] dv \)

where \( v_0 \) is a characteristic volume the choice of which fixes the additive constant in entropy. Entropy (10) is entropy per one grain, while the total entropy of microstructure \( NS^* \) referred to unit volume is

11. \( S_m = S^*/\bar{v}. \)

The modified Hillert theory yields the following answers to the above-posed questions:

- The entropy per unit volume, \( S_m \), after, possibly, some initial time interval, decays in the course of grain growth indeed.
- Most details of the initial grain size distribution are forgotten, and a universal equation of state holds that links entropy, energy and average grain volume. This equation has the form

\[ S_m = \frac{1}{\bar{v}} \left( \ln \frac{\bar{v}}{v_0} + S_0(X, n) \right), \quad X \equiv \frac{2 U_m}{3 \gamma} \left( \frac{\bar{v}}{4\pi/3} \right)^{1/3}. \]

The memory of the initial grain size distribution enters only through the dimensionless parameter \( n \) which characterizes the distribution of the largest grains. There are indications that the distribution of largest grains has profound effect on other properties of metals as well. Function \( S_0(X, n) \) is shown in Figure 4.
Figure 4. Equation of state of grain boundary structures: the dependence of entropy $S_0$ on dimensionless energy $X$ for various inhomogeneities of the distribution of largest grains $n$. For a given $n$, the evolution follows the thin line which ends at the bold line; the end point on the bold line corresponds to the self-similar growth.

Temperature of microstructure, $T_m$, defined by the usual thermodynamic formula $1/T_m = \partial S/m/\gamma \varphi a$, characterizes the scatter of grain boundary energies of the grain ensemble.

The issues discussed here for grain growth pertain to any macroscopic description of solids whose microstructure evolves.

References