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Phonons and specific heat of linear dense phases of atoms physisorbed in the grooves of carbon nanotube bundles

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The vibrational properties (phonons) of a one-dimensional periodic phase of atoms physisorbed in the external groove of the carbon nanotube bundle are studied. Analytical expressions for the phonon dispersion relations are derived. The derived expressions are applied to Xe, Kr, and Ar adsorbates. The specific heat pertaining to dense phases of these adsorbates is calculated.

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I. INTRODUCTION

Adsorption of gases in nanotube materials has been investigated extensively in recent years, both from the experimental[1–6] and theoretical[7–13] standpoints. A very special geometry of the nanotube materials provides a possibility for realization of unique adsorbate phases with reduced effective dimensionality.[9,10,13,14] The behavior of adsorbates depends on whether they are adsorbed within the tubes,[8] in the interstitial channels,[9] or in the grooves.[10,11] For samples consisting of nanotubes with closed ends, the adsorption in the tube interior is not possible, and for sufficiently large adsorbates, the adsorption potential in the interstitial channel is purely repulsive.[7] Thus, for the case of large atoms adsorbed in the material made of closed-end carbon nanotubes, the only positions available for gas adsorption are the grooves of the bundles of carbon nanotubes.

In this paper we consider a dense, periodic phase of noble gas atoms physisorbed in the groove positions of a nanotube bundle. This phase can be visualized as a one-dimensional chain of atoms arranged in a periodic array within a groove (see Fig. 1). While the single particle properties of quantum adsorbates in grooves have been considered in Ref. 10, in this article we concentrate on the many-particle excitations (phonons) of the dense, periodic adsorbate phase, that crucially depend on the interactions between adsorbates.

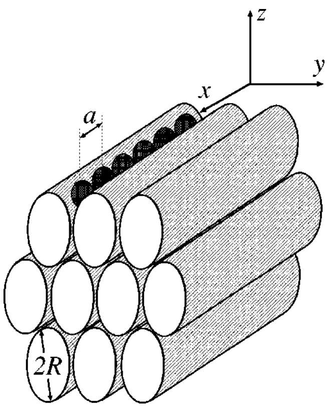

FIG. 1. A sketch of a small bundle of carbon nanotubes with the one-dimensional adsorbate phase in one of its grooves. The choice of the coordinate system is denoted. The adsorbate atoms are denoted by small dark circles.

Recently, measurements of the specific heat of atoms adsorbed in nanotube materials have been reported.[5,6] In this respect, it is important to theoretically consider the specific heat of a dense phase and its signature in the overall specific heat of the sample (nanotube material + adsorbates).

The outline of the article is as follows. In Sec. II, we present a simple lattice dynamics approach to the vibrations of adsorbates in a groove. We show how the phonon frequencies are related to the interadsorbate interaction potential and the interaction of an adsorbate with the surrounding nanotube medium. In Sec. III, we apply the model from Sec. II to adsorption of Xe, Kr, and Ar atoms and we calculate the characteristic vibrational frequencies pertaining to these adsorbates. In Sec. IV, we use this information to calculate the specific heat of dense adsorbate phases. Section V summarizes the main results.

II. VIBRATIONS OF DENSE PHASES OF ADSORBATES IN THE GROOVES

To study the vibrations of the adsorbates in a groove we introduce a simplifying assumption of rigid substrate, i.e., we do not consider phonons of the nanotube material. In this case, the total potential energy Φ of the adsorbate system is given as

$$\Phi=\frac{1}{2}\sum_{l,l'}^{l\neq l'} v(\mathbf{r}_l-\mathbf{r}_{l'})+\sum_{l} V(\mathbf{r}_l). \tag{1}$$

Here, $v(\mathbf{r}_l-\mathbf{r}_{l'})$ represents the interaction between the adsorbates at $\mathbf{r}_l$ and $\mathbf{r}_{l'}$ positions. The indices l and l' denote the adsorbed atoms, and $V(\mathbf{r}_l)$ represents the interaction of the lth adsorbate with the surrounding nanotube medium (substrate). We assume that in the absence of vibrations, the adsorbates are positioned in an infinitely long one-dimensional lattice (with the lattice parameter a, see Fig. 1) within a groove. We also neglect all the interactions between the adsorbates which are not in the same groove. This is an excellent approximation, due to a large diameter of carbon nanotubes.

