# THERMODYNAMIC CHARACTERISTICS OF GRAPHENE

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## INTRODUCTION

The paper analyzes the monolayer graphene and dispersion laws for phonons and electrons, and on the basis of these dispersion laws temperature dependences of the internal energies and specific heats of graphene are calculated. In dispersion laws for phonons, all three branches of acoustic phonons are included (while much lower contribution of three optical phonon branches is neglected). In dispersion laws for electrons, the cases of pure graphene and graphene with impurities and defects are considered (with accounted screened Coulomb interaction between the charge carriers in the second case). The temperature dependences of thermodynamic properties are given in graphical form and compared with the available experimental data.

## PHONON SPECIFIC HEAT OF GRAPHENE

The main thermodynamic variable that is examined is specific heat (phonon and electronic), because it is easy to determine experimentally and to compare with theoretical predictions. Characteristics of phonon spectrum are hereby determined for 2D structure of graphene, which has a hexagonal structure with two carbon atoms per unit cell. This determines the appearance of six phonon branches in the dispersion spectrum: three acoustic (LA, TA, ZA) and three optical (LO, TO, ZO). The main contribution to specific heat of graphene is provided by acoustic phonon branches, while contribution of optical phonon branches may be neglected. LA and TA acoustic modes correspond to longitudinal and transverse phonon oscillations in a graphene plane, and have linear dispersion laws, $\omega_1 = v_1 q$, $\omega_2 = v_2 q$, while ZA acoustic mode corresponds to oscillations of phonons in the direction normal to the direction of LA and TA oscillation modes, and has nonlinear dispersion law, $\omega_3 = v_3 q^{1.5}$ .

Phonon specific heat is determined by:

$$C_{ph} = \frac{3N_A}{k_B T^2} \int_{\omega_{min}}^{\omega_{max}} \frac{e^{\hbar\omega/k_B T}}{\left(e^{\hbar\omega/k_B T}-1\right)^2}(\hbar\omega)^2 f_s(\omega)d\omega; \quad f_s(\omega) = \frac{g_s(\omega)}{\int_0^{\omega_{max}} g_s(\omega)d\omega}; s \in (LA, TA, ZA)$$

where $N_A$ is Avogadro number, $k_B$ is Boltzmann constant, and $g_s(\omega)$ is phonon density of states.

Calculations are performed using software package *Mathematica* (cf. Figs. 1 and 2, for partial and total contribution of phonon branches, up to 400 K and 1500 K, respectively). Index $s$ has values $s \in (TA, LA, ZA)$, while relevant parameters are given in Table below:

