Singular behavior of the Debye-Waller factor of graphene

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It is shown that the mean-square displacement or the exponent of the Debye-Waller factor of graphene has a singularity except at zero temperature. The zero-temperature values of the mean-square displacement are calculated separately for planar and out-of-plane phonon modes for graphene. These values give the Debye-Waller factor that can be used to model various scattering processes at temperatures much lower than the Debye temperature of graphene. Since the Debye temperature of graphene is about 2300 K for planar modes, the calculated values should provide a useful estimate of the Debye-Waller factor at temperatures of practical interest. Finally, it is shown qualitatively that the singularity can be removed by accounting for the finite size of real graphene crystals.

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I. INTRODUCTION

We derive an expression for the Debye-Waller (DW) factor[1] of graphene and show that its exponent has an inherent singularity except at zero temperature. The DW factor of graphene is, therefore, undefined at all temperatures except zero. We calculate the zero-temperature value by using a recently derived set of force constants,[2] which provides a good agreement with the experimentally observed phonon frequencies in graphene.

The DW factor is an important quantity needed for modeling all scattering processes in materials in which ionic displacements are involved.[1] Examples are scattering of x-rays, neutrons, electrons, gamma rays, etc., which can also be used to measure the DW factor.[3–5] Scattering is a very powerful tool for interrogating the physical characteristics of a material. Hence, the singular behavior of the DW factor raises a problem in the interpretation of scattering data in graphene. In view of the strong topical interest in exploring the physical characteristics of graphene, it is important to identify the problem and have at least an estimate of the DW factor for graphene, which is the objective of this paper. Further, as a possible solution of the singularity problem, we show qualitatively that it is possible to remove the singularity by accounting for the finite size of the graphene crystals. Since all real crystals are finite, it may be the appropriate solution of the problem created by the unphysical singularity.

In Sec. II, we calculate the mean-square displacement (MSD) of atoms in graphene by using the phonon Green's-function method and identify the nature of the singularity in the MSD. The DW factor is exponentially related to the MSD,[1] which can be calculated in terms of the phonon spectrum or the phonon Green's function of the solid.[1,6–8] The phonon spectra of graphene have been calculated recently by Zimmermann *et al.*[9] and Mohr *et al.*,[10] but calculations of phonon Green's functions or the DW factor have not been reported in the literature. In Sec. III, we show qualitatively that it is possible to remove the singularity by accounting for the finite size of graphene crystals. A crude estimate of the effect of finite size of the crystal is also provided in Sec. III. Finally, conclusions are presented in Sec. IV.

Our calculated value of the MSD, which gives the DW factor at zero temperature, should be useful for modeling the scattering processes at low temperatures. By low temperature we mean a temperature T, which is much less than the effective Debye temperature $\hbar\omega_m/k_B$, where k_B is the Boltzmann constant, $\hbar$ is the Planck's constant in units of 2π, and ω_m is the maximum angular frequency of phonons in the solid. The values of ω_m are different for planar and out-of-plane phonon modes. Since the Debye temperatures for graphene are 2300 and 1287 K, respectively, for planar and out-of-plane modes, the low-temperature approximation may be adequate for many practical purposes.

II. PHONON GREEN'S FUNCTION AND MEAN-SQUARE DISPLACEMENT OF ATOMS

We assume the Born–von Karman model for the infinite graphene lattice subject to the Born's cyclic boundary conditions. We assume the crystallographic axes of graphene as the frame of reference with the X-axis along a C-C bond. We denote the Cartesian components of a vector by the Greek indices α, β, etc. that stand for x, y, or z. Summation over repeated indices is not assumed and will be written explicitly. We label an atom in the lattice by a pair of indices $L\kappa$, where L labels a unit cell and κ labels the atom inside a unit cell. Each unit cell of the graphene lattice contains two atoms so $\kappa=0$ or 1. The atom $\kappa=0$ is assumed to be at the origin of the unit cell.

