ON FLEXURAL PHONONS IN GRAPHENE.
THERMAL CONDUCTIVITY AND SPECIFIC HEAT

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ABSTRACT. We analyzed the phonon spectrum of graphene. The flexural phonon contribution on thermal properties of graphene is discussed. The thermal conductivity has been calculated using the Boltzmann equation in the relaxation time approximation. The temperature dependence of the thermal conductivity and of the phonon specific heat has been calculated in the low temperatures domain.

Keywords: Graphene, Flexural phonons, Thermal conductivity, Specific heat

Phonons play a fundamental role in the physics and the characterization of graphene and carbon nanotubes. Phenomena as charge, spin, and heat transport, infrared and Raman spectra, electron-phonon scattering, and related effects as electric conduction can be understand, in most situations, by phononic spectrum. The simplest calculation of phononic spectra is based on the continuum elastic theory based on the known isotropy of the honeycomb lattice. Many experimental data as thermal conductance and specific heat have been explained using models of the harmonic theory for the lattice dynamics. In two dimensional (2D) systems the lattice long range order is destroyed by the thermal fluctuations, known as the Mermin-Wagner theorem [1-5], reconsidered for flexural phonons [6]. If the dynamics of lattice is treated in the harmonic approximation the concept of "phonon" is introduced and used to describe the thermal properties [7]. Although the exact dispersion law of the acoustic modes is apparently irrelevant in the quantified thermal conductance [8], the quadratic dispersion of the flexural modes is important in describing the low-temperature specific heat [9]. Most of the results [10-12] cover a wide temperature interval and provide approximative estimation of the power low of the T-dependence, but only few works [9, 13] extended the temperature

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range down to 0.1 K and provide a more precise analysis and proposed $C(T) \sim T^{1/2}$. The out-of-plane distortions, called flexural phonons, are important for the theory of transport in graphene because of the anharmonicity effect [14, 15]. The anharmonic coupling of flexural phonons to the in-plane modes give the stable 2D graphene to rippling. An important effect of anharmonicity is the enhancement of dispersion relation of the long- wavelength flexural modes. The effect of anharmonicity has been considered by Mariani and von Oppen [17] using an effective energy functional including corrections to the harmonic potential that are lowest order in the wave vector, which then couple to flexural modes. Using the Renormaliztion Group (RNG) method they calculated the energy of the flexural modes on the continuum model. The main result is the modification of the dispersion dependence from $\omega \sim q^2$ at low temperatures, to $\omega \sim q^{3/2}$ at high temperatures. In this paper we concentrate on the contribution of the flexural phonon on the thermal properties of graphene.

The mechanical distortions of graphene are described by the vector **u(r)** by the scalar h(**r**) associated with in-plane and flexural (out-of-plane) deformations, respectively. The physics of mechanical distortions is captured in the elastic Lagrangian density. In the harmonic approximation the Lagrangian yields two in-plane phonons modes, longitudinal (*l*), transverse (*t*) and one flexural branch (*f*) with dispersions

$$\omega_l(q) = v^l q \tag{1}$$

$$\omega_t(q) = v^t q \tag{2}$$

$$\omega_f(q) = \sqrt{((\gamma q^2 + \kappa q^4)/\rho)} \tag{3}$$

and group velocities $v^l = [(2\mu + \lambda)/\rho]^{1/2}$ $v^t = [\mu/\rho]^{1/2}$. The flexural branch has a quadratic dispersion in the absence of external strain and introduce a new vector scale $q_s = [\gamma/\kappa]^{1/2}$ discriminating a strain-induced linear dispersion

$$\omega_f(q) \simeq [\gamma/\rho]^{1/2} q \equiv v^f q \tag{4}$$

where $\gamma = 2u(\mu + \lambda)/\rho$, u being the strain, for $q \ll q_s$, and

$$\omega_f(q) \simeq [\kappa/\rho]^{1/2} q^2 \tag{5}$$

for $q \gg q_s$. In the absence of strain: $v^l \simeq 21\ km/s$, and $v^t \simeq 14\ km/s$. There is no agreement for v^f but near the Brillouin zone boundary: $v^f \simeq 8\ km/s$. The flexural phonons dominate the phonon contribution in resistivity [17], and the divergence

