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Extending cluster dynamics to concentrated and disordered alloys: The linear-chain case

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Abstract

Cluster dynamics is often used in the multi-scale procedure to link atomistic and macroscopic approaches, in particular when modelling precipitation processes. To extend its use to concentrated alloys, it is necessary to take into account accurately the exclusion zones and their overlap. By investigating the one-dimensional case, one obtains an exact formula for these zones, and its generalization to higher dimensions is proposed. By integrating cluster fragmentation/coagulation processes into cluster dynamics equations, a perfect agreement between atomistic simulations (Kinetic Monte Carlo) and cluster dynamics is reached on the whole range of concentrations for kinetics which govern microstructure in one dimension.

Keywords: Cluster dynamics; Kinetic Monte Carlo simulations; Linear chain; Local order; Nanowires

1. Introduction

The expansion of multiscale modelling in materials sciences requires, in particular, the development of mesoscale methods in order to make a connection between the atomistic and macroscopic models. Among the mesoscopic approaches, cluster dynamics (CD) [1–7] is a chemical kinetics method which can model numerous kinetics, such as precipitation in alloys [8–10] or the time evolution of the concentration of point defect clusters under irradiation [11–14]. For precipitation in binary alloys, CD has almost always been used in the domain of dilute alloys with a low solubility limit. Bypassing this limit raises numerous problems, one of the main difficulties being to compute the available space to form new clusters by considering both the exclusion zone due to present clusters and the overlapping of these zones [15,16]. This issue, which is tightly linked to the computation of the entropy of the cluster gas [15–17], has recently aroused two studies which brought significant progress: (i) Lépinoux proposed a formalism which takes into account the exclusion zones due to each cluster and their overlap, in two dimensions (2D) and three dimensions (3D) [15,16]. This framework has been successfully compared with Kinetic Monte Carlo simulations (KMC) for precipitation kinetics in a concentration range <10%. Nevertheless, the range of higher concentrations has not been studied, although it is a more severe test to validate the proposed formulation. (ii) For the one-dimensional (1D) Ising model, M.B. Yilmaz and F.M. Zimmermann (denoted YZ in the following) obtained analytical formulas which provide the equilibrium size distribution of clusters on the whole range of temperature and concentration. These results have been confirmed by equilibrium Monte Carlo simulations [18]. Recall that the 1D Ising model induces a nil critical temperature, and the cluster description consequently amounts to describing the local order in a disordered solid solution [19].

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In order to develop a CD that is likely to deal with concentrated alloys, the present study considers the linear-chain case by extending the equilibrium description of YZ [18] to its kinetic part. More precisely, the case of 1D adsorption that can take place along the steps of a surface, either dense or vicinal, is investigated. The system under study is denoted $A_\theta V_{1-\theta}$, where A stands for the atoms, and V for the unoccupied sites, θ being the coverage (or alloy concentration). Note that the study of the time evolution of the pseudo-1D microstructure is also precious for alloy nanowires and for cases where the segregation of one of the components is close to 1D, as can occur in the core of dislocations or grain boundaries.

Investigating the 1D case enables the formula given by Lépinoux for the entropy of the cluster gas [15,16] to be tested, and a correction of the overestimation of the overlapping of the exclusion zones that this study revealed is proposed. This also leads to integration of the cluster fragmentation and coagulation processes into the CD. The resulting agreement with the KMC simulations is remarkable.

The paper is organized as follows. The equilibrium description using clusters is detailed in Section 2, including in particular the computation of the exclusion zones. Section 3 presents different formulations of the CD which include these exclusion zones, and the fragmentation/coagulation processes. Section 4 compares the 1D deposition kinetics obtained by CD and KMC.

