

## Renormalization Group Approach on Nanostructured Systems \*

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*The electronic spectra of one-dimensional nanostructured systems are calculated within the pure hopping model on the tight-binding Hamiltonian. By means of the renormalization group Green's function method, the dependence of the density of states on the distributions of nanoscaled grains and the changes of values of hopping integrals in nanostructured systems are studied. It is found that the frequency shifts are dependent rather on the changes of the hopping integrals at nanoscaled grains than the distribution of nanoscaled grains.*

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There is much current interest in nanostructured systems.<sup>1</sup> The sizes of the grains in these systems are intermediate between the sizes of macro-crystals and those of atoms or molecules or atomic clusters. Previous experiments<sup>2-4</sup> showed that in these systems there exist many singular properties that are much different from those of bulk crystals or amorphous with the same compositions. However, there is few theoretical understanding due to the fact that the limit of the finite sizes of nanoscaled grains makes theoretical calculations of their lattice dynamics difficult.<sup>5</sup> Recently, we used renormalization group (RG) approach to study vibrational properties of nanostructured systems.<sup>6</sup> It provides somewhat an intuitive and coherent picture about the vibrational spectrum.

A nanostructured system is piled up with many nanoscaled grains of which the sizes are distributed randomly in a certain extension. In order to construct one-dimensional (1D) version of nanostructured systems, we consider a kind of model chains based on the chain-like Si-backbone polymer.<sup>7</sup> In a nanostructured chain,  $L$  nanoscaled building blocks with various numbers  $\{K_i\}$  ( $i = 1, 2, \dots, L$ ) of atoms are arranged randomly by using the Monto-Carle method. For a certain building block,  $K_i$  takes value with possibility. The possibility is determined by a distribution function such as the Poisson function. Each distribution function has two character factors, the most-possible number  $K_m$  and the half-maximum breadth  $\Delta_K$ . Here, we take the Poisson distribution function [see Figs. 1(a) and 1(b)] to generate the atomic numbers of the building blocks, which are arranged in a sequence by using the Monto-Carle method.

Let us consider the electronic tight-binding Hamiltonian

$$H = \sum_i |i\rangle \varepsilon_i \langle i| + \sum_{i,j} |i\rangle t_{ij} \langle j|, \quad (1)$$

where the site energy  $\varepsilon_i$  takes  $\varepsilon_1$  at a crystalline site, or  $\varepsilon_2$  at a second neighbor boundary site, or  $\varepsilon_3$  at a nearest-neighbor boundary site, and the hopping integral  $t_{ij}$  takes  $T_1$  between

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two crystalline sites, or  $T_2$  between a crystalline site and a boundary site, or  $T_3$  between two boundary sites. Introducing the Green's function  $G(Z) = 1/(ZI - H)$ , we can get, from Eq. (1), the matrix element equation of the Green's function

$$(Z - \varepsilon_i)G_{ij} = \delta_{ij} + \sum_k t_{ik}G_{kj}, \quad i, j = 0, \pm 1, \pm 2, \dots (i \text{ no sum}) \quad (2)$$

with the Kronecker delta  $\delta_{ij}$ , where  $Z = E + i\eta (\eta \rightarrow 0)$ . One remembers that the crystalline sites are ordered in each building block. Thus, some RG transformations can be used to decimate the atoms with the same local environments. Analogously, the site parameters  $\{\varepsilon_i\}$  and  $\{t_{ij}\}$  are changed to be the renormalized site parameters  $\{\varepsilon'_i\}$  and  $\{t'_{ij}\}$ . From Eq. (2), one can get the recursion relations of the renormalized site parameters  $\{\varepsilon'_i\}$  and  $\{t'_{ij}\}$  to the original site parameters  $\{\varepsilon_i\}$  and  $\{t_{ij}\}$ , which are similar to the sets of RG equations in Ref. 6. As a transformation used, tens of sites in each building block of the original system are decimated. So the original nanostructured systems are transferred to be simple systems only consisting of the boundary sites which have the same local environments in original system. As the series of RG transformations are iterated successively, the hopping integral  $t_{i,i\pm 1}$  between two nearest-neighbor pseudosite in the renormalized chain gets smaller and smaller. When  $t_{i,i\pm 1} \rightarrow 0$  after iterations of RG transformations, one can calculate, from Eq. (2), the local Green's function  $G_{ii} = 1/(Z - \varepsilon'_i)$  at every site  $i$  of the studied nanostructured system.