in scattering rate is logarithmical if the quadratic dispersion of flexural phonons is considered. This divergence is cut off by coupling between bending and stretching degrees of freedom contained in the Lagrangian. At finite temperature, this coupling reorganize the bending rigidity including a stiffening of the flexural dispersion at long wavelength. The energy of flexural phonons $\omega_f(q)$ is modified by this interaction and in lowest order is

$$\omega_F^2(q)= \omega_f^2(q)+ \Re\, \Sigma(\omega_f(q))/\rho \tag{6}$$

In the high-temperature limit, the self-energy $\Sigma(\omega_f(q))$ has been calculated by Amorim et al. [16] as

$$\Re\Sigma(\omega_f(q))= C\,k_B\,T\,q^2 \tag{7}$$

where C depends on μ and λ. The energy can be approximated in terms of temperature momentum scale $q_c^2= (\gamma+ C\,k_B\,T)/\kappa$ as

$$\omega_F(q)= \alpha_0\left[1+\frac{q_c^2}{q^2}\right]^{1/2} q^2 \tag{8}$$

where $\alpha_0= \sqrt{\kappa/\rho}$. This expression can be approximated as:

$$\omega_F(q)\simeq\alpha_0\, q^2 \tag{9}$$

for $q > q_c$, and:

$$\omega_F(q)\simeq\alpha_0\, q_c\, q \tag{10}$$

for $q < q_c$. Mariani and von Oppen [17] studied the effect of anharmonicity on the flexural modes starting with the energy of nearly flat graphene, including lowest order corrections to the harmonic potential which couple the flexural modes to the in-plane modes. Following the RNG strategy they intergraded out the in-plane modes leaving an effective temperature-dependent interaction among the flexural modes. In the one-loop approximation the energy of flexural modes was calculated as

$$\omega_F(q)= \alpha_r(T,q)\, q^2 \tag{11}$$

where

$$\alpha_r(T,q)= \alpha_0\left[1+\frac{\bar{q}_c^2}{q^2}\right]^{1/4} \tag{12}$$

and q_c is $T^{1/2}$ dependent. These results show that $\omega_F(q) \sim q^2$ at low temperatures, while $\omega_F(q) \sim q^{3/2}$ at high temperatures, which is different to the linear dependence given by Eq.(10). This difference is given by the simple correction to the flexural energy $\omega_F(q)$ given by the self- energy term. We mention that the quadratic dispersion is important because it gives a constant density of states for phonons, but the linear dependence lead to a linear energy dependent density of states. The $q^{3/2}$ dispersion has been proposed in a phenomenological model by Jacimovski et al. [18] for calculation of the thermal conductivity of graphene. This dispersion is supposed to be more realistic than the q-dependence in the temperature interval 15K- 400K, and it is agrement with experimental data.

The phonon thermal conductivity is determined from Boltzmann transport equation as

$$K(T) = \frac{1}{(4\pi h k_B T^2)} \int_{q_m}^{q_M} q\,dq\,\Omega^2(q)\tau_F \frac{\left(\exp\left(\frac{(\hbar\omega_F(q))}{(k_B T)}\right)\right)}{\left(\exp\left(\frac{(\hbar\omega_F(q))}{(k_B T)}\right) - 1\right)^2}$$

(13)

where $\Omega(q) = \hbar\omega_F(q)\dfrac{(d\,\omega_F(q))}{dq}$, h – the thickness of graphene, and I_F is the phonon scattering rate, which is given by different contributions. Klements and Pedraza [19] developed a model for the scattering rate considering the intrinsic phonon-phonon scattering, taking for the three-phonon scattering processes rate

$$\frac{1}{\tau_F} = \gamma_s^2 \frac{(k_B T)}{(M v^2)} \frac{\omega^2}{\omega_D}.$$

(14)

where γ_s, M and ω_D are the Gruneisen parameter, the mass of an atom, and the maximum frequency of the acustic mode in the Debye approximation respectively. v represent the average phonon velocity. Nika et al. [20] calculated the scattering rate considering three-phonon scattering that satisfy momentum and energy conservation. Linsday et al. [21] considered the three-phonon scattering processes involving the flexural modes with an even number of phonons, neglecting the four-scattering processes, considered by De Martino et al. [22], and Feng and Ruan [23]. The recent analysis from [23] suggested that four-scattering processes, quadratically dependent with temperature, are more important than the three-scattering processes.

