Chin. Ann. Math.
28B(6), 2007, 665–676
DOI: 10.1007/s11401-006-0447-2

Chinese Annals of Mathematics, Series B

The Elastic Continuum Limit of the Tight Binding Model***

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Abstract The authors consider the simplest quantum mechanics model of solids, the tight binding model, and prove that in the continuum limit, the energy of tight binding model converges to that of the continuum elasticity model obtained using Cauchy-Born rule. The technique in this paper is based mainly on spectral perturbation theory for large matrices.

Keywords Continuum limit, Elasticity theory, Cauchy-Born rule, Tight binding model
2000 MR Subject Classification 74B20, 35Q72

1 Introduction

We consider a topic that has been of considerable interest in recent years, the continuum limit of atomistic models for solids. We limit our attention at zero temperature in which case both the atomistic and the continuum models reduce to energy minimization problems. By atomistic model, we mean either quantum mechanics based models or models based on classical potentials. The purpose of this study is two-fold: To understand the microscopic origin of the continuum elasticity theory and to understand when elasticity theory breaks down. This study is also relevant to the vast amount of effort that has been devoted to developing modeling strategies that combine continuum and atomistic models (see [7]). Questions of this type were considered in the classic works of Cauchy and Born [3]. Indeed the most well-known strategy for deriving nonlinear elasticity models from atomistic models carry the name of "Cauchy-Born rule". One main purpose of this work is to study when the Cauchy-Born rule can be applied.

There are two kinds of results that have been established. The first type of results were established in the work of Blanc, Le Bris and Lions [2]. They assumed that the displacement of the atoms follows a smooth vector field, and proved that in the continuum limit, the difference between the energies of the atomistic and continuum models obtained using the Cauchy-Born rule goes to zero. The second type of results were established in the work of E and Ming [8]. They proved that in the continuum limit, the local minimizers representing elastic states of the atomistic model converge to the local minimizers of the continuum model representing its elastic states. A consequence of this result is a proof of the main assumption of the Blanc, Le Bris and Lions's result, namely that the displacement of the atoms does follow a smooth vector field, and this smooth vector field is close to the solution of the continuum model. Adopting the

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***Project supported by the Natural Science Foundation (No. DMS 04-07866) and the "Research Team on Complex Systems" of Chinese Academy of Sciences.

terminology from numerical analysis, one may say that the Blanc, Le Bris and Lions's result is a consistency statement, whereas the E and Ming's result is a statement of convergence. The difference between the two results lies in stability. Indeed, one main component of the E-Ming's work is to identify the correct stability conditions for the atomistic models. E and Ming also gave examples for which the stability conditions do not hold, and in that case, the Blanc, Le Bris and Lions's results fail to reveal that the crystal is not in an elastic regime.

At this stage, the E-Ming's results are only proved for classical atomistic models. The Blanc-Le Bris-Lions's results have also been proved for the Thomas-Fermi-von Weizäker model. For the perfect crystal, the similar results (the thermodynamic limit in this case) have been established for the Thomas-Fermi type model (see [4, 11]) and the modified Hartree and Hartree-Fock models (see [5, 6]). Unfortunately, these models are rarely used in practice. Therefore it remains to be of great interest to establish such results for the kind of quantum mechanics models that are really used.

This paper will focus on the tight binding model, a commonly used model for insulations. In the tight binding model, one makes an independent electron approximation except that the Pauli exclusion principle has to be obeyed. One approximates the wave function of the electrons by a linear combination of a finite number of atomic orbitals, which are solutions of the Schrödinger equations for the hydrogen atom. Under these approximations, the Hamiltonian operator becomes a matrix. The eigenvalues are computed and Pauli exclusion principle is used to assign electrons to the lowerest states.

The main purpose of this paper is to extend the Blanc-Le Bris-Lions type of results to tight binding models. The main obstacle that we need to overcome is the nonlocality of the tight binding model: Continuum elasticity models are certainly local whereas the tight binding model, which involves diagonalization of the Hamiltonian matrix, seems quite nonlocal. However, using spectral perturbation theory for large matrices, we will show that to leading order, the tight binding model is also local, and this leads to the desired result.

At this point, it remains open to extend the E-Ming type of results to tight binding models. We will return to this point in the conclusion section.

2 Tight Binding Model

The tight binding (TB) model has its origin in the linear combination of atomic orbitals (LCAO) method pioneered by Slater and Koster. It is widely used in total energy calculation and band structure determination. Here we summarize the key elements of TB model, followed by two specific examples.

2.1 Abstract formulation

In this work, we denote by Ω the domain occupied by the material in the undeformed state; $\boldsymbol{x}_j$ the position of the j-th atom in equilibrium; and $\boldsymbol{y}_j = \boldsymbol{x}_j + \boldsymbol{u}(\boldsymbol{x}_j)$ the position of j-th atom in the deformed state, where the continuous vector field $\boldsymbol{u}$ is the displacement field.

