Rigidity of Layered Random Alloys

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Abstract

Randomly intercalated layered alloys are excellent models for two-dimensional microporous systems. We have studied the nonlinear gallery expansion and the gallery height fluctuations by constructing a double layer model that describes the layer rigidity and the size and stiffness of the intercalant species. Exact solutions, simulations and an effective-medium theory (EMT) results are compared. Applications of the results to ternary intercalation compounds are discussed.

Introduction

There is a large variety of ternary layered alloys whose chemical composition can be written as $A_{1-x}B_xL$, where $L$ represents the host layer such as graphite, dichalcogenide and layered sheet silicate (vermiculite). Two distinct atoms (ions) $A$ and $B$ are intercalated into the galleries between the host layers. All these alloys show a composition dependence of the average interlayer spacing $\langle h \rangle$ which increase with the concentration of the largest constituent. The linear variation of $\langle h \rangle$ with $z$ is the well known Vegard’s law, although most alloys exhibit a complex nonlinear (superlinear, sublinear, sigmoidal) behavior. The physical origin of this nonlinear behavior is a subject of considerable theoretical interest. Furthermore these layered alloys, particularly those associated with the sheet silicates are excellent models for two-dimensional microporous systems which are potentially useful for solid state catalysis.

In this paper, we discuss our recent theoretical work on the structural properties of these layered alloys. We will introduce a harmonic model that describes both the layer rigidity and the size and stiffness of the intercalant ions in these alloys. We give an exact solution for the case when $A$ and $B$ have the same stiffness. We will also give an EMT solution and compare the results with numerical simulations. Finally we apply the results to experiments in ternary intercalated graphite and in layered sheet silicates.

The Model

The basic idea of our microscopic model is that the $z$-dependence of $\langle h \rangle$ depends on the competition between local and global energies associated with forming a solid solution. These energies depend upon the relative size and compressibility of the different atomic species and overall rigidity of the system. The host layer-intercalant interaction is approximated by a harmonic spring of strength $K_1$($= K_A$ or $K_B$), characterizing the compressibilities of the intercalant atoms (ions), and equilibrium height
The intercalants are assumed to occupy randomly a set of well-defined lattice sites (Fig. 1). The energy associated with the host layer deformation has two types of contributions. The first one, proportional to $K_T$, is the transverse layer rigidity,\textsuperscript{4,7} and the second one, proportional to $K_F$ is the bending layer rigidity.\textsuperscript{3,11} Therefore the total elastic energy of the layer-intercalant system can be written as

$$E = \frac{1}{2} \sum_i K_i (h_i - h^\rho_i)^2 + \frac{1}{2} K_T \sum_i \sum_{<ij>} (h_i - h_{i,j+})^2 + \frac{1}{2} K_F \sum_i \left[ \sum_{d} (h_i - h_{i,d}) \right]^2, \quad (1)$$

where $h_i$ is the gallery height at the site $i$ where an intercalant (either A or B) sits. If we define a local dimensionless height $d_i$ such that $h_i = h^\rho_i + d_i (h^A_i - h^B_i)$, then the heights and the energy are scaled by $(h^A_i - h^A_i)$ and $(h^B_i - h^A_i)^2$, respectively.\textsuperscript{7}

We minimize the energy $E$ given in Eq. (1) with respect to the heights $\{h_i\}$ for a given realization of the random variables $K_i (= K_A, K_B)$ and $h^\rho_i (= h^\rho_A, h^\rho_B)$ to determine the stable structure of the random alloys. We calculate the average heights $(d)$, $(d_A)$, $(d_B)$, the average energy per site $e$, the fluctuations in height $(\langle (d - d)^2 \rangle)$, $(\langle (d_A - d) \rangle)^2$ etc., as functions of $x$, $K_A$, $K_B$, $h^\rho_A$, $h^\rho_B$, $K_T$, $K_F$ and the structure of the host lattice by averaging over different configurations.

(a) Top view of a hexagonal lattice host layer where the intercalants form a triangular lattice. (b) Side view of the intercalants.