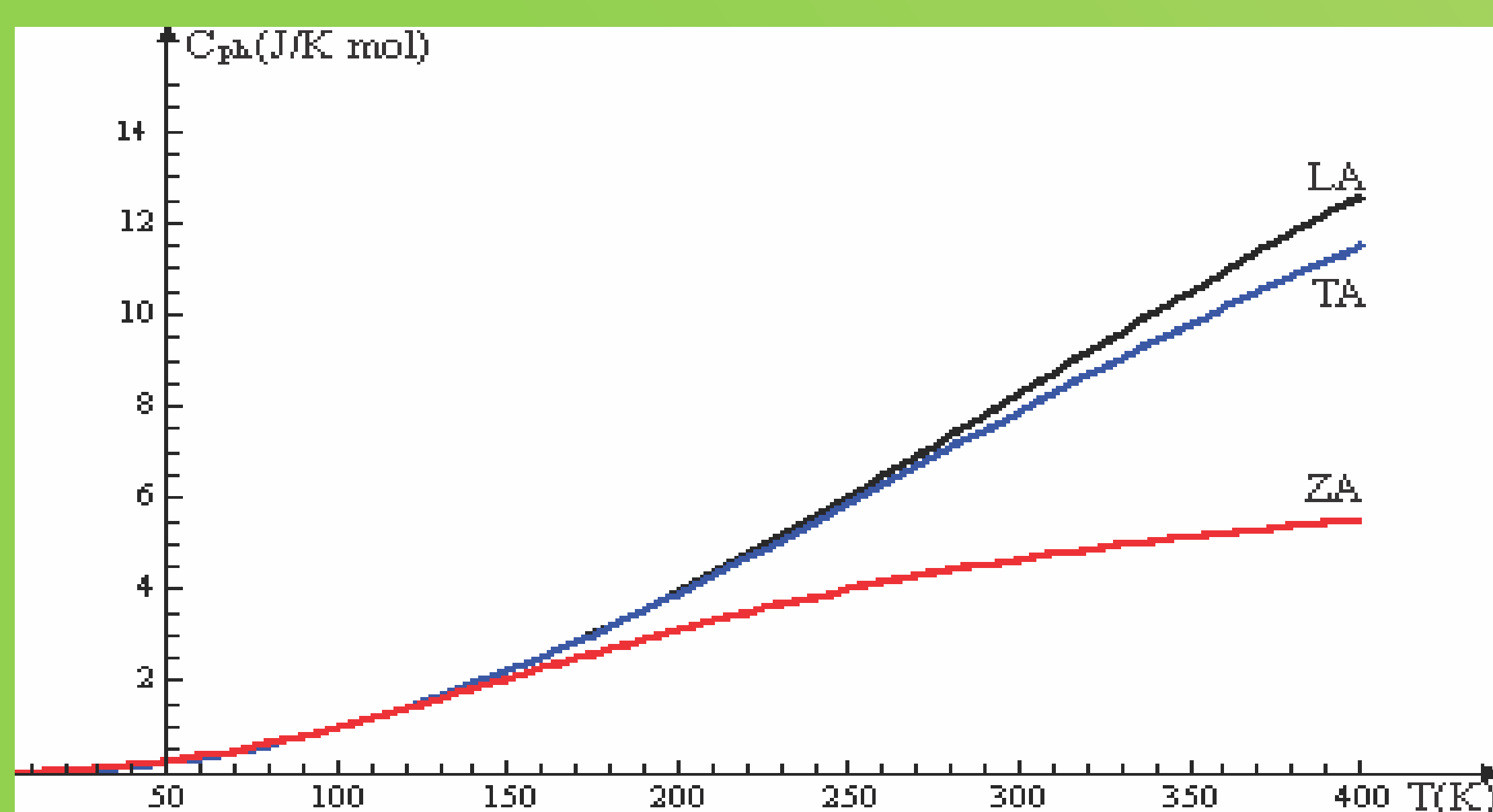| $v_{LA}$ km/s | $v_{TA}$ km/s | $v_{ZA}$ km/s | $l(\omega_s, T) = \frac{1}{2\gamma_s^2}\upsilon\frac{M\upsilon^2}{k_B T}\frac{\omega_D}{\omega_s^2} < L_x.$ |
|---|---|---|---|
| 18.4 | 16.5 | 9.2 | $\omega_{min} = f(\omega, T)$ |
| $\omega_{D,LA}$ Hz | $\omega_{D,TA}$ Hz | $\omega_{D,ZA}$ Hz | $\omega_{s,max} = \omega_{s,D}$ |
| $2.66\cdot10^{14}$ | $2.38\cdot10^{14}$ | $1.32\cdot10^{14}$ | ------- |