The starting point of TB is an approximation of total electron wave function using linear combination of atomic-like orbitals $|j\alpha\rangle = \phi_\alpha(\cdot - \boldsymbol{y}_j)$, where j is a site index and α is an orbital index:

$$|\psi\rangle = \sum_{j\alpha} C_{j\alpha}|j\alpha\rangle. \tag{2.1}$$

The coefficients $C_{j\alpha} = \langle j\alpha|\psi\rangle$ are determined by solving an effective single particle Schrödinger

equation:

$$\widehat{H}|\psi\rangle = \lambda|\psi\rangle. \tag{2.2}$$

When applying TB model to real systems, we need to choose a basis of atomic-like orbitals $\{\phi_\alpha\}$. In most cases, the set of valence orbitals are used, for exmaple, $3s$, $3p_x$, $3p_y$, $3p_z$ for Silicon. We assume that the overlap between two different atomic orbitals can be neglected, i.e.,

$$\langle j\alpha|k\beta\rangle = \delta_{jk}\delta_{\alpha\beta}. \tag{2.3}$$

In this case, the Hamiltonian can be represented as a matrix whose elements $H_{j\alpha,k\beta}$ are

$$H_{j\alpha,k\beta} = \langle j\alpha|\widehat{H}|k\beta\rangle. \tag{2.4}$$

Therefore, we can rewrite (2.2) in the matrix form:

$$\sum_{k\beta} H_{j\alpha,k\beta}C_{k\beta} = \lambda C_{j\alpha}. \tag{2.5}$$

Note that the eigenvalue λ and eigenvector $(C_{j\alpha})$ can always be made real, since the atomic orbitals are real. This is assumed from now on.

The total energy of the system may be written as

$$U_{\text{tot}} = U_{\text{band}} + U_{\text{rep}} = 2\sum_{n(\text{occ})} \lambda_n + \frac{1}{2}\sum_{j\neq k}\phi(r_{jk}), \tag{2.6}$$

where the first sum runs over the occupied states, and $\phi(r_{jk})$ is a repulsive pair potential between ionic cores, which has contributions from electrostatics, and from Pauli exclusion principle. Since the band energy depends on the displacement field, the domain and also the number of atoms, the band energy can be written as

$$E_{\text{p}}(\boldsymbol{u}, \Omega, N) = 2\sum_{n(\text{occ})} \lambda_n(\boldsymbol{u}, \Omega, N), \tag{2.7}$$

where the subscript p denotes periodic boundary condition we will use for the domain.

Calculating the band energy E_{p} using TB model amounts to diagonalizing the Hamiltonian matrix $H_{j\alpha,k\beta}$. The eigenvalue problem of a matrix is highly nonlocal. However, we will show in this work that in the continuum limit, the total energy can be represented in a local way.

2.2 Example 1: A one-dimensional chain

To illustrate the ideas of the TB model, we now consider a one-dimensional periodic chain of atoms with one valence electron per atom, and choose a tight binding orbital basis that consists of one s-orbital per site. Periodicity means that the solid is invariant under the translation of $x \to x + L$. Suppose that in one supercell $\Omega = [0, L]$, there are N atoms with $x_j = j\epsilon$ and $y_j = x_j + u(x_j)$. $\epsilon = \frac{L}{N}$ will be the small parameter in our analysis, and can be understood as the ratio of the lattice constant to the length scale of the system. By periodicity, we have $y_{N+1} = y_1 + L$. $E_{\text{p}}(u, \Omega, N)$ will be calculated using TB model.

For simplicity, all interactions beyond those at the nearest-neighbor level are neglected and we assume that the on-site coupling constant (i.e., $\langle j|H|j\rangle$) is zero. Since the basis consists of only one orbital, the index α is not needed in this case. Therefore, we have

$$|\psi\rangle = \sum_j C_j|j\rangle, \tag{2.8}$$

and (2.5) is simplified as

$$\sum_k H_{j,k}C_k = \lambda C_j, \tag{2.9}$$

where $H_{j,k}$ is an $N \times N$ tridiagonal matrix:

$$H_{j,k} = \begin{cases} h(y_{j+1}-y_j)\delta_{k,j+1} + h(y_j - y_{j-1})\delta_{k,j-1}, & 2 \le j \le N-1, \\ h(y_2 - y_1)\delta_{k,2} + h(y_1 + L - y_N)\delta_{k,N}, & j = 1, \\ h(y_N - y_{N-1})\delta_{k,N-1} + h(y_1 + L - y_N)\delta_{k,1}, & j = N. \end{cases} \tag{2.10}$$

Same as ϕ, h also has the scaling ϵ, i.e.,

$$h(y_{j+1} - y_j) = h_0\Big(\frac{y_{j+1} - y_j}{\epsilon}\Big).$$

By the minimal energy principle and Pauli exclusion principle, the $\frac{N}{2}$ states with least energy are filled with electrons at zero temperature. (We assume here N is even, this will not lead to any loss of generality since we mainly focus on the case that N is large.)