**Exact Solution**

When the layers are either completely floppy or perfectly rigid, the model can be solved exactly.\textsuperscript{4,7} If $K_T = K_F = 0$, we have $(d) = \varepsilon$; the usual Vegard's law with $(d_A) = 0$ and $(d_B) = 1$. The corresponding fluctuations are given by $(\langle (\Delta d)^2 \rangle) = (d^2) - (d)^2 = \varepsilon (1 - \varepsilon)$, and the site-specific fluctuations are zero. On the opposite end, in the limit of infinite layer rigidity\textsuperscript{4} the energy $E$ is minimised by having all the $d_i$ equal $(d_A = d_B = d)$, i.e.,

$$d = (d_A) = (d_B) = \frac{x}{\varepsilon + (1 - \varepsilon)K_A/K_B}, \quad (2)$$

and fluctuations in all the three heights vanish in this limit.

When the stiffness of the A and B ions are equal $(K_A = K_B = K)$, the model can also be solved exactly. The non-trivial exact solution in this case can be expressed in terms of Watson integrals $W_0(K) \equiv W_0(K), W_1(K)$ and $W_2(K)$, which are related to the rigidities of the layers.\textsuperscript{7} We write
\[(d_B) = 1 - (1 - x)[1 - W(K)], \quad (d_A) = x[1 - W(K)], \quad (3)\]
\[\langle (d_B - d_B)^2 \rangle = \langle (d_A - d_A)^2 \rangle = x(1 - x)[W_1(K) - W(K)^2], \quad (4)\]
\[\langle (d - d)^2 \rangle = x(1 - x)W_1(K), \quad (5)\]
\[e = \frac{1}{2} K x(1 - x)[1 - W(K)], \quad (6)\]

where the Watson integrals are defined by
\[W_n(K) = \int \frac{dq}{(2\pi)^D} \left( \frac{K}{\lambda_q} \right)^{n+1}, \quad (7)\]
where \(D\) is the dimension (\(D = 1\) for linear chain, \(D = 2\) for square and triangular lattices), and the factor \(\lambda_q\) is given by
\[\lambda_q = K + K T x(1 - \gamma_q) + K F [x(1 - \gamma_q)]^2, \quad (8)\]
where \(\gamma_q = \frac{1}{x} \sum_{q} e^{i nq}, \) and \(x\) is the number of nearest neighbors (\(x = 2\) for linear chain, \(x = 4\) for the square lattice, \(x = 6\) for the triangular net). Clearly the geometry of the lattice will determine \(\lambda_q\) and hence the layer distortion characteristics. In Fig. 2 we plot \(W(K)\) and \(W_1(K)\) for various lattices as a function of \(K/(xK_T)\) for \(K_F = 0\). The average heights \(\langle d \rangle, \langle d_A \rangle, \langle d_B \rangle\) show straight line behavior, with \(\langle d \rangle\) obeying Vegard’s law. The fluctuations and average energy are symmetric about \(z = 0.5\). The difference \(\langle d_B \rangle - \langle d_A \rangle = W(K)\) is independent of \(z\). It depends only on the transverse layer rigidity parameters and decreases as the rigidity of the layer increases.\(^7\)

![Fig. 2](image)

The Watson integrals \(W_n(K)\) are shown for various lattices as a function of \(K/(xK_T)\) and for \(K_F = 0\).

**Effective Medium Theory**

We have developed an EMT to handle the case of unequal stiffness \((K_A \neq K_B)\). In this approximation,\(^7,12\) the effect of the layer on the intercalant ions is contained within an effective local spring constant \(K_s\). This can be found by applying a force \(F\) to a single site in the non-random system where \(K = K_A = K_B\) as shown in Fig. 3(a), where the effective spring constant for this kind of displacement \(K_s\) is given by
\[ K_e = \frac{K}{W(K)}. \] (9)

The whole system is now replaced by a single spring \( K_e \) as shown in Fig. 3(b). The problem is now reduced to just two springs in parallel as shown in Fig. 3(c). One of these springs is \( K_{e\alpha} \), where \( \alpha \) can be either \( A \) or \( B \) with probability \( 1 - z \) or \( z \) respectively. The other spring is \( K'_{e\alpha} = K - K \) formed by removing the spring \( K \). From variational procedures, we obtain the self-consistency condition that determines the effective spring constant \( K \)

\[ x \frac{K - K_B}{K'_e + K_B} + (1 - x) \frac{K - K_A}{K'_e + K_A} = 0. \] (10)