*Figure 1. Temperature dependence of graphene phonon specific heat calculated separately for all three acoustic phonon branches, up to 400 K.*
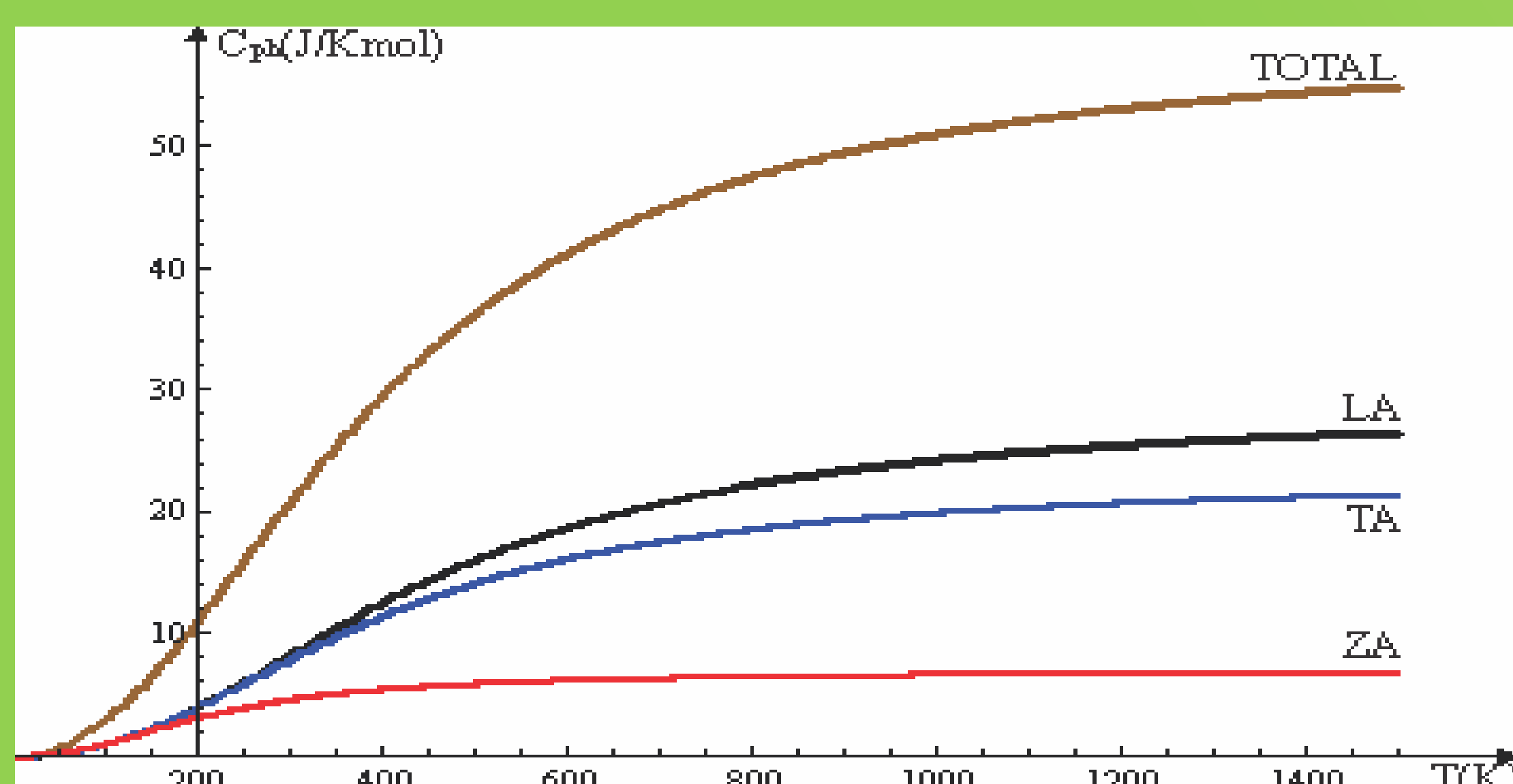


*Figure 2. Temperature dependence of graphene phonon specific heat calculated separately for all three acoustic phonon branches and in total, up to 1500 K.*

## ELECTRONIC SPECIFIC HEAT OF GRAPHENE

The graphene dispersion low for charge carriers, in case we take into account only area in the vicinity of Dirac points, can be significantly simplified: $E = \hbar v_F k$. For this dispersion law, electronic specific heat is obtained from general thermodinamic relations:

$$\Phi = -k_B T \sum_{\vec{k},\sigma} \ln\left(1 + e^{-(\varepsilon_{\vec{k}}-\mu)/k_B T}\right) = -2k_B T \sum_{\vec{k}} \ln\left(1 + e^{-(\varepsilon_{\vec{k}}-\mu)/k_B T}\right)$$

$$C_e = -T\frac{\partial^2\Phi}{\partial T^2} = \frac{2}{k_B T^2}\sum_{\vec{k}}\frac{\left(\varepsilon_{\vec{k}}-\mu\right)e^{(\varepsilon_{\vec{k}}-\mu)/k_B T}}{\left(e^{(\varepsilon_{\vec{k}}-\mu)/k_B T}\right)^2}\left[\left(\varepsilon_{\vec{k}}-\mu\right)+T\frac{\partial\mu}{\partial T}\right]$$