2.3 Example of two-dimensional graphite

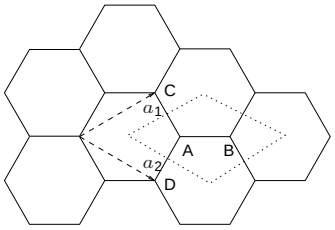


Figure 1 Two-dimensional graphite

Graphite is a three-dimensional layered hexagonal lattice of carbon atoms. A single layer of graphite forms a two-dimensional material, called 2D graphite or a graphene layer. The equilibrium 2D graphite (as in Figure 1) has a complex lattice structure. The underlying Bravais lattice has basis vectors

$$\boldsymbol{a}_1 = \Big(\frac{\sqrt{3}}{2}\epsilon, \frac{1}{2}\epsilon\Big), \quad \boldsymbol{a}_2 = \Big(\frac{\sqrt{3}}{2}\epsilon, -\frac{1}{2}\epsilon\Big), \tag{2.11}$$

where $\epsilon = |\boldsymbol{a}_1| = |\boldsymbol{a}_2|$ is again the small parameter (understood as the ratio of lattice constant to the length scale of the system). $\boldsymbol{p} = (\frac{\sqrt{3}}{3}\epsilon, 0)$ is the shift vector between the two Bravais lattices.

We consider the π-bonds of two-dimensional graphite (see [9]). Notice that the unit cell contains two atoms (e.g., A and B in Figure 1), the orbital basis contains two $2p_z$ orbitals that concentrate on atom A and B respectively. Suppose that the system consists of N unit cells with periodic boundary condition, with $\sqrt{N}$ unit cells in each direction ($\boldsymbol{a}_1$ and $\boldsymbol{a}_2$), so the system contains $2N$ atoms. At zero temperature, the lowest N orbitals will be occupied by the electrons. Here, we assume that $\sqrt{N}$ is an integer.

As in the one-dimensional example, only nearest-neighbor interaction will be counted, i.e., the nonzero entries of Hamiltonian matrix corresponding to the interaction between $2p_z$ orbitals

belonging to atom pairs like A and B, A and C, or, A and D in Figure 1. Again, we use h to denote the interaction term. h depends on the distance between the neighboring atoms and has the scaling

$$h(|\mathrm{AB}|) = h_0\Big(\frac{|\mathrm{AB}|}{\epsilon}\Big).$$

While we do not write the explicit form of the Hamiltonian matrix for 2D graphite under general deformation, we will see in the next subsection that when the system is at equilibrium or under uniform deformation, it can be characterized more clearly using the k-space tight binding method.

2.4 k-Space tight binding model for 2D graphite

When the system has translational symmetry, TB model can be combined with Fourier analysis to calculate the energy spectrum in Fourier space. This is so called the k-space TB model. In k-space, the Hamiltonian matrix decouples into smaller matrix, which is easier to diagonalize.

Consider a 2D graphite at equilibrium or under uniform defomation. In this case the system has translational symmetry. By Bloch's theorem, the coefficients of (2.1) may be chosen as

$$C_{j\alpha} = e^{i\boldsymbol{k}\cdot\boldsymbol{y}_j} C_\alpha, \tag{2.12}$$

where $\boldsymbol{k}$ is a point in the k-space. Since we use the periodic boundary condition, $\boldsymbol{k}$ satisfies $e^{i\sqrt{N}\boldsymbol{k}\cdot\boldsymbol{y}_j} = 1$ as the 2D graphite has $\sqrt{N}$ unit cells in each direction.

Therefore, (2.5) becomes

$$\sum_\beta H_{\alpha\beta} C_\beta = \lambda C_\alpha, \tag{2.13}$$

where

$$H_{\alpha\beta} = \Big(\frac{1}{N}\sum_j \sum_l e^{i\boldsymbol{k}\cdot(\boldsymbol{y}_l - \boldsymbol{y}_j)} H_{j\alpha,l\beta}\Big).$$

Hence, for each admissible $\boldsymbol{k}$, we only need to diagonalize a 2×2 matrix instead of $2N\times 2N$ matrix.

We use A and B as orbital index corresponding to $2p_z$ orbitals centered at atoms A and B in Figure 1. Assuming that the on-site coupling constants satisfy $H_{AA} = H_{BB} = 0$ and restricting to the nearest-neighbor interaction, for fixed $\boldsymbol{k}$, the decoupled Hamiltonian matrix becomes

$$H(\boldsymbol{k}) = \begin{bmatrix} 0 & H_{AB}(\boldsymbol{k}) \\ H^*_{AB}(\boldsymbol{k}) & 0 \end{bmatrix} \tag{2.14}$$

for

$$H_{AB}(\boldsymbol{k}) = h(r_{AB}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{AB}} + h(r_{AC}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{AC}} + h(r_{AD}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{AD}}, \tag{2.15}$$

where $\boldsymbol{r}_{AB}$ is the vector pointing from A to B, and r_{AB} is its length. Here we suppose that the interaction between two neighboring atoms could be decouple to angle-independent part h and angle-dependent part. Clearly, the eigenvalues of $H(\boldsymbol{k})$ are $\pm|H_{AB}(\boldsymbol{k})|$. Then the band energy of the system is

$$E_{\mathrm{p}}(\boldsymbol{u}, \Omega, N) = -2\sum_{\boldsymbol{k}} |H_{AB}(\boldsymbol{k})|. \tag{2.16}$$

3 Cauchy-Born Rule

The Cauchy-Born (CB) rule is a standard recipe for obtaining the stored energy functional in elasticity theory from atomistic models.