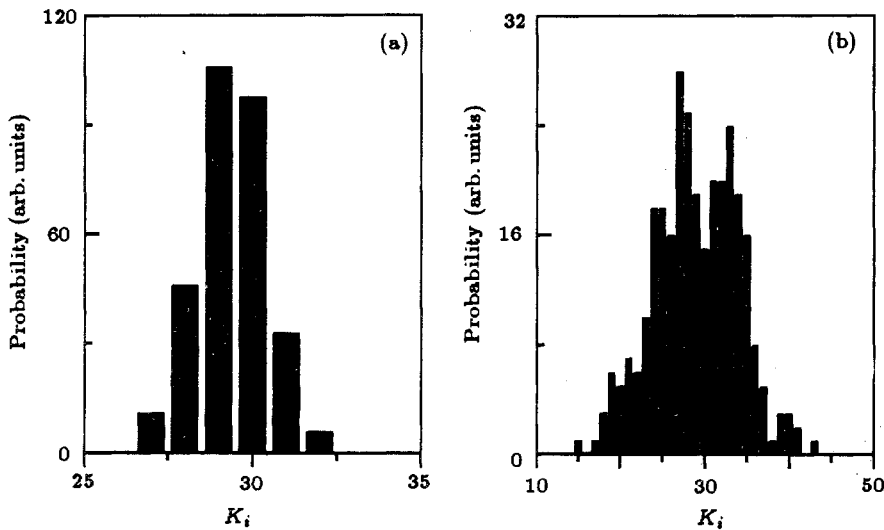


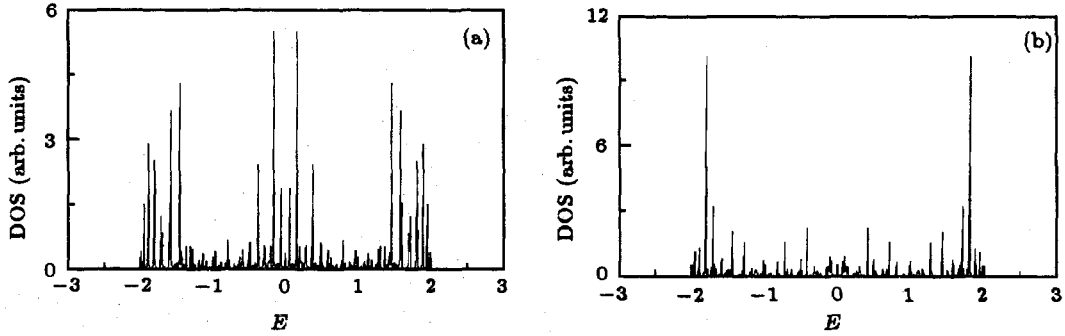
Fig. 1. Schematic bar representations of the Poisson distribution of atomic numbers of nanoscaled building blocks in nanostructured systems, in which the distribution factors  $K_m/\Delta_K$  are (a) 30/1; (b) 30/5.

Once the local Green's functions  $\{G_{ii}\}$  at all kinds of sites are known, many physical properties of the nanostructured systems can be calculated. For instance, the electronic density of states (DOS) is given by

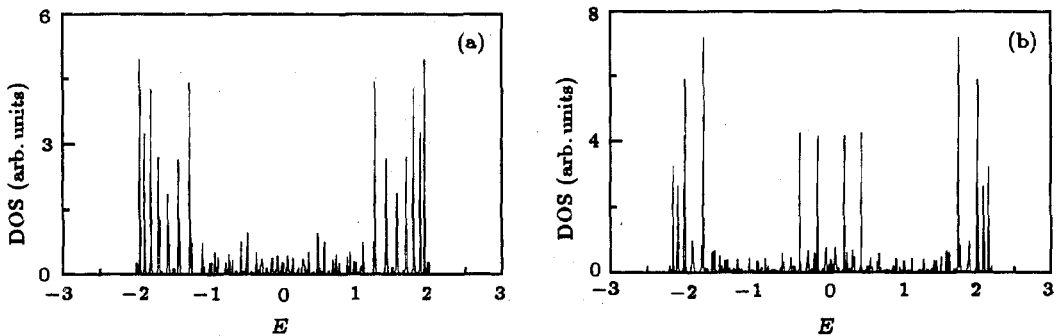
$$\rho(E) = - \lim_{N \rightarrow \infty} \left( \frac{1}{N\pi} \left\{ \lim_{n \rightarrow 0} \left[ \text{Im} \sum_i G_{ii}(E + i\eta) \right] \right\} \right), \quad (3)$$

where "Im" denotes the imaginary part of a complex quantity, and  $N = \sum_{i=1}^L K_i$  is the total

number of sites of the studied system. As  $N$  tends to infinite, the model systems with infinite number  $L \rightarrow \infty$  of building blocks are big enough to be compared to real nanostructured materials. Here, we present the DOS of nanostructured systems mainly on the pure hopping model for which the on-site energies  $\{\varepsilon_i\}$  are the zero of energy. As typical example, the number of blocks in the studied system is  $L = 300$ , and the infinitesimal is  $\eta = 0.001$ . The DOSs for some types of nanostructured systems with the site parameters  $\{T_1, T_2, T_3\}$  and the distribution factors  $K_m/\Delta_K$ , are shown in Figs. 2 and 3, respectively.