Proposing that chemical potential is small and temperature-independent, the electronic specific heat is determined by (cf. Figure bellow as well):

$$C_e = \frac{10.8 k_B^3 T^2}{\pi\hbar^2 v_F^2};$$
$$n_0 = 1.2\cdot10^{16}\, 1/m^2;$$
$$T_F = 1294\, K$$
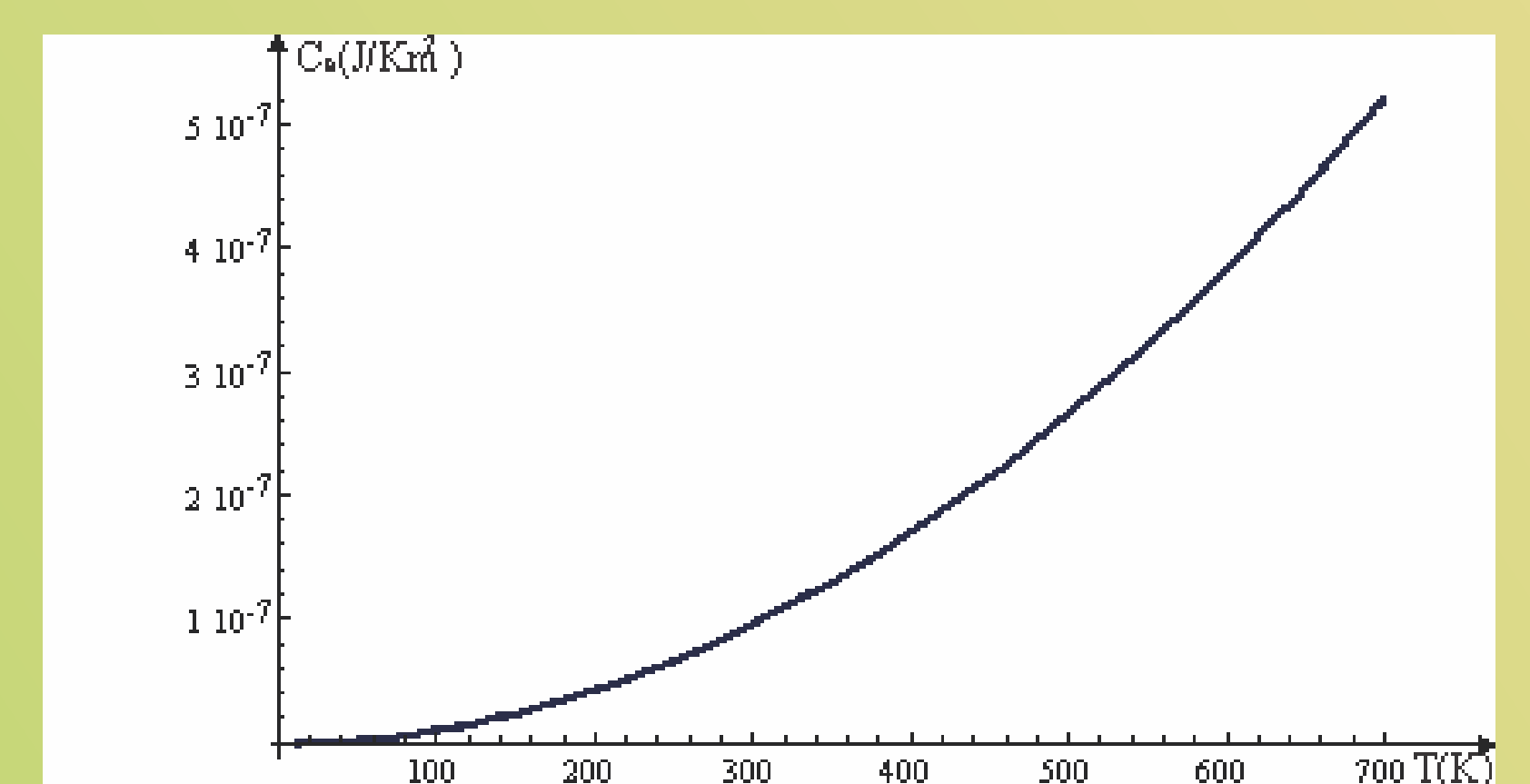


When taking into account temperature dependence of chemical potential,

$$\mu = \varepsilon_F\left(1 - \frac{\pi^2}{6}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right)$$

following expression for graphene electronic specific heat is obtained (cf. Fig. 3):