3.1 General formulation

The idea of CB rule is that the stored energy density for elastic deformations of a crystal can be obtained through computing the energy per atom for the uniformly deformed crystal. In particular, for simple lattice, the stored energy density $W_{\rm CB}$ is a function of $d \times d$ matrices, where d is the dimension. Given a $d \times d$ matrix A, $W_{\rm CB}(A)$ is computed by first deforming an infinite crystal uniformly with deformation gradient A, and then setting $W_{\rm CB}(A)$ to be the energy of the deformed unit cell

$$W_{\rm CB}(A) = \lim_{k\to\infty} \frac{U_{\rm tot}(\{\, \boldsymbol{y}_j \mid \boldsymbol{y}_j \in (I+A)L \cap kD \,\})}{|(I+A)L \cap kD|}, \tag{3.1}$$

where D is an open domain in $\mathbb{R}^d$, L denotes the Bravais lattice, and $|\cdot|$ is the number of elements in a set. The key point here is that the lattice is uniformly deformed, i.e., no internal relaxation is allowed for the atoms in kD.

For complex lattice, besides the deformation gradient A, the lattice structure has additonal degrees of freedom: the shift vectors between the different Bravais sublattices. Therefore, the stored energy density $W_{\rm CB}$ is a function of not only $d \times d$ matrices, but also d-dimensional shift vectors. We restrict our consideration to the case that the complex lattice consists of two Bravais sublattices. Thus there is only one shift vector $\boldsymbol{p}$. Then we have

$$W_{\rm CB}(A, \boldsymbol{p}) = \lim_{k\to\infty} \frac{U_{\rm tot}(\{\, \boldsymbol{y}_j \mid \boldsymbol{y}_j \in \{(I+A)L \cup \{(1+A)L + \boldsymbol{p}\}\} \cap kD \,\})}{|\{(I+A)L \cup \{(1+A)L + \boldsymbol{p}\}\} \cap kD|}. \tag{3.2}$$

We can also eliminate $\boldsymbol{p}$ by defining

$$W_{\rm CB}(A) = \min_{\boldsymbol{p}} W_{\rm CB}(A, \boldsymbol{p}). \tag{3.3}$$

In this work, we will use the former definition, but the result can be easily extended to the latter case.

3.2 Cauchy-Born rule for the 1D chain

As a specific example, we now derive the expression of $W_{\rm CB}$ for the one-dimensional chain considered in Subsection 2.2. The atomistic energy takes the form

$$U_{\rm tot} = E_{\rm p}(u, \Omega, N) + U_{\rm rep} = 2 \sum_{n({\rm occ})} \lambda_n + \sum_{j=1}^{N} \phi(r_{j,j+1}).$$

In this setting, $\{\lambda_n\}_{n({\rm occ})}$ are the smallest $\frac{N}{2}$ eigenvalues of the Hamiltonian matrix (2.10), or in the matrix form

$$H = \begin{bmatrix} 0 & h(D^+y_1) & & & h(D^+y_N) \\ h(D^+y_1) & 0 & h(D^+y_2) & & \\ & \ddots & \ddots & \ddots & \\ & & h(D^+y_{N-2}) & 0 & h(D^+y_{N-1}) \\ h(D^+y_N) & & & h(D^+y_{N-1}) & 0 \end{bmatrix}, \tag{3.4}$$

where we have introduced the notation

$$D^+ y_k = y_{k+1} - y_k.$$

In the equilibrium state, the atoms are located at $x_j = j\epsilon$. For uniform deformation, we have

$$y_j = (1+A)x_j = (1+A)j\epsilon \quad \text{and} \quad D^+ y_j = (1+A)\epsilon.$$

Therefore, $E_{\rm p}(u,\Omega,N) = E_{\rm p}(Ax,\Omega,N)$. Note that, in the one dimensional case, A is actually a number rather than a matrix. The H matrix (3.4) becomes

$$H_A = \begin{bmatrix} 0 & h_0 & & & h_0 \\ h_0 & 0 & h_0 & & \\ & \ddots & \ddots & \ddots & \\ & & h_0 & 0 & h_0 \\ h_0 & & & h_0 & 0 \end{bmatrix}, \tag{3.5}$$

where h_0 takes value at $(1+A)$.

The following fact is well known.