We define the two-dimensional (2D) position vector of an atom $L\kappa$ in the plane of the graphene lattice as follows:

$$\mathbf{r}(L\kappa) = \mathbf{r}(L0) + \mathbf{r}'(\kappa), \tag{1}$$

where $r'(\kappa)$ is the position vector of the atom κ with respect to the origin of its own unit cell. We denote the 3×3 force-constant matrix[1] between atoms $L\kappa$ and $L'\kappa'$ by $\boldsymbol{\phi}(L\kappa,L'\kappa')$. For a perfect lattice that has translation symmetry, $\boldsymbol{\phi}(L\kappa,L'\kappa')$ depends upon L and L' only through their difference. The elements of the dynamical matrix[1,11]

$\mathbf{D}(\mathbf{k})$ in the reciprocal space for the perfect graphene lattice is then given by

$$D_{\alpha\beta}(\mathbf{k};\kappa,\kappa') = (1/M)\sum_L \phi_{\alpha\beta}(0\kappa,L\kappa')\exp[\imath\mathbf{k}\cdot\{\mathbf{r}(L\kappa')-\mathbf{r}(0\kappa)\}], \tag{2}$$

where the sum is over all the lattice sites, M is the mass of a carbon atom, and $\mathbf{k}$ is a 2D vector in the Brillouin zone of graphene. Note that the vectors $\mathbf{r}$ and $\mathbf{k}$ are 2D but the matrix $\boldsymbol{\phi}$ is 3×3 and $\mathbf{D}$ is 6×6. The eigenvalues of $\mathbf{D}(\mathbf{k})$ will be denoted by $\omega^2(\mathbf{k}j)$, where $\omega(\mathbf{k}j)$ is the phonon frequency and $j=1-6$ labels the six eigenvalues.

In order to calculate the MSD or the DW factor, we need the equal time correlation function $\langle u_\alpha(L\kappa)u_\beta(L'\kappa')\rangle$ which is related to the phonon Green's function[1] as follows:

$$\langle u_\alpha(L\kappa)u_\beta(L'\kappa')\rangle = \frac{\hbar}{\pi}\int_0^{\omega_m}[2n(\omega)+1]\mathrm{Im}\, G_{\alpha\beta}(L\kappa,L'\kappa';\omega^2-\imath0^+)d\omega, \tag{3}$$

where ω_m is the maximum phonon frequency, $\mathbf{u}(L\kappa)$ denotes the 3D instantaneous displacement of the atom $L\kappa$, $\langle\ \rangle$ denotes the ensemble average, $\mathbf{G}$ denotes the phonon Green's-function matrix, $\imath$ is $\sqrt{-1}$, Im denotes the imaginary part, and 0^+ indicates that the imaginary part of ω^2 is zero in the limit, which is reached from the upper half complex ω plane,

$$n(\omega) = 1/[\exp(\eta\hbar\omega)-1], \tag{4}$$

and

$$\eta = 1/(k_BT). \tag{5}$$

The elements of the Green's-function matrix[1,12] are given in terms of the dynamical matrix as follows:

$$G_{\alpha\beta}(L\kappa,L'\kappa';\omega^2) = \frac{1}{NM}\sum_{\mathbf{k}}[I\omega^2-D(\mathbf{k})]^{-1}_{\alpha\kappa,\beta\kappa'}\exp[-\imath\mathbf{k}\cdot\{\mathbf{r}(L'\kappa') - \mathbf{r}(L\kappa)\}], \tag{6}$$

where $\mathbf{I}$ is the unit matrix, N is the total number of unit cells, and the sum in Eq. (6) is over the entire Brillouin zone.