$$C_e = \frac{2}{\pi k_B T^2 \hbar^2 v_F^2}\int_0^\infty \frac{e^{(\varepsilon-\mu)/k_B T}}{\left(e^{(\varepsilon-\mu)/k_B T}+1\right)^2}\varepsilon(\varepsilon-\mu)\left[(\varepsilon-\mu)-\varepsilon_F\frac{\pi^2}{3}\left(\frac{T}{T_F}\right)^2\right]d\varepsilon$$
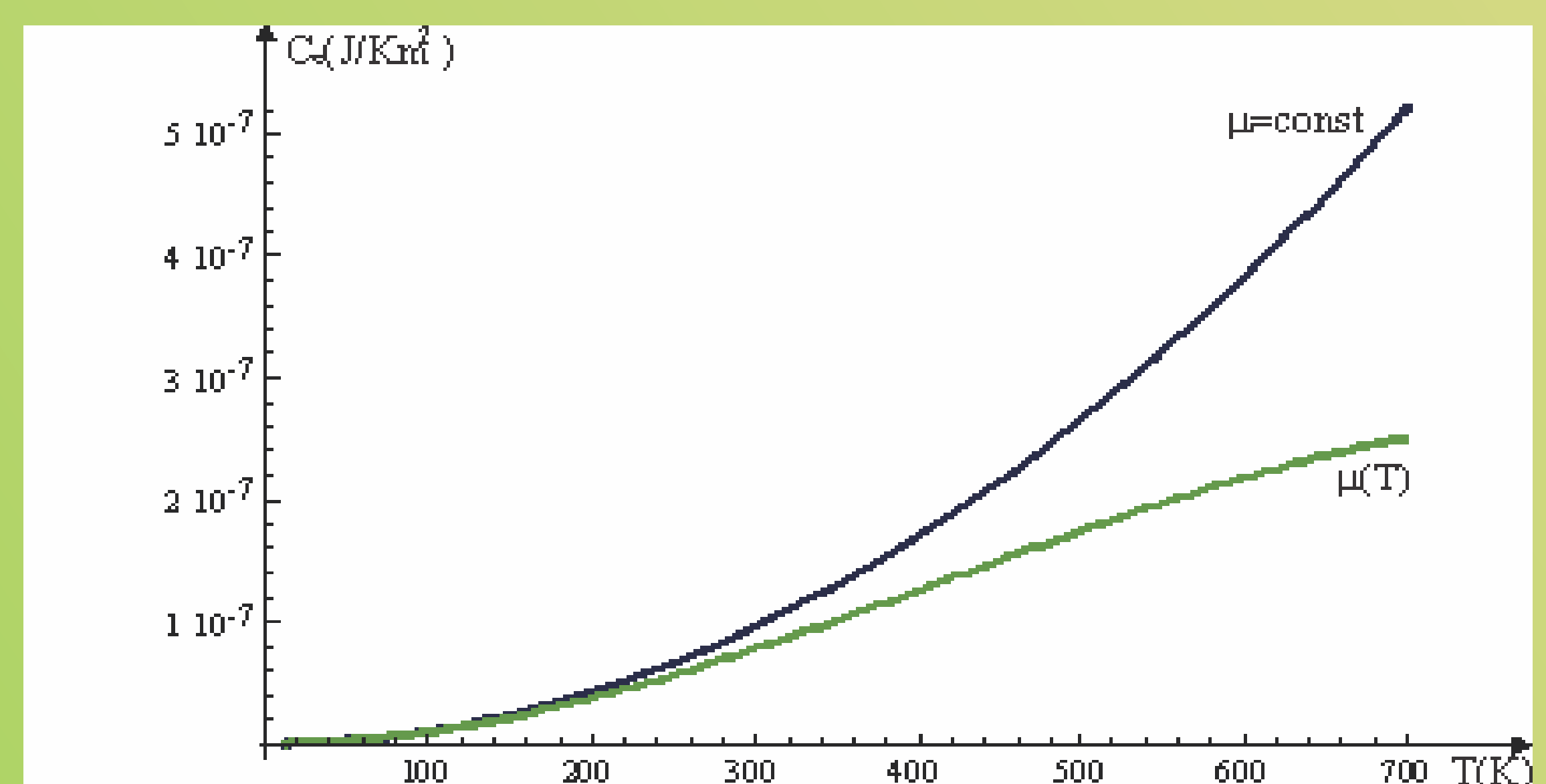


*Figure 3. Temperature dependence of graphene electronic specific heat up to 700 K, for temperature-independent and temperature-dependent chemical potentiials.*

When taking into account modified electronic dispersion law due to screening effect,

$$\varepsilon = \hbar v_F q(1 + g\ln\frac{p_0}{p}); g = 0.0367; p_0 = 5\cdot10^9\, 1/m^2; p = \hbar q$$

temperature dependence for graphene electronic specific heat is additionaly modified (cf. Fig. 4, with all three analyzed cases presented).