2. Equilibrium

2.1. Energetic model

The linear chain of the atom–vacancy system is described via an Ising Hamiltonian in the grand-canonical ensemble:

$$H = E_{ads}\sum_n p_n + V_{AA}\sum_{n\neq m} p_n p_m - \mu\sum_n p_n \tag{1}$$

where E_{ads} stands for the adsorption energy of an isolated atom, and p_n is the occupation number, which equals 1 if the site n is occupied by an atom, and 0 otherwise. The attractive interactions between atoms are restricted to the nearest-neighbour sites and are denoted by V_{AA} (<0). μ is the chemical potential which imposes the coverage $\theta = (\sum_{n=1}^{N_s} p_n)/N_s$, where N_s is the number of the chain sites. With reference to previous work on silver deposited on copper, the results presented here are obtained with parameters determined for this system, which are: $V_{AA} = -0.277$ eV and $E_{ads} = -2.56$ eV [20–22].

In contrast to the Ising model in 2D or 3D which is characterized by a first-order transition and the presence of a miscibility gap in the canonical ensemble, the 1D case does not display any phase transition [19,23]. The presence of attractive interactions is only depicted by the existence of atomic and vacancy clusters whose size distribution has been widely studied. In particular, YZ's investigation leads to an analytical expression of these distributions [18]. Before details are given of the time evolution of these cluster distributions via CD, its equilibrium properties are recalled, and it is linked with other descriptions of local order.

2.2. Cluster approach

The cluster description relies on the knowledge of the size distribution of atomic and vacancy clusters. An atomic cluster of size n consists of a chain of n adjacent occupied sites terminated by unoccupied sites at both ends, with an analogous definition for a vacancy cluster. Note, N_n is the number of atomic clusters of size n, N_n^v is the number of vacancy clusters made of n connected unoccupied sites, and $C_n = N_n/N_s$ is the density of clusters of size n (respectively $C_n^v = N_n^v/N_s$). The coverage and the total cluster density can be written from the cluster size distribution:

$$\theta = \sum_{n=1}^{N_s} nC_n \quad \text{and} \quad C_{tot} = \sum_{n=1}^{N_s} C_n \tag{2}$$

Using the maximum-term approach in the partition function [24], YZ show that the dependence of the total cluster density C_{tot} on θ can be expressed at equilibrium as:

$$C_{tot} = \frac{\sqrt{1 + 4\theta(1-\theta)\left(\exp\left(-\frac{V_{AA}}{kT}\right) - 1\right)} - 1}{2\left(\exp\left(-\frac{V_{AA}}{kT}\right) - 1\right)} \tag{3}$$

where T is the temperature, and k is the Boltzmann constant. Fig. 1 shows perfect agreement between the Monte Carlo simulations (obtained for a chain of $N_s = 1000$ sites limited by periodic boundaries) and the values of the total cluster density as predicted by Eq. (3). This relation underlines two features of the total cluster density: (i) C_{tot} is symmetric with respect to $\theta = ½$ and displays a maximum at this value. This symmetry originates from the atom–vacancy symmetry of the Ising model used. In other words, there are as many atomic clusters as vacancy clusters for

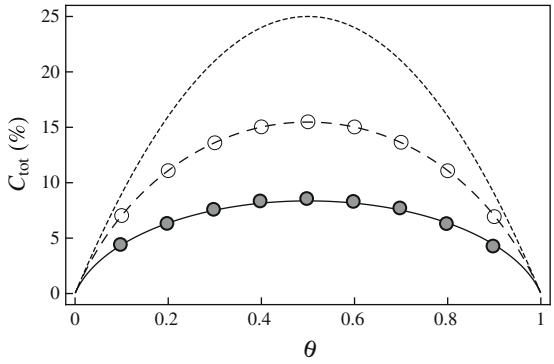

Fig. 1. Comparison between MC simulations (symbols) and analytical computation with the help of formula (3) (lines) of the equilibrium total cluster density C_{tot} as a function of the coverage θ for different temperatures: $T = 1000$ K (continuous lines and full dots) and 2000 K (dashed lines and empty circles). The totally disordered system described by $C_{tot} = \theta(1-\theta)$ is recalled as the dotted lines.