The DW factor for the 3D scattering vector $\mathbf{K}$ is usually written as $\exp(-2W)$. The exponent $2W$ is define[1,8] in terms of the equal time auto correlation function as

$$2W = \sum_{\alpha\beta}K_\alpha K_\beta\langle u_\alpha(L\kappa)u_\beta(L\kappa)\rangle. \tag{7}$$

For a perfect lattice, $\mathbf{u}(L\kappa)$ is independent of L. We also make it independent of κ by taking the average over all κ in the unit cell and assuming that the value for each κ is equal to the average value. The DW factor for graphene is isotropic in the plane of the lattice due to hexagonal symmetry but will be different for out-of-plane displacements. We will refer to these displacements, respectively, as the planar and the Z modes. The anisotropy of the DW factor for the planar and the Z modes in graphene is similar to the anisotropy in highly oriented pyrolytic graphite.[13,14]

For graphene, Eq. (7) reduces to the following:

$$2W = K_P^2U_P^2 + K_Z^2U_Z^2, \tag{8}$$

where

$$U_P^2 = (1/4)\sum_\kappa[\langle u_x(L\kappa)^2\rangle + \langle u_y(L\kappa)^2\rangle], \tag{9}$$

$$U_Z^2 = (1/2)\sum_\kappa\langle u_z(L\kappa)^2\rangle, \tag{10}$$

where the summation in Eqs. (9) and (10) is over two atoms in each unit cell, K_P is the magnitude of the planar component of $\mathbf{K}$ defined as

$$K_P^2 = K_x^2 + K_y^2, \tag{11}$$

and K_Z as its Z component. The quantities U_P^2 and U_Z^2 are the MSDs and determine the DW factor for graphene in the planar and the Z modes, respectively.

For graphene lattice the dynamical matrix in Eq. (2) factorizes[15] into a 4×4 block matrix corresponding to the XY plane and a 2×2 block matrix corresponding to Z displacements. As we see from Eq. (6), the Green's-function matrix will also be factorized in two block diagonal matrices: a 4×4 planar part corresponding to x and y components and a 2×2 Z part. By symmetry of the graphene lattice, the off-diagonal elements $\alpha\neq\beta$ of $\mathbf{G}$ in Eq. (3) are zero. From Eqs. (3), (6), and (9), we can write the following for the planar part of the Green's-function matrix:

$$U_P^2 = \frac{\hbar}{4\pi}\int_0^{\omega_{mP}}[2n(\omega)+1]\mathrm{Im}\sum_{\alpha_p,\kappa}G_{\alpha_p\alpha_p}(L\kappa,L\kappa;\omega^2-\imath0^+)d\omega, \tag{12}$$

where ω_{mP} is the maximum phonon frequency for the planar modes and $\alpha_p=x$ or y is the Cartesian component in the XY plane. The trace of the planar part of the Green's-function matrix in Eq. (6) is given by

$$G_{\mathrm{TP}}(\omega^2) = \sum_{\alpha_p,\kappa}G_{\alpha_p\alpha_p}(L\kappa,L\kappa;\omega^2) = \frac{1}{NM}\sum_{kj}[\omega^2-\omega_p^2(kj)]^{-1}, \tag{13}$$

where $\omega_P^2(kj)$ is the jth ($j=1-4$) eigenvalue of the planar block of the dynamical matrix.

From Eqs. (12) and (13), we obtain

$$U_P^2 = \frac{\hbar}{M}\int_0^{\omega_{mP}}\coth\left(\frac{\eta\hbar\omega}{2}\right)F_P(\omega^2)d\omega, \tag{14}$$

where

$$F_P(\omega^2) = \frac{1}{4N}\sum_{kj}\delta[\omega^2-\omega_p^2(kj)] = \frac{M}{4\pi}\mathrm{Im}\, G_{TP}(\omega^2-\imath0^+) \tag{15}$$

is the spectrum of squared frequencies for the planar mode and δ is the Dirac's delta function. In deriving Eq. (14), we have used the following standard relation:

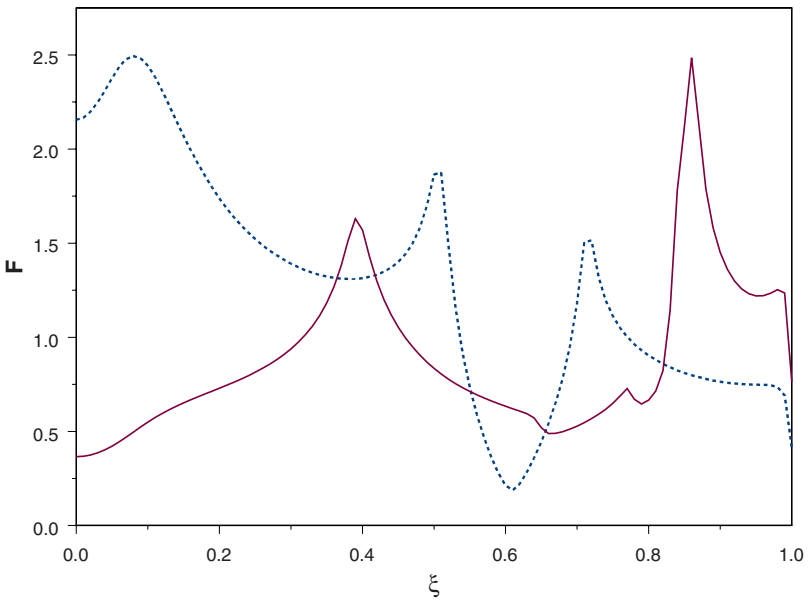

FIG. 1. (Color online) Normalized distribution functions for squared frequencies as a function of normalized square frequencies. The normalization is defined in Eqs. (22) and (23). Solid line: planar modes and dashed line: Z modes.

$$\mathrm{Im}[1/(c-\imath 0^+)] = \pi\delta(c) \tag{16}$$

for any real c.

The functions $F_P(\omega^2)$ are related[1] to the frequency distribution function (density of states) as follows:

$$F_P(\omega^2) = g_P(\omega)/2\omega, \tag{17}$$

where $g_P(\omega)$ is the phonon frequency distribution functions for the planar modes.

Since $\coth(x)$ varies as $1/x$ near $x=0$, we note that the integrand in Eq. (14) varies as $g_P(\omega)/\omega^2$ near $\omega=0$ for nonzero T. In a normal 3D lattice, $g(\omega)$ varies as ω^2 near $\omega=0$ so the integrand is well behaved at $\omega=0$. In a 2D solid $g_P(\omega)$ varies as ω, which makes the integrand singular at $\omega=0$ unless $T=0$.

In order to further illustrate the nature of the singularity, we express the Green's function in k space. Using Eq. (15) into Eq. (14), we can write

$$U_P^2 = \frac{\hbar}{8NM}\sum_{kj}\frac{1}{\omega_p(kj)}\coth\left[\frac{\eta\hbar\omega_p(kj)}{2}\right]. \tag{18}$$

At low frequencies near the center of the Brillouin zone (k close to zero), hyperbolic cotangent behaves as $1/\omega_p(kj)$, so the summand behaves like $1/[\omega_p(kj)]^2$. For acoustic modes that dominate at low frequencies, $\omega_p(kj)$ is proportional to k near $k=0$. Hence, the summand has a $1/k^2$ singularity at $k=0$.

In a 3D lattice, the k space is 3D and the number of k points in a spherical shell of radius k is proportional to k^2. Hence, the singularity cancels out at $k=0$ for a 3D lattice when summed over k. In a 2D lattice such as graphene, the k space is 2D and the number of k points in the circular shell of radius k is proportional to k, which does not cancel the singularity. Hence, the sum in Eq. (18) is singular.