If the interaction with the substrate were vanishingly small, the problem would reduce to three-dimensional vibrations of an unsupported chain of atoms. This problem can be easily solved analytically as shown, e.g., in Ref. 15. Even with the external field V, the problem can be analytically solved, following the lattice dynamics approach.[15–17] The eigenfrequencies of the adsorbate system can be found from the matrix equation

$$[\mathcal{D}(q)-M\omega(q)^2]\mathbf{e}(q)=0, \tag{2}$$

where M is the adsorbate mass, $\omega(q)$ is the vibrational frequency, q is the phonon wave vector parallel to the groove, and $\mathbf{e}(q)$ is the 3D phonon polarization vector. Note that the phonon wave vector q is a one-dimensional quantity since the adsorbate lattice exhibits a 1D translational invariance. The polarization vector $\mathbf{e}(q)$ is a three-dimensional quantity since the displacements of adsorbate atoms in all three spatial directions are allowed. If we take into account only pair interactions v between the nearest neighboring adsorbates and neglect the discrete nature of the tubes surrounding a groove by effectively "smearing" the carbon atoms along the tube surface,[7,8] the 3×3 dynamical matrix, $\mathcal{D}(q)$ is given as

$$\mathcal{D}=\begin{bmatrix} 2\beta[1-\cos(qa)]+f_{xx} & f_{xy} & f_{xz} \\ f_{xy} & 2\alpha[1-\cos(qa)]+f_{yy} & f_{yz} \\ f_{xz} & f_{yz} & 2\alpha[1-\cos(qa)]+f_{zz} \end{bmatrix}. \tag{3}$$

The x axis is oriented along the chain of adsorbates, the y axis passes through the centers of the two tubes surrounding a groove, and the z axis in perpendicular to both x and y axes and points outward from the bundle, as denoted in Fig. 1. The external force constants $f_{\mu,\nu}$ are given by

$$f_{\mu,\nu}=\left(\frac{\partial^2 V}{\partial\mu\partial\nu}\right)_0, \mu,\nu=x,y,z, \tag{4}$$

where the subscript zero signifies that the derivatives should be taken at the equilibrium position of the adsorbate. As the tubes surrounding a groove are assumed to be smooth, the external potential, $V(\mathbf{r}_l)$ does not depend on the adsorbate x coordinate and there is no external (substrate induced) restoring force associated with the adsorbate displacements in the x direction. That is why all $f_{\mu,\nu}$ constants with $\mu=x$ or $\nu=x$ vanish in Eq. (3). Additionally, due to the symmetry of the external potential with respect to the displacements parallel to the line joining the centers of the two tubes surrounding a groove (y direction, see Fig. 1), the constant f_{yz} also vanishes.

The force constants associated with the adsorbate-adsorbate interactions [α and β in Eq. (3)] are given as

$$\alpha=\frac{1}{a}\left(\frac{dv}{dr}\right)_{r=a},$$

$$\beta=\left(\frac{d^2v}{d^2r}\right)_{r=a}, \tag{5}$$

where r is the coordinate of relative distance between the neighboring adsorbates. The phonon dispersion relations, $\omega(q)$ for $-\pi/a\leqslant q\leqslant\pi/a$, obtained as the solutions to Eq. (2) with $f_{xx}=f_{xy}=f_{xz}=f_{yz}=0$ are given as

$$\omega_L(q)=2\sqrt{\frac{\beta}{M}}\sin\left(\frac{qa}{2}\right),$$

$$\omega_{T1}(q)=\sqrt{\frac{f_{yy}+2\alpha[1-\cos(qa)]}{M}},$$

$$\omega_{T2}(q)=\sqrt{\frac{f_{zz}+2\alpha[1-\cos(qa)]}{M}}, \tag{6}$$

where the subscripts $L,T1,T2$ denote the longitudinal (L) and the two transverse phonon branches ($T1,T2$). The $L,T1$ and $T2$ modes are polarized exclusively in $x,y,$ and z directions, respectively. Similar equations have been derived in Ref. 12. The authors of this reference considered an isotropic oscillator model, $V(x,y,z)=\overline{f}[(y-y_0)^2+(z-z_0)^2]/2$. The two transverse modes are degenerate in this approximation, which, however, is not always the case, because generally $f_{yy}\neq f_{zz}$, as will be shown in the next section.