In order to calculate the contribution of the flexural phonons to the thermal conductivity we use $\omega_F(q) = \alpha_0\, q^2$ valid in the low temperature case. To calculate the temperature dependence of the thermal conductivity we consider the scattering time as: $\tau_F = A\omega_F^{-2} T^{-\gamma}$ (see also, Lindsay et al. [21]), and using $\hbar\omega_F = x\, k_B T$, Eq.(13) becomes

$$K(T) = \frac{(A k_B T^{-\gamma})}{(2\pi h)} \int_{\Theta_m/T}^{\infty} dx\, \frac{(x e^x)}{(e^x - 1)^2}$$

(15)

where $\Theta_m = \hbar\omega_m / k_B$. The integral from Eq.(15) can be analytically performed and we get

$$K(T) = \frac{(A k_B)}{(2\pi h)} \left(\frac{1}{T}\right)^{\gamma} \left[\frac{(\Theta_m/T)}{(e^{\Theta_m/T} - 1)} - \ln\left(1 - e^{-\Theta_m/T}\right) \right]$$

(16)

which can be approximated as

$$K(T) \simeq \frac{(A k_B)}{(2\pi h)} \left(\frac{1}{T}\right)^{\gamma} \frac{\Theta_m}{T} e^{-\Theta_m/T}$$

(17)

The contribution to specific heat of the phonons is given by:

$$C_p = \int_0^{\omega_{max}} k_B \left(\frac{(\hbar\omega)}{(k_B T)}\right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \rho(\omega)\, d\omega$$

(18)

The specific heat temperature dependence is sensitive to characteristics of the phonon spectrum and on its density of states [24, 25]. In the case of low temperatures we use the energy of the flexural phonons given by $\omega \equiv \omega_F \simeq \alpha_0 q^2$, which gives the density of states: $\rho \simeq 1/4\pi\alpha_0$. In this case the specific heat is calculated from Eq.(18) as:

$$C_p(T) \simeq \frac{(\pi k_B^2 T)}{(12\,\alpha_0\, \hbar)}$$

(19)

We presented an analytical theory of the flexural phonon contribution on thermal properties of graphene. The continuum elasticity approach giving the flexural modes with dispersion $\omega_F(q) \sim q^2$ has been discussed, using the renormalization

group method [17], to include the anharmonicity of the dispersion relation in the long-wavelength flexural modes. The q-dependence of the dispersion $\omega(q)$ has a temperature dependence, at low temperatures as $\omega(q)\sim q^2$ and at high temperatures as $\omega(q)\sim q^{3/2}$. The thermal conductivity has been calculated using the Boltzmann equation along with the relaxation time approximation. The linear ($\gamma = 1$) and quadratic temperature dependence ($\gamma = 2$) in relaxation time, given by three-phonon and four-phonon processes have been considered. The temperature dependence of the thermal conductivity $K(T)$ is affected by the dispersion $\omega(q)$ and the scattering rate I_F. The temperature dependence of dispersion appears due to the anharmonicity effect considered in Ref.[22], but the temperature dependence of scattering rate was introduced phenomenologically [21], or estimated theoretically considering the phonon-interaction[22,23]. Using the RNG results we obtained $K(T)\sim T^{-\gamma-1}\exp(-1/T)$ in the low temperatures limit, where $\gamma = 1,2$ for three, respectively four phonon processes. At low temperatures the phonon specific heat scales as $C_p \sim T^{d/2}$, for a phonon dispersion $\omega \sim q^2$, in d-dimensions [9,26]. We obtained that the specific heat $C_p(T)$, which is sensitive to dispersion, is linear in the low temperatures domain $C_p(T) \sim T$. These results could be of interest in low dimensional graphene systems, and could be extended to other properties of graphene and graphene layers, such as the superconductivity of graphene layers at magic angle [27] (with associated properties [28-30]).

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