The integrand in Eq. (14) has finite value[1] at $T=0$ or $\eta=\infty$ if T approaches 0 before ω. Since $\coth(x)=1$ for $x=\infty$, U_P can be well behaved at $T=0$ and is given below:

$$U_P^2 = \frac{\hbar}{M}\int_0^{\omega_{mP}} F_P(\omega^2)d\omega. \tag{19}$$

Proceeding in a similar manner, we obtain for the Z modes,

$$U_Z^2 = \frac{\hbar}{M}\int_0^{\omega_{mZ}} \coth\left(\frac{\eta\hbar\omega}{2}\right)F_Z(\omega^2)d\omega, \tag{20}$$

where ω_{mZ} is the maximum value of ω and $F_Z(\omega^2)$ is the spectrum of squared frequencies for the Z modes, defined similar to Eq. (15). The same considerations apply to the singularity in Z modes given by Eq. (20). However, in the special case of graphene, the nature of the singularity for the Z modes is different because $\omega_z(kj)$ is proportional to k^2 near $k=0$.[15]

Proceeding in a similar manner, we find the value of U_Z at $T=0$,

$$U_Z^2 = \frac{\hbar}{M}\int_0^{\omega_{mZ}} F_Z(\omega^2)d\omega. \tag{21}$$

We calculate $F_{P,Z}(\omega^2)$ by using a fourth-neighbor interaction model given in an earlier paper.[2] This model gives a very good fit between the calculated and the observed phonon frequencies in graphene in the three symmetry directions ΓM, ΓK, and MK. Using the force constants given in Ref. 2, we calculate $\mathbf{D}(\mathbf{k})$ from Eq. (2) and the Green's function from Eq. (13). The eigenvalues of $\mathbf{D}(\mathbf{k})$ give the phonon frequencies. The maximum values of ω for the planar and the Z modes are found to be, respectively, 3.01 and 1.68 in units of 10^{14} Hz. These values correspond to Debye temperatures 2300 and 1287 K, respectively. We calculate $F_P(\omega^2)$ from Eq. (15) and $F_z(\omega^2)$ by using an analogous equation. Finally, we calculate U_P^2 and U_Z^2 at $T=0$ by using Eqs. (19) and (21).

We show the variation in the normalized functions $F_{P,Z}(\omega^2)$ with normalized frequencies in Fig. 1. The functions and the frequencies have been normalized separately for the planar and the Z modes such that

$$\int_0^1 F_{P,Z}(\xi_{p,z}^2)d\xi_{p,z}^2 = 1, \tag{22}$$

and

$$\xi_{p,z}^2 = \omega^2/\omega_{mP,mZ}^2. \tag{23}$$

We see from Fig. 1 that both the functions are well behaved in the entire range. The two peaks in the planar mode function near the middle and at the end and in the Z mode near the middle are features of the phonon frequency spectrum of graphene.[11]

Finally, we obtain the following values of the MSD for the planar and the Z modes at $T=0$: $U_P^2=1.59\times10^{-3}$ Å^2 and $U_Z^2=4.04\times10^{-3}$ Å^2. For a given value of the scattering vector, these values give the DW factor by using Eq. (8).

Note that the calculated values of the MSDs are their zero-temperature values but not their zero-temperature limits. The mathematical limit of a function with respect to a parameter is the value to which the function approaches continuously as the parameter approaches its limiting value. As is apparent from Eqs. (14) and (20), the MSD is infinite at any arbitrarily small but nonzero value of T. The singularity is an essential feature of the 2D structure of graphene and makes the DW factor undefined at nonzero temperatures. Since the DW factor is a physical parameter that must exist at all temperatures, a new physical insight is needed for defining the DW factor for graphene.

One possibility is to include the effect of the finite size of the crystal that has been neglected in the above analysis. In Sec. III, we show qualitatively that it can, in principle, remove the above singularity in the MSD and lead to a well-defined low-temperature limit of the DW factor.

III. EFFECT OF THE FINITE SIZE OF THE CRYSTAL ON THE SINGULARITY IN THE MSD

Since the singularity in the MSD arises at low frequencies or long wavelengths, we consider only the phonon modes near $k=0$ or $\omega=0$. For low values of k and ω, we can use the continuum model for phonons.[12] We assume that the dimensions of the crystal are $L\times L$ along the X and Y axes. The longest wavelength permissible in such a solid will be of the order of L. Hence the smallest value of k is of the order of $1/L$. Since the phonon frequency is proportional to k for low k, the minimum frequency of the phonons will be of the order of c/L, where c is the velocity of sound. Of course $k=0$ is also included but that corresponds to rigid body translation of the crystal and does not contribute to the phonon energy.