Lemma 3.1 *The eigenvalues of the matrix H_0 are*

$$\lambda_n = 2h_0(1+A)\cos\frac{2\pi n}{N}, \quad n = 1, \cdots, N,$$

and the corresponding eigenvectors are

$$\mathbf{w}_n = \sqrt{\frac{1}{N}}\Big(\exp i\frac{2\pi n}{N}, \exp i\frac{4\pi n}{N}, \cdots, \exp i\frac{2N\pi n}{N}\Big).$$

From Lemma 3.1, we get

$$W_{\rm CB}(A) = \phi_0(1+A) - \frac{4}{\pi}|h_0(1+A)|, \tag{3.6}$$

since by simple calculation,

$$\lim_{N\to\infty}\frac{1}{N}E_{\rm p}(u,\Omega,N) = -\frac{4}{\pi}\left|h_0(1+A)\right|.$$

Therefore, the total energy given by the continuum model is

$$\int_\Omega \phi_0(1+u'(x))\,dx - \frac{4}{\pi}\int_\Omega |h_0(1+u'(x))|\,dx. \tag{3.7}$$

3.3 Cauchy-Born rule for 2D graphite

We then consider the example of two-dimensional graphite. Again, we will derive $W_{\rm CB}$ from the atomistic model

$$U_{\rm tot} = E_{\rm p}(\boldsymbol{u},\Omega,N) + U_{\rm rep}.$$

Since we only need to consider uniform deformation, we may use k-space tight binding model and this will simplify the computation. From §2.4, to calculate $E_{\rm p}$, we only have to determine $H_{AB}(\boldsymbol{k})$ for each admissible $\boldsymbol{k}$. To see more clearly the geometrical idea behind the computation, we choose an alternative way of characterizing the deformation which is equivalent to the deformation matrix A.

Consider a unit cell in a 2D graphite sheet as shown in Figure 2. In the figure, $\boldsymbol{a}_1 = \boldsymbol{r}_{AE}$ and $\boldsymbol{a}_2 = \boldsymbol{r}_{AF}$ are basis vectors of one of the Bravais sublattice and $\boldsymbol{p}$ is the shift vector between the Bravais sublattices. We denote by θ_1 the angle formed by atoms EAB and by θ_2 the angle

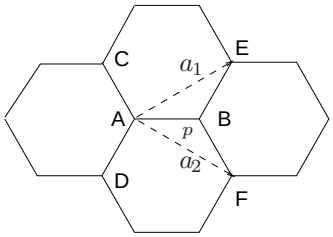


Figure 2 Two-dimensional graphite

formed by atoms FAB. We can use p, a_1, a_2, θ_1 and θ_2 to characterize the deformation (we choose $\boldsymbol{p} = (p, 0)$ to eliminate one degree of freedom which corresponds to uniform rotation).

At equilibrium, we have $p = \frac{\sqrt{3}}{3}$, $a_1 = a_2 = \epsilon$, $\theta_1 = \frac{\pi}{6}$ and $\theta_2 = -\frac{\pi}{6}$. When the lattice is uniformly deformed, we may represent the positions of atoms in the parameters $B(p, 0)$, $C(p - a_1 \cos\theta_1, -a_1 \sin\theta_1)$ and $D(p - a_2 \cos\theta_2, -a_2 \sin\theta_2)$. Therefore, $r_{AB} = p$, $r_{AC} = \sqrt{p^2 + a_1^2 - 2a_1 p \cos\theta_1}$ and $r_{AD} = \sqrt{p^2 + a_2^2 - 2a_2 p \cos\theta_2}$. Substituting these into (2.15), we get

$$\begin{aligned} H_{AB}(\boldsymbol{k}) &= h(r_{AB}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{AB}} + h(r_{AC}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{AC}} + h(r_{AD}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{AD}} \\ &= h(p) e^{ik_x p} + h\Big(\sqrt{p^2 + a_1^2 - 2a_1 p \cos\theta_1}\Big) e^{ik_x(p - a_1\cos\theta_1) - ik_y a_1 \sin\theta_1} \\ &\quad + h\Big(\sqrt{p^2 + a_2^2 - 2a_2 p \cos\theta_2}\Big) e^{ik_x(p - a_2\cos\theta_2) - ik_y a_2 \sin\theta_2}. \end{aligned}$$

The band energy E_{p} is twice the sum of $-|H_{AB}(\boldsymbol{k})|$ for every possible $\boldsymbol{k}$. From the constraint $e^{i\sqrt{N}\boldsymbol{k}\cdot\boldsymbol{y}_j} = 1$, we know $\boldsymbol{k} = 2\pi\big(\frac{n_1\boldsymbol{b}_1}{\sqrt{N}} + \frac{n_2\boldsymbol{b}_2}{\sqrt{N}}\big)$, where n_1 and n_2 can be 0, 1, $\cdots$, $\sqrt{N} - 1$. $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ are basis vectors of the reciprocal lattice:

$$\begin{aligned} \boldsymbol{b}_1 &= \Big(\frac{1}{a_2 \sin(\theta_1 - \theta_2)} \sin\theta_1, -\frac{1}{a_2 \sin(\theta_1 - \theta_2)} \cos\theta_1 \Big), \\ \boldsymbol{b}_2 &= \Big(-\frac{1}{a_1 \sin(\theta_1 - \theta_2)} \sin\theta_2, \quad \frac{1}{a_1 \sin(\theta_1 - \theta_2)} \cos\theta_2 \Big). \end{aligned} \tag{3.8}$$

While the summation does not have a simple closed form, we can calculate explicitily the band energy for the system under uniform deformation. From now on, we assume that E_{p} is known for systems under uniform deformation with E_{p} either represented in the summation form or calculated using some numerical methods.