A brief comment concerning the neglect of corrugation of the holding potential, i.e., discreteness of the nanotube, is in order here. If the adsorbate phase is commensurate with the holding potential provided by the substrate, the longitudinal mode will exhibit a zone center gap which can be related to the magnitude of the corrugation. This effect has been experimentally confirmed for Xe overlayers on Cu(111) surface[22,23] and should in principle be observable for all commensurate systems.

III. VIBRATIONS OF Xe, Kr, AND Ar ADSORBATES

The ingredients necessary for the calculation of phonon modes are obviously the force constants α,β and f_{yy},f_{zz}. The first two can be calculated from the presumably known interadsorbate interaction potential, while the f-force constants can be calculated from the asdsorbate-substrate interaction potential.

The adsorbate-substrate interaction can be calculated as a superposition of the adsorbate-nanotube interactions. It is sufficient to consider only the two nanotubes surrounding the groove, since the interaction of adsorbate atom with other nanotubes is vanishingly small due to a large diameter of the carbon nanotubes typically encountered in experiments.[28]

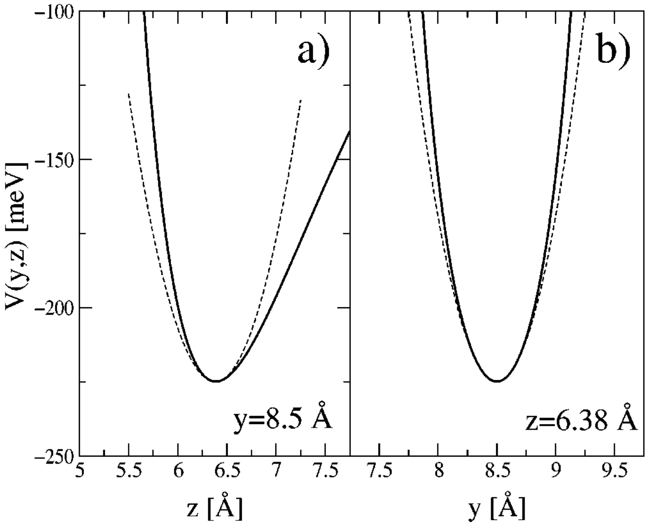

FIG. 2. Full lines: External potential for Xe atom in the groove. (a) Potential along the z direction. (b) Potential along the y direction. Both curves pass through the absolute minimum of the potential located at ($y=8.5$ Å, $z=6.38$ Å). Dashed lines: Harmonic approximation to the potential.

Neglecting the discrete nature of the carbon nanotube, the adsorbate-single wall nanotube interaction can be written as[7,8]

$$V(\rho)=3\pi\theta\epsilon\sigma^2\left[\frac{21}{32}\left(\frac{\sigma}{R}\right)^{10}\eta^{11}M_{11}(\eta)-\left(\frac{\sigma}{R}\right)^{4}\eta^{5}M_{5}(\eta)\right], \tag{7}$$

where ϵ and σ are the energy and range parameter of the effective adsorbate-carbon site interaction which is assumed to be of a Lennard-Jones form. The variable ρ denotes the distance of the adsorbate atom from the axis of the tube, θ is the effective coverage of C atoms on the tube surface ($\theta=0.38$ 1/Å^2), R is the tube radius, and the variable η is defined as $\eta=R/\rho$ when $\rho>R$. The function $M_n(\eta)$ is defined as

$$M_n(\eta)=\int_0^{\pi}\frac{d\phi}{(1+\eta^2-2\eta\cos\phi)^{n/2}}. \tag{8}$$

The external potential can be constructed as a sum of the adsorbate interactions with two tubes surrounding a groove. From the thus constructed potential, the relevant external force constants can be obtained using Eq. (4).