Various solutions for \( K \) from Eqs. (10) and (11) are shown in Fig. 4 for the triangular net (Fig. 1) and compared to the virtual crystal result \( K_o = zK_B + (1 - z)K_A \). The averages can also be obtained from the same variational procedures. We write

\[ \langle d \rangle = x + z(1 - z) \frac{K_eK'_e(K_B - K_A)}{K(K'_e + K_A)(K'_e + K_B)}, \] (11)

\[ \langle d_B \rangle = 1 - (1 - z) \frac{K_eK'_eK_A}{K(K'_e + K_A)(K'_e + K_B)}, \quad \langle d_A \rangle = z \frac{K_eK'_eK_B}{K(K'_e + K_A)(K'_e + K_B)}, \] (12)

\[ \epsilon = z(1 - z) \frac{K'_eK_eK_AK_B}{2K(K'_e + K_A)(K'_e + K_B)}. \] (13)

We note that when \( K_B > K_A \) the average height shows superlinear behavior and the partial heights \((\langle d_A \rangle, \langle d_B \rangle)\) are no longer linear. The fluctuations can be obtained using the Feynman-Hellman theorem,

\[ (\langle d_A - \langle d_A \rangle \rangle^2) = z(1 - z) \frac{K_AK_BK'_e^2}{W(K)^2} \left[ \frac{K(K'_e + K_A)(K'_e + K_B)(K'_e + K_o)}{W(K)^2 + (K - K_A)(K - K_B)} \right]^2. \] (14)

Fig. 3 Illustrating how (a) the equivalent spring \( K_{e\alpha} \), (b) the local rigidity, and (c) the effective coupling constant \( K \) are determined within the EMT.
\[
((d - \langle d \rangle)^2) = z(1 - z) \frac{W_1(K)}{W_1(K) - W(K)^2} \left[ \frac{K_A K_B K_D}{K(K_A + K_A)(K_A + K_B)} \right]^2 + \frac{K_A K_B K_D}{K_A + K_A}(K_A + K_B).
\]

These EMT results contain the previous exact results as special cases.

**Numerical Simulation**

We test the above EMT results via a direct numerical simulation method. We have performed extensive simulations for the triangular lattice where typical lattice sizes used were \(N = 50 \times 50 = 2500\) nodes with periodic boundary conditions. The simulations were carried out by first generating an initial configuration of random system and then relaxing it by use of the conjugate gradient total energy minmization method.\(^7\) In Fig. 5 we show a typical configuration of a relaxed layer obtained from the simulation at \(z = 0.2\) and \(K_A \neq K_B\). One sees that the relaxed surface is not flat, but rather have the appearance of "waves on the ocean". However, in the limit of very large \(K_F\) or \(K_P\), the layers do become flat, similar to the "flat phase" of polymerized membranes.\(^1\) The simulation results of the average heights, average fluctuations for both the \(A\) and \(B\) intercalants, and the average energy are shown as solid dots in Fig. 6 and compared with

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**Fig. 4** The effective spring constant \(K\) for a triangular lattice.

**Fig. 5** A configuration of a relaxed triangular layer.

**Fig. 6** Showing (a) average height, (b) fluctuations in height and (c) the average energy. The solid lines are EMT results and the solid dots are simulation results.
the EMT results. We see that the EMT gives very good agreement with the simulation results.

The two ternary graphite intercalation systems whose average c-axis separation can be understood within our model are \( V_1 \rightarrow Li_xC_6 \) (\( V \) is a vacancy) and \( K_{1-x}Rb_xC_6 \) (Ref. 3, 15). For the lithium ternary, where the gallery expands from 3.36\( \bar{\AA} \) for \( z = 0 \) to 3.78\( \bar{\AA} \) for \( z = 1 \), the \( A \) atom is actually a vacancy so that \( K_A/K_B \gg 1 \). A choice of \( K_A/K_B = 0.1 \), and \( K_I/K_B = 0.1 \) can semi-quantitatively fit the experimental data excepting for \( z = 1 \) where anharmonicity effects may be important. The potassium-rubidium ternary data, where the gallery expands from 5.47\( \bar{\AA} \) for \( z = 0 \) to 5.68\( \bar{\AA} \) for \( z = 1 \), shows nearly a Vegard's law behaviour.\(^{18}\) This can be understood if we assume that \( K_A/K_B \approx 1 \) which seems physically reasonable.

In summary, we have set up an elastic model that describes the structural properties of random layered alloys. This model incorporates both the layer rigidity and the compressibilities of the intercalants. Vegard's law is only obtained when \( K_A = K_B \) (Ref. 16).

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References