4 The Continuum Limit

Using asymptotic analysis, we will show that in the continuum limit as $\epsilon \to 0$ and $N \to \infty$, the total energy of the TB model is to leading order given by the CB rule. We will follow the set up of Blanc, Le Bris and Lions. This proves that the two models are consistent. The E-Ming type of stronger results remain open.

4.1 One-dimensional case

We first discuss the case of one-dimensional chain, since one can understand the mathematics involved more clearly in this case. Calculation of the total band energy by TB model requires diagonalizing a matrix with the form (3.4). Except in the uniformly deformed case,

the eigenvalues cannot be explicitly computed. Nevertheless, asymptotically, the sum of the eigenvalues has a nice and simple relation in terms of h.

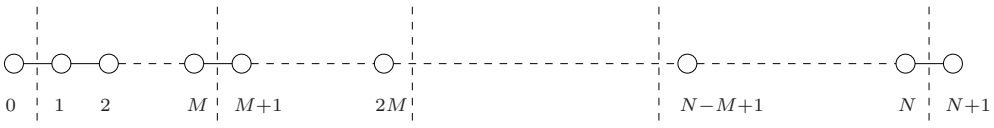
Theorem 4.1 *Let $\lambda_1, \lambda_2, \cdots, \lambda_N$ be eigenvalues of matrix (3.4), and $\{\lambda_n\}_{n(\mathrm{occ})}$ be the smallest $\frac{N}{2}$ eigenvalues. Then as N tends to infinity, we have*

$$\lim_{N\to\infty} \frac{1}{N} E_{\mathrm{p}}(u, \Omega, N) = \lim_{N\to\infty} \frac{2}{N} \sum_{n(\mathrm{occ})} \lambda_n = -\frac{4}{\pi} \int_{\Omega} |h_0(1 + u'(x))| \, \mathrm{d}x.$$

The entries of the Hamiltonian matrix $h(D^+ y_i)$ can be viewed as a smooth function evaluated at x_i. To recover Cauchy-Born rule which is concerned only with linear displacement fields, we approximate the displacement field u by piecewise linear functions. This idea is implemented as follows.

Proof of Theorem 4.1

Step 1 Let M be an integer such that $M|N$. $M|N$ is required just for simplicity, the argument can be generalized with slight modification. The domain $\Omega = [0, L]$ is divided into $\frac{N}{M}$ subdomains $\Omega_k = [\frac{kLM}{N} + \frac{\epsilon}{2}, \frac{(k+1)LM}{N} + \frac{\epsilon}{2}]$, where $k = 0, 1, \cdots, \frac{N}{M} - 1$. Ω_k consists of atoms y_{kM+1}, y_{kM+2}, $\cdots$, $y_{(k+1)M}$. $E_{\mathrm{p}}(u, \Omega, N)$ is approximated by $\sum\limits_k E_{\mathrm{p}}(u, \Omega_k, M)$.



For the k-th subsystem on Ω_k, the elements of the Hamiltonian matrix $\widehat{H}_k$ are

$$(\widehat{H}_k)_{j,l} = \begin{cases} h\Big(y_{kM+1} - y_{(k+1)M} + \frac{LM}{N}\Big), & (j,l) = (1,N) \text{ or } (j,l) = (N,1), \\ H_{kM+j,kM+l}, & \text{otherwise}, \end{cases}$$

where the term $h(y_{kM+1} - y_{(k+1)M} + \frac{LM}{N})$ originates from the periodic boundary condition of Ω_k. Clearly, $E_{\mathrm{p}}(u, \Omega_k, M)$ is determined by $\widehat{H}_k$.

Define

$$\widehat{H} = \begin{bmatrix} \widehat{H}_0 & & & \\ & \widehat{H}_1 & & \\ & & \ddots & \\ & & & \widehat{H}_{N/M-1} \end{bmatrix}.$$

Then $\widehat{H}$ is the Hamiltonian matrix for the system consisting of these $\frac{N}{M}$ subsystems. $\widehat{H}$ is a block matrix. Its set of eigenvalues consists of eigenvalues of the sub-matrices $\widehat{H}_k$.

Let $\widehat{\lambda}_1, \widehat{\lambda}_2, \cdots, \widehat{\lambda}_N$ be eigenvalues of matrix $\widehat{H}$. Then

$$\sum_{k=0}^{N/M-1} E_{\mathrm{p}}(u, \Omega_k, M) = 2 \sum_{n(\mathrm{occ})} \widehat{\lambda}_n.$$

Let $\mu_1, \mu_2, \cdots, \mu_N$ be the eigenvalues of matrix $\Delta H = H - \widehat{H}$. According to Vieta's theorem, the sum of the squares of the μ's is equal to the sum of all second order principle minors, i.e.,

$$\sum_{n=1}^{N} \mu_n^2 = \sum_{k=0}^{N/M-1} h(D^+ y_{kM})^2 + \sum_{k=0}^{N/M-1} h\Big(y_{kM+1} - y_{(k+1)M} + \frac{LM}{N}\Big)^2. \tag{4.1}$$