To illustrate the shape of the holding external potential, we plot in Fig. 2 the potential for Xe adsorbate along the y and z directions. In this figure and in all subsequent calculations, we consider single wall carbon nanotubes with the diameter of 13.8 Å, arranged within a bundle in a triangular lattice with the lattice constant of 17 Å.[28] The origin of the coordinate system is chosen in such a way that the centers of the two tubes surrounding a groove are positioned at ($y=0$ Å, $z=0$ Å) and ($y=17.0$ Å, $z=0$ Å). The parameters of the Xe-C site potential are obtained from the so-called combination rules, as explained in Ref. 7. We adopt all the relevant parameters of adsorbate-adsorbate and adsorbate-substrate interactions from Table I of Ref. 7. Since the two curves displayed in panels (a) and (b) of Fig. 2 pass through the absolute minimum of the external potential ($y=8.5$ Å, $z=6.38$ Å), the external force constants can be obtained as second derivatives of the potential curves presented in Fig. 2 at their minimum positions. Note that the potential is significantly more anharmonic in the z than in the y direction which means that the harmonic approximation to the potential is less satisfactory in the z direction as can be seen from inspection of thin dashed lines in Fig. 2 which represent the harmonic approximation. It should be mentioned that the minimum value of the potential we obtain is consistent with the one reported in Ref. 7. However, the binding energy of a single Xe adsorbate in this potential is not consistent with the experimental result[2] (-282 ± 11 meV) which is lower than the absolute minimum of the potential we obtain here (-225 meV). A possible small difference in the tube separations at the surface of the bundle with respect to the corresponding separation in the bundle interior may be responsible for this discrepancy. In addition, as shown and discussed in Ref. 10, small changes in the adsorbate-carbon site effective potential may cause relatively large change in the adsorbate binding energy.

The total adsorbate-adsorbate interaction encompasses direct adsorbate-adsorbate interaction and the indirect interaction mediated by the polarizable substrate material and other adsorbates.[18,19] This interaction is generally different from the corresponding interaction between the atoms in the gas phase. The most critical adsorbates to be considered in the remainder of this paper are Xe adatoms which have the highest polarizability of all the adsorbates we shall consider. While the substrate mediated forces can be calculated for a planar substrate material, it is more difficult to calculate them and assess their importance for the substrate of present interest, i.e., a bundle of carbon nanotubes. This issue has been discussed in the case of interstitial adsorption in Ref. 20.

Even though the many body forces should play a role in dynamics of Xe monolayers on crystal surfaces,[18] it is often found that the gas phase Xe-Xe potentials provide very reliable phonon dispersions.[18,21] This is in part due to the fact that phonon dispersions are not determined by the potential itself, but by its derivatives which may be less influenced by many-body effects. The only exception to this "rule" seems to be the somewhat puzzling dynamics of Xe overlayers on Cu surfaces.[22–27] In all the calculations to be presented, we shall assume that the adsorbate-adsorbate interactions can be well represented by the corresponding gas phase potentials.

We shall model the adsorbate-adsorbate interaction also by the Lennard-Jones potential $4\epsilon_{gg}[(\sigma_{gg}/r)^{12}-(\sigma_{gg}/r)^{6}]$, where r is the interadsorbate separation, and ϵ_{gg} and σ_{gg} are the energy and range parameters of the potential, respectively. The equilibrium positions of the adsorbates can be found from the static equilibrium condition, i.e., by minimizing expression (1) with respect to the lattice parameter a. Following this procedure, we find that the 1D lattice parameter is given by

TABLE I. Force constants and phonon frequencies of L, $T1$, and $T2$ modes (Brillouin zone center and Brillouin zone edge) for Xe, Kr, and Ar adsorbates in groove positions of the carbon nanotube bundle.

	Xe	Kr	Ar
a [Å]	4.59	4.03	3.81
f_{yy} [N/m]	7.13	6.50	5.58
f_{zz} [N/m]	4.01	3.19	2.58
α [N/m]	-0.003	-0.003	-0.0024
β [N/m]	1.10	1.10	0.87
$\hbar\omega_L(q=0)$ [meV]	0	0	0
$\hbar\omega_L(q=\pi/a)$ [meV]	3.06	3.83	4.93
$\hbar\omega_{T1}(q=0)$ [meV]	3.899	4.660	6.253
$\hbar\omega_{T1}(q=\pi/a)$ [meV]	3.895	4.655	6.247
$\hbar\omega_{T2}(q=0)$ [meV]	2.924	3.264	4.251
$\hbar\omega_{T2}(q=\pi/a)$ [meV]	2.919	3.258	4.244

$$a=\sigma_{gg}\pi\left(\frac{1382}{675675}\right)^{1/6}\approx 1.1193\sigma_{gg}. \tag{9}$$

