

Short Note

A Paradox of Decreasing Entropy in Multiscale Monte Carlo Grain Growth Simulations

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Abstract: Grain growth in metals is driven by random thermal fluctuations and increases the orderliness of the system. This random process is usually simulated by the Monte Carlo (MC) method and Cellular Automata (CA). The increasing orderliness results in an entropy decrease, thus leading to a paradoxical apparent violation of the second law of thermodynamics. In this paper, it is shown that treating the system as a multiscale system resolves this paradox. MC/CA simulations usually take into consideration only the mesoscale entropy. Therefore, the information entropy of the system decreases, leading to an apparent paradox. However, in the physical system, the entropy is produced at the nanoscale while it is consumed at the mesoscale, so that the net entropy is growing.

Keywords: grain growth, Monte Carlo simulation, Cellular Automata, multiscale modeling.

The entropy as a measure of irreversibility and dissipation in a thermodynamic system was introduced by R. Clausius in the 1850s. According to the second law of thermodynamics, the entropy of a closed system cannot decrease. In 1877, L. Boltzmann suggested a definition of the entropy using the statistical thermodynamics approach and the concept of microstates Ω corresponding to a given macrostate,

$$S = k_B \ln \Omega \quad (1)$$

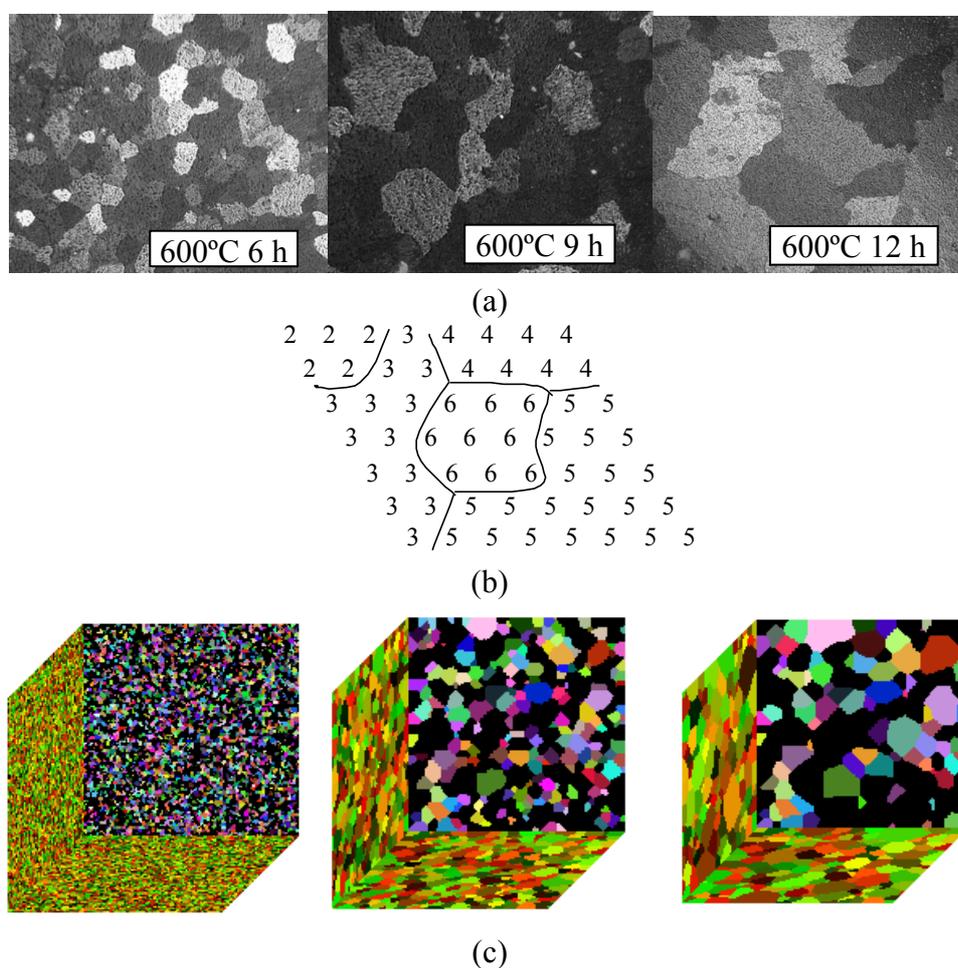
where k_B is Boltzmann's constant and Ω is the number of microstates.

About 70 years later, the concept of information entropy was introduced by C. Channon, who defined it as

$$H = K \ln(1/p) \tag{2}$$

where K is a constant and p is the probability associated with the information. The relationship between the two types of the entropy remains a matter of debate [1]. The extensive study of self-organizing systems since 1960 attracted attention to situations when the entropy decreases. However, these self-organizing systems are not closed and operate far from the equilibrium, with the entropy being driven away from the system.

Figure 1. MC simulation of grain growth (a) experimental observation of grains in aluminum at different time intervals (b) simulation lattice (c) simulation results for grain growth [2].



An interesting example of a self-organizing process is the thermally activated grain growth in metals (Fig. 1, [2]). It is well known that metal crystals form grains, characterized by different orientations of the lattice [3]. The typical grain size is in the range between microns and millimeters. There is an additional energy associated with the grain boundaries due to the misorientation of the neighboring grains. Therefore, it is energetically profitable for larger grains to grow and to absorb smaller grains, thus reducing the total number of grains and the total boundary area. The ideal state of

a perfect crystal with only one grain corresponds to the minimum energy. The grain growth is a thermally activated diffusion-like process with the Arrhenius type of kinetics. For normal isotropic grain growth, theoretical considerations predict a parabolic dependence of the average grain radius r on time

$$r^2 - r_0^2 = K_0 \exp\left(-\frac{Q}{RT}\right)t \quad (3)$$

where Q is the activation enthalpy, R is the universal gas constant, K_0 is a proportionality constant and r_0 is the initial grain size [4].