Without loss of generality, we assume that $\lambda_1 \le \lambda_2 \le \cdots \le \lambda_N$ and $\widehat{\lambda}_1 \le \widehat{\lambda}_2 \le \cdots \le \widehat{\lambda}_N$. Using the Wielandt-Hoffman theorem in [10], we have

$$\sum_{n(\mathrm{occ})} (\lambda_n - \widehat{\lambda}_n)^2 \le \sum_{n=1}^{N} \mu_n^2 = \mathcal{O}\Big(\frac{N}{M}\Big). \tag{4.2}$$

Therefore

$$\frac{1}{N}\Big|E_{\mathrm{p}}(u,\Omega,N) - \sum_{k=0}^{N/M-1} E_{\mathrm{p}}(u,\Omega_k,M)\Big| = \Big|\frac{2}{N}\sum_{n(\mathrm{occ})}(\widehat{\lambda}_n - \lambda_n)\Big| \le \mathcal{O}\Big(\frac{1}{\sqrt{M}}\Big). \tag{4.3}$$

Step 2 For each subsystem, we approximate the displacement by linear function. Consider the k-th subsystem on Ω_k. We will use $E_{\mathrm{p}}(u_k,\Omega_k,M)$ to approximate $E_{\mathrm{p}}(u,\Omega_k,M)$, where $u_k = u'(x_{kM+1})x$ is the linear approximation of u in Ω_k. For elements of $\widehat{H}_k$, Taylor expansion gives

$$\begin{aligned} h(D^+ y_{kM+j}) &= h_0\Big(\frac{y(x_{kM+j+1}) - y(x_{kM+j})}{\epsilon}\Big) \\ &= h_0\Big(1 + \frac{1}{\epsilon}(u(x_{kM+j+1}) - u(x_{kM+j}))\Big) \\ &= h_0 + h_0' u''(x_{kM+1})\Big(j - \frac{1}{2}\Big)\epsilon + \mathcal{O}(\epsilon^2), \end{aligned}$$

where in the right hand side, h_0 and h_0' are evaluated at $1 + u'(x_{kM+1})$. The expansion for terms like $h(y_{kM+1} - y_{(k+1)M} + \frac{LM}{N})$ is similar. We define

$$\widetilde{H}_k = \begin{bmatrix} 0 & h_0 & & & h_0 \\ h_0 & 0 & h_0 & & \\ & \ddots & \ddots & \ddots & \\ & & h_0 & 0 & h_0 \\ h_0 & & & h_0 & 0 \end{bmatrix}.$$

$\widetilde{H}_k$, as defined, is the Hamiltonian matrix for a system containing M atoms with uniform deformation u_k, which can be solved using Lemma 3.1

$$\lim_{M\to\infty} \frac{1}{M} E_{\mathrm{p}}(u_k,\Omega_k,M) = -\lim_{M\to\infty} \frac{4}{\pi}|h_0(1 + u'(x_{kM+1}))|.$$

By Gerschgorin's circle theorem, all the eigenvalues of the matrix $\widehat{H}_k - \widetilde{H}_k$ are of order $\mathcal{O}(\frac{M}{N})$, since the entries of $\widehat{H}_k - \widetilde{H}_k$ are of that order. Hence, using the Wielandt-Hoffman theorem again, we have

$$\frac{1}{M}|E_{\mathrm{p}}(u,\Omega_k,M) - E_{\mathrm{p}}(u_k,\Omega_k,M)| \le \mathcal{O}\Big(\frac{M}{N}\Big). \tag{4.4}$$

Step 3 We finally prove the asymptotic result for $E_{\mathrm{p}}(u,\Omega,N)$ and hence the claim of Theorem 4.1. This is a result of matrix perturbation theory.

From (4.3) and (4.4), we have

$$\begin{aligned} &\frac{1}{N}\Big|E_{\mathrm{p}}(u,\Omega,N) - \sum_k E_{\mathrm{p}}(u_k,\Omega_k,M)\Big| \\ &\le \frac{1}{N}\Big|E_{\mathrm{p}}(u,\Omega,N) - \sum_k E_{\mathrm{p}}(u,\Omega_k,M)\Big| + \frac{M}{N}\sum_k \frac{1}{M}|E_{\mathrm{p}}(u,\Omega_k,M) - E_{\mathrm{p}}(u_k,\Omega_k,M)| \\ &= \mathcal{O}\Big(\frac{1}{\sqrt{M}}\Big) + \mathcal{O}\Big(\frac{M}{N}\Big). \end{aligned}$$

Let $M = N^{2/3}$. We get

$$\begin{aligned}\lim_{N\to\infty}\frac{1}{N}E_{\rm p}(u,\Omega,N) &= \lim_{N\to\infty}\frac{1}{N}\sum_{k=0}^{N/M-1}E_{\rm p}(u_k,\Omega_k,M)+\mathcal{O}(N^{-1/3})\\ &= -\lim_{N\to\infty}\frac{M}{N}\frac{4}{\pi}\sum_{k=0}^{N/M-1}|h_0(1+u'(x_{kM+1}))|\\ &= -\frac{4}{\pi}\int_\Omega |h_0(1+u'(x))|\,dx.\end{aligned}$$

This completes the proof for this one dimensional model.