The force constants α and β [Eq. (5)] are then given as

$$\alpha=-0.1665\frac{\epsilon_{gg}}{\sigma_{gg}^2},$$

$$\beta=60.615\frac{\epsilon_{gg}}{\sigma_{gg}^2}. \tag{10}$$

Force constant α determines the dispersion of the transverse modes. It is negative due to the fact that the lattice parameter a is smaller than the equilibrium separation of the binary Lennard-Jones potential ($1.122\ \sigma_{gg}$). Note also that $|\alpha| \ll |\beta|$, which means that the transverse modes have negligible dispersion in comparison with the longitudinal mode.

If the adsorbates form a chain that is commensurate with the substrate corrugation, the periodicity of the one-dimensional chain of atoms may be different from the one obtained here by neglecting the substrate corrugation. In this case, all the force constants may change. On the other hand, for the incommensurate chain, our model should provide reliable results.

In Table I, we summarize the lattice parameters and the force constants needed for calculation of the phonons in the specific cases of Xe, Kr, and Ar atoms adsorbed in a groove. We also summarize the mode frequencies at the Brillouin zone center ($q=0$) and the zone edge ($q=\pi/a$). As can be seen from the table, the transverse modes for all adsorbates considered have completely negligible dispersion throughout the Brillouin zone. We also find that $\omega_{T1}(q)<\omega_{T2}(q)$ which is a consequence of a specific shape of the potential experienced by adsorbates in the groove. This means that the potential is "softer" with respect to adsorbate displacements in the z direction (see Fig. 2).

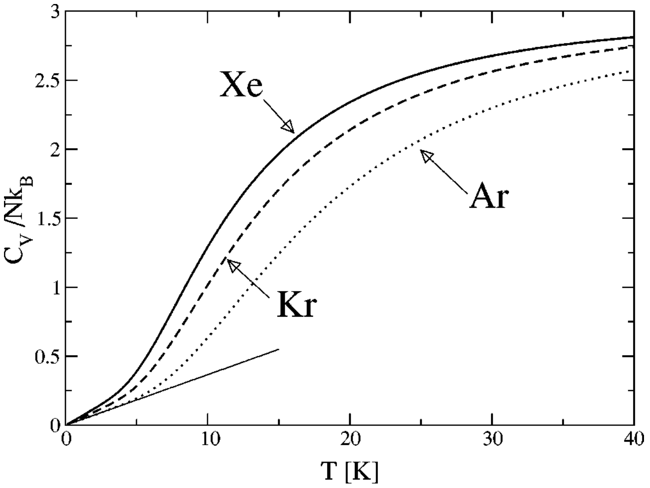

FIG. 3. Specific heat of Xe (thick full line), Kr (thick dashed line), and Ar (thick dotted line) adsorbate chains in a groove as a function of the temperature. The thin full line represents the linear low-temperature behavior of specific heat for Ar as predicted by Eq. (13), with $\hbar\omega_L(q=\pi/a)=4.93$ meV (see Table I).

IV. SPECIFIC HEAT OF DENSE ONE-DIMENSIONAL ADSORBATE PHASES

Knowing the dispersion relations for the adsorbate phonons, we can now proceed to calculate the specific heat pertaining to a dense phase of the adsorbates in a groove. The heat capacity at constant volume, C_V, for a collection of independent oscillators (phonons) is given by[17]

$$C_V=k_B\sum_i \frac{\left(\frac{\hbar\omega_i}{k_BT}\right)^2 e^{\hbar\omega_i/k_BT}}{(e^{\hbar\omega_i/k_BT}-1)^2}, \tag{11}$$

where k_B is the Boltzmann constant, T is the temperature, and index i counts the harmonic oscillators of frequencies ω_i. In our case, the index i is replaced by the phonon wave vector, q and the phonon branch index s ($s=L,T1,T2$). Relation (11) is thus rewritten as