Modeling the grain growth is a challenging task. Since it is a random process, deterministic modeling is difficult. Monte Carlo (MC) simulations and Cellular Automata (CA) approaches are often used [5-6]. CA algorithms describe the spatial and temporal evolution of a complex system by applying deterministic or probabilistic local rules to the cells of a regular lattice. They are based on finite difference formulations of local interaction laws. The MC method uses randomly generated orientation numbers associated with a regular lattice. The latter is initialized by randomly assigning to each lattice point an integer number representing its orientation. Reorientations are randomly and sequentially attempted for all lattice sites. If a new orientation is characterized by lower energy, then it is accepted [5-11].

The grains of a metal represent a typical example of a partially ordered system that occupies an intermediate position between the complete disorder (a random collection of atoms) and complete order (a perfect single crystal, which is close to the state of complete order, although it may have thermal equilibrium defects introducing disorder). The grain growth is also a self-organizing process system, which naturally evolves from a disordered to an ordered state, while being driven by random thermal fluctuations. Consider an array of N cells, representing lattice cells in the simulation method, with each cell being in one of M microstates. The total number of microstates of this system would then be:

$$\Omega = M^N \quad (4)$$

When the system reaches its final state with all cells having the same orientation, the total number of microstates becomes:

$$\Omega = M \quad (5)$$

Using the statistical mechanics definition of the entropy, one can find the initial entropy S_0 and the final entropy S_f of the system as:

$$S_0 = \ln(MN) = N \ln M = NS_f \quad (6)$$

$$S_f = \ln M \quad (7)$$

Based on Eqs. 6 and 7, the entropy decreases between the initial and the final states by an amount of

$$\Delta S = (N - 1)\ln M \quad (8)$$

This result constitutes an apparent paradox, because it seems to contradict the second law of thermodynamics, which states that the entropy of a closed system does not decrease. Another formulation of the paradox is that the randomness of thermal fluctuations leads to an increased orderliness of the system.

In order to solve this paradox, one has to take into account that the system under consideration can be studied at different scale levels, and also that it is not a closed system. At the macroscale, the continuum system is characterized by certain bulk mechanical properties (e.g., yield strength, elastic modulus) that depend upon the average grain size. At the macroscale, no change of entropy is expected, i.e. $\delta S_{macro} = 0$. The mesoscale (or microscale) is governed by grains that tend to grow. Therefore, the mesoscale entropy is essentially the configuration entropy, and with increasing grain size it decreases due to the increased orderliness of the system, i.e. $\delta S_{meso} < 0$. At the molecular scale (or nanoscale), energy barriers for grain growth and random thermal fluctuations exist. Every time when a lattice site is reoriented, a certain amount of energy is dissipated because the energy barrier must be overcome. However, if the system's temperature is maintained constant, then the heat is removed from the system due to its contact with the surroundings, and thus the system is not closed. This results in an increase in the system's temperature and entropy, i.e. $\delta S_{nano} > 0$. In other words, the random fluctuations at the nanoscale lead to the orderliness increase at the mesoscale, which is compensated by the entropy increase at the nanoscale. The net entropy of the system can therefore be written as

$$S_{net} = S_{macro} + S_{meso} + S_{nano} \tag{9}$$

Since $|\delta S_{nano}| > |\delta S_{meso}|$, the net entropy decreases and the second law of thermodynamics is satisfied (Table 1).

Table 1. Hierarchy levels in the physical system and simulation.

	Physical system			Simulation		
	Objects	Driving force	Entropy	Objects	Driving force	Entropy
Macroscale	Continuum material	–	$\delta S_{macro} = 0$	–	–	–
Mesoscale	Grains	Decreasing boundary energy	$\delta S_{meso} < 0$	Cells	Decreasing energy functional	$\delta S < 0$
Nanoscale	Atoms	Thermal fluctuations	$\delta S_{nano} > 0$	–	–	–

Therefore, we deal with the two different systems: the physical system that is characterized by the thermodynamic entropy and the simulation system that models the physical system and is

characterized by the information entropy. Concerning the information entropy of the system, several interesting observations can be made with regard to the self-organizing properties of this system. The numerical CA/MC models consider only the mesoscale structure of the system, and thus only the mesoscale (configurational) entropy S_{meso} can be determined from the CA/MC models. This is the reason for the apparent entropy decrease. The physical system is not insulated. The heat and entropy are removed from the system, and thus, it is not a closed system. However, the numerical CA/MC models do not take into account that aspect, because they are concentrated on the mesoscale description of the physical system. As a result, the second law of thermodynamics is apparently violated in the simulation system in a paradoxical manner. The second law is valid for closed physical systems. However, there is no reason why it cannot be violated for CA/MC models during computer simulation. One should keep in mind that computers require energy dissipation (i.e. computer processors require permanent cooling), and therefore, the decrease of entropy in the information system is compensated by an increase of the thermodynamic entropy.

The conclusion is that there is a correspondence between the physical system (a metal crystal) and the information system, used for the simulation (e.g. CA). However, the physical system is a multiscale system, with the entropy produced at the nanoscale and consumed at the mesoscale, so that the net sum of the entropy grows. The information system simulates only the mesoscale level, thus leading to the apparent reduction of the entropy. Consequently, the second law of thermodynamics is not observed within the computer simulation network. It is noted that such a common dissipative process as dry friction also has a hierarchical (multiscale) organization [12-13], and therefore the hierarchical approach to the entropy is important for a broad class of physical systems.

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