4.2 Multi-dimensional case

The analysis in one dimension can be carried over to multi-dimension with small amount of modifications. In what follows, we will try to make clear the required modifications in the analysis. The underlying idea is again to divide the system into subsystem and apply linear approximation on every subsystem. We divide the system into subsystems each of which contains M unit cells, using hyperplanes

$$\Gamma_{j,k} = \Big\{\boldsymbol{r} = \Big(kM^{1/d}+\frac{1}{2}\Big)\boldsymbol{a}_j + \sum_{l\neq j}\mu_l\boldsymbol{a}_l \,\Big|\, \mu_l\in\mathbb{R}\Big\},$$

where $j = 1, 2, \cdots, d$, $k = 1, 2, \cdots, (\frac{N}{M})^{1/d}$ and $\boldsymbol{a}_j$'s are basis vectors of the Bravais lattice.

As in the one-dimensional case, we can prove the consistency of CB rule with the atomistic model, once we find an upper bound for

$$\Big|E_{\rm p}(\boldsymbol{u},\Omega,N) - \sum_k E_{\rm p}(\boldsymbol{u},\Omega_k,M)\Big| \quad\text{and}\quad |E_{\rm p}(\boldsymbol{u},\Omega_k,M) - E_{\rm p}(\boldsymbol{u}_k,\Omega_k,M)|,$$

where Ω_k's are the subsystems, and $\boldsymbol{u}_k$ is the linear approximation of displacement $\boldsymbol{u}$ on Ω_k. The analysis for the latter is almost the same as the one-dimensional case (4.4), from which we get

$$\frac{1}{M}|E_{\rm p}(\boldsymbol{u},\Omega_k,M) - E_{\rm p}(\boldsymbol{u}_k,\Omega_k,M)| \le \mathcal{O}\Big(\Big(\frac{M}{N}\Big)^{1/d}\Big). \tag{4.5}$$

Next we consider the error caused by dividing the system. Similar to the one-dimensional case, the error comes from the nonzero entries of the Hamiltonian matrix ΔH, which is the difference between the Hamiltonian matrices for the original and the decoupled systems. It is clear that all the atoms except those on the boundary of the subsystems will not be affected by the division. The nonzero terms arise from the modification of the environment of these boundary atoms. It is easy to see that there are totally $\mathcal{O}(\frac{N}{M^{1/d}})$ atoms located near the hyperplanes $\Gamma_{j,k}$ of these subsystems. Since each atom interacts only with its nearest neighbors, we can bound the sum of all second order principle minors of ΔH by $\mathcal{O}(N/(M^{1/d}))$. Therefore, by the Wielandt-Hoffman theorem, we have

$$\frac{1}{N}\Big|E_{\rm p}(\boldsymbol{u},\Omega,N) - \sum_k E_{\rm p}(\boldsymbol{u},\Omega_k,M)\Big| \le \mathcal{O}\Big(\frac{1}{M^{1/2d}}\Big). \tag{4.6}$$

Combining (4.5) and (4.6), and choosing $M = N^{2/3}$, we get

$$\lim_{N\to\infty}\frac{1}{N}E_{\rm p}(\boldsymbol{u},\Omega,N) = \lim_{N\to\infty}\frac{1}{N}\sum_{k=0}^{N/M-1}E_{\rm p}(\boldsymbol{u}_k,\Omega_k,M)+\mathcal{O}(N^{-1/3d}),$$

where $E_{\rm p}(\boldsymbol{u}_k, \Omega_k, M)$ converges to the Cauchy-Born result when N goes to infinity. For example, in the 2D graphite case, the results from §3.3 gives us the asymptotics of $E_{\rm p}$ in large N.

5 Conclusion

We considered the simplest quantum mechanics model for solids, the tight binding model, and proved that in the continuum limit, it is consistent with the nonlinear elasticity model obtained using the Cauchy-Born rule, in the sense that if we assume that the displacement of the atoms follows a smooth vector field, then the energy of the two systems approaches each other in the continuum limit. As explained earlier, as far as the continuum limit of atomistic models are concerned, this is a weaker form of the results that we would like to obtain. In the stronger form of the results along the lines of E-Ming, rather than assuming it, one would prove that the displacement of the atoms follows a smooth vector field. Moreover, this smooth vector field is close to a local minimizer of the elasticity model obtained from the Cauchy-Born rule. The ingredients for proving the stronger results are: (1) the stability analysis for both the discrete and continuum models, (2) high order asymptotic expansion for the atomistic model. The first step seems possible. It is not clear how to carry out the second step.

In addition, it is important to extend these results to more general quantum mechanics models such as the Kohn-Sham density functional theory. This important question also remains open.

Acknowledgement The authors are grateful to Pingbing Ming for helpful discussions.

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