$$C_V=\frac{Nk_Ba}{\pi}\sum_s\int_0^{\pi/a}\frac{\left[\frac{\hbar\omega_s(q)}{k_BT}\right]^2 e^{\hbar\omega_s(q)/k_BT}}{[e^{\hbar\omega_s(q)/k_BT}-1]^2}dq, \tag{12}$$

where we have transformed the sum over wave vectors into an integral as $\Sigma_q\rightarrow(L_x/\pi)\int_0^{\pi/a}dq$. Here, L_x is the length of the adsorbate chain (or groove) and the number of adsorbates within a particular groove is $N=L_x/a$. It is easy to check that in the limit of high temperatures [$k_BT\gg\hbar\omega_s(q)$, $s=L,T1,T2$], the specific heat in Eq. (12) reduces to its classical value $C_V=3Nk_B$.

In Fig. 3 we plot the specific heat for Xe, Kr, and Ar adsorbates obtained from Eq. (12) by using information on the adsorbate phonons summarized in Eq. (6) and Table I. As can be seen, at high temperatures all the three curves tend to the classical limit.

To separate the influence of transverse modes, we plot in Fig. 4 the three different contributions to the specific heat of

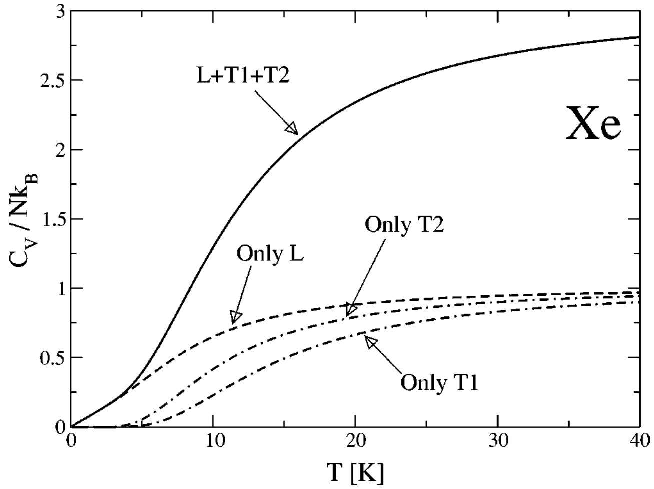

FIG. 4. Separate contributions of three modes of Xe chain to the specific heat. Dashed line: *L* mode. Dash-dotted line: *T*2 mode. Dash-dash-dotted line: *T*1 mode. Full line: total specific heat of the Xe chain.

a chain of Xe atoms, i.e., in the sum in Eq. (12) we consider only one mode (either *L*, *T*1, or *T*2). As can be inferred from this figure, the low-temperature behavior of the specific heat ($T<4$ K) is completely determined by the longitudinal mode. At temperatures higher than about 4 K (for Xe), all the modes in the sum in Eq. (12) must be considered. Due to the fact that the transverse modes have higher frequencies for Kr and Ar adsorbates, their contribution to the specific heat becomes significant at somewhat higher temperatures. The specific heat at low temperatures, where only the *L* mode contributes, is proportional to the temperature and the following relation holds:

$$C_V \approx 2.095 N k_B \frac{k_B T}{\hbar \omega_L (q=\pi/a)}. \tag{13}$$

The linear dependence of specific heat on temperature is a consequence of effectively 1D behavior of the chain at low temperatures and can be easily seen from Fig. 3 at temperatures lower than ≈ 4 K. Equation (13) also implies that the measurement of specific heat at low temperatures would yield an information on the maximum frequency of the longitudinal mode (Brillouin zone edge frequency). As this frequency crucially depends on the interadsorbate potential [Eq. (5) and Eq. (6)], these measurements could yield an information on the effective interaction between the adsorbate atoms which may be modified by the presence of the substrate material, as discussed in Sec. III.

V. SUMMARY

We have studied the vibrational properties of linear dense phases of adsorbates in the grooves of the carbon nanotube bundles. The three modes characterizing the adsorbate vibrations have been identified and their frequencies have been calculated for Xe, Kr, and Ar adsorbates. We have also calculated the specific heat corresponding to the linear phase and identified the temperature regimes in which the transverse modes begin to significantly contribute to the specific heat. The presented results should serve as a useful guidance in the measurements of specific heat of gases adsorbed in the nanotube materials.[5,6]

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