**Fig. 2.** Electronic DOS of the nanostructured systems with the site parameters  $\{T_1, T_2, T_3\} = \{1.0, 0.9, 0.5\}$ , where the distribution factors  $K_m/\Delta_K$  are (a) 30/1; (b) 30/5.



**Fig. 3.** Electronic DOS of the nanostructured systems with the distribution factors  $K_m/\Delta_K = 30/1$ , where the site parameters  $\{T_1, T_2, T_3\}$  take (a)  $\{1.0, 0.8, 0.3\}$ , (b)  $\{1.1, 1.0, 0.6\}$ .

In Figs. 2(a) and 2(b), the site parameters  $\{T_1, T_2, T_3\}$  are chosen to be  $\{1.0, 0.9, 0.5\}$ , while the distribution factors  $K_m/\Delta_K$  take 30/1 and 30/5, respectively. The increase of  $\Delta_K$  in a nanostructured system corresponds to the increase of the proportion which is of the number of boundary sites to the total number of sites. Comparing Fig. 2(b) with Fig. 2(a), one can see that the number of sharp peaks decreases as well as that the structures of amplitudes of electronic DOS are reconstructed when the proportion of the number of boundary sites to the total number of sites in nanostructured system increases. For example, the center peak at  $E = 0.0$  in Fig. 2(a) disappears in Fig. 2(b) as  $\Delta_K$  increases. This result supports the conclusions obtained for vibrational spectrum of nanostructured systems by using the pure numerical LMTO (linear Muttin-Tin orbit) method.<sup>5</sup> However, the edge  $E = \pm 1.9701034$  of the spectrum is not extended as the half-maximum breadth  $\Delta_K$  increases. We also calculate the electronic DOSs of the nanostructured systems with the distribution factors  $K_m/\Delta_K = 20/1$

and 50/1, for which the site parameters  $\{T_1, T_2, T_3\}$  are the same as those in Fig. 2(a). Due to limited space, we do not show them here. The results show that the edge of the spectrum is fixed on  $E = \pm 1.9701034$ , i.e., is not extended, too, when the most-possible number  $K_m$  changes. It means that the changes of the distribution factors  $K_m/\Delta_K$  do not affect the shifts of the edges of electronic spectra of nanostructured systems. The "blue shift" phenomena found experimentally are caused neither by the numbers of atoms in nanoscaled grains nor by the distribution of atomic numbers of nanoscaled grains in nanostructured systems.

As we know, experiments show that the decrease of average diameters of grains in nanostructured systems makes frequency shift.<sup>4,7</sup> How are the theoretical discussions in qualitative agreement with the experimental results? it is noted that, besides the decrease of atomic number in nanoscaled grains, the contractions of lattice constants may reduce the diameters of nanoscaled grain. So we calculate numerically the electronic DOS of the nanostructured system with the distribution factors  $K_m/\Delta_K = 30/1$  and the site parameters  $\{T_1, T_2, T_3\} = \{1.0, 0.8, 0.3\}$  and  $\{1.1, 0.9, 0.6\}$  in Figs. 3(a) and 3(b), respectively. Comparing Fig. 3(a) with Fig. 3(b), one can find that when the hopping integral  $T_1$  between crystalline sites does not change the decreases of  $T_2$  and  $T_3$  lead to the decrease of number of sharp peaks, and the wider bands at energy region  $[-1.5, 1.5]$  of the spectrum of nanostructured systems. However, at the energy regions  $[-1.5, -2.0]$  and  $[1.5, 2.0]$ , the number and the positions of sharp peaks do not change except the change of the amplitude distribution. The edge of the spectrum is also fixed on the energies  $E = \pm 1.9701034$ . Similar conclusion to above paragraph can be obtained as the hopping integrals  $T_2$  and  $T_3$  at the boundary of nanoscaled grains decrease. In Fig. 3(b), all of  $T_1$ ,  $T_2$ , and  $T_3$  are larger than those in Fig. 2(a). It is shown that as the gaps become wider the edge of the spectrum is extended when the hopping integral  $T_1$ , as well as  $T_2$  and  $T_3$ , increase. It means that the edges of the spectrum shift to the direction where  $|E|$  is higher as the hopping integrals  $\{T_1\}$  between crystalline atoms increase. For a nanostructured system with certain composition, the decreases of the distances between two nearest-neighbor atoms may not only reduce the diameter of a grain, but also enhance the interactions between atoms. The changes of the hopping integrals  $T_1$ ,  $T_2$ , and  $T_3$  in a nanoscaled grain are due to lattice distortions. It indicates that the lattice distortions of nanoscaled grains in a nanostructured system, which can reduce the diameters of nanoscaled grains, may raise the frequency shifts of spectra in nanostructured systems. Otherwise, the distribution of atomic numbers of grains in nanostructured systems does not take the effect of frequency shifts. It only modulates the amplitude structures of electronic DOS. It should be mentioned that similar conclusions can be obtained from the DOSs of nanostructured systems for the case  $\varepsilon_i \neq 0$  either on the basis of pure hopping model or on the combined model.

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