We first consider only the planar modes and denote the minimum phonon frequency by ω_0. The lower limit of the integral in Eq. (14) now becomes ω_0. We expand the coth function in a series of exponentials for $\eta\to\infty$ corresponding to $T\to0$. The first term in the expansion is just unity that leads to Eq. (19). The contribution ΔU_P^2 of the second term in the expansion of coth to the integral is given below:

$$\Delta U_P^2 = \frac{2Ck_B\mathrm{T}}{M}[\exp(-T_{mP}/T) - \exp(-T_0/T)], \tag{24}$$

where

$$T_{mP} = \hbar\omega_{mP}/k_B, \tag{25}$$

and

$$T_0 = \hbar\omega_0/k_B. \tag{26}$$

In deriving Eq. (24), we have used Eq. (5), and using the continuum approximation, we assumed $F_P(\omega^2)$ to be a constant equal to C. The temperature T_{mP} can be identified as the Debye temperature for the planar modes and T_0 as the effective temperature corresponding to the minimum size-dependent phonon energy. Assuming $c\approx2.2\times10^4$ m/s corresponding to the longitudinal wave along the ⟨100⟩ direction in graphene and $L=1$ micrometer, we estimate $T_0\approx1$ K.

Equation (24) gives the first-order correction to the MSD given by Eq. (19). It is obviously not singular at $T=0$. The correction term goes to zero continuously as $T_0\gg T\to0$. This shows that the effect of the finite size of the crystal, which makes ω_0 nonzero, is to remove the singularity in the MSD. Moreover, it shows that Eq. (19) is the genuine zero-temperature limit of the MSD rather than just the zero-temperature value.

Equation (24) shows that the effect of the finite size of the crystal is temperature dependent. For $T\ll T_0\ll T_{mP}$, the size effect varies with temperatures as $T\exp(-T_0/T)$. Since $\exp(-x)<1$ for $x>0$, the expansion of the coth function in a series of exponentials is valid even for $T>T_0$ but in that case more terms need to be retained in the expansion. Strictly speaking the values of the MSD given in Sec. II are valid only for $T<T_0$ but should provide a reasonable estimate of the MSD for $T\ll T_{mP}$. It should be possible to experimentally verify the effect of the finite size of the crystal by measuring the temperature dependence of the DW factor.

The above analysis is only qualitative. A more precise estimate of the size effect will require a detailed calculation of the phonon spectra in finite systems by using a method such as the phonon Green's function. In the present context, the most important implication of the above analysis is that the DW factor does exist for graphene, and Eq. (19) is the genuine zero-temperature limit of the MSD.

A similar analysis is applicable to the Z modes but the form of the frequency spectrum will be different. The long-wavelength Z modes in graphene correspond to plate modes in the continuum approximation. The correspondence between the continuum plate modes and the lattice Green's functions for graphene has been discussed in an earlier paper.[15]

IV. CONCLUSIONS

We have shown that the MSD or the exponent of the DW factor for graphene has a singularity at all temperatures except at $T=0$. The singularity is a characteristic of the 2D structure of infinite graphene. Since the MSD, which is the exponent of the DW factor, is a physical parameter, it cannot be singular at any temperature. A new physical insight is

needed to either redefine the DW factor or include a contribution in the formulation that can remove the unphysical singularity. We show qualitatively that the singularity can be removed by accounting for the finite size of the crystal. Detailed calculations of the phonon spectra in finite systems are needed to calculate a more precise value of the MSD.

We have calculated the zero-temperature values of the MSD separately for the planar and the out-of-plane modes, which give the corresponding DW factors for a given scattering vector. These values can be used to model scattering processes at temperatures much lower than the Debye temperature for graphene. Since the effective Debye temperatures of graphene are quite high, 2300 and 1287 K, respectively, for the planar and the Z modes, the calculated values should be useful for interpreting the scattering data at temperatures of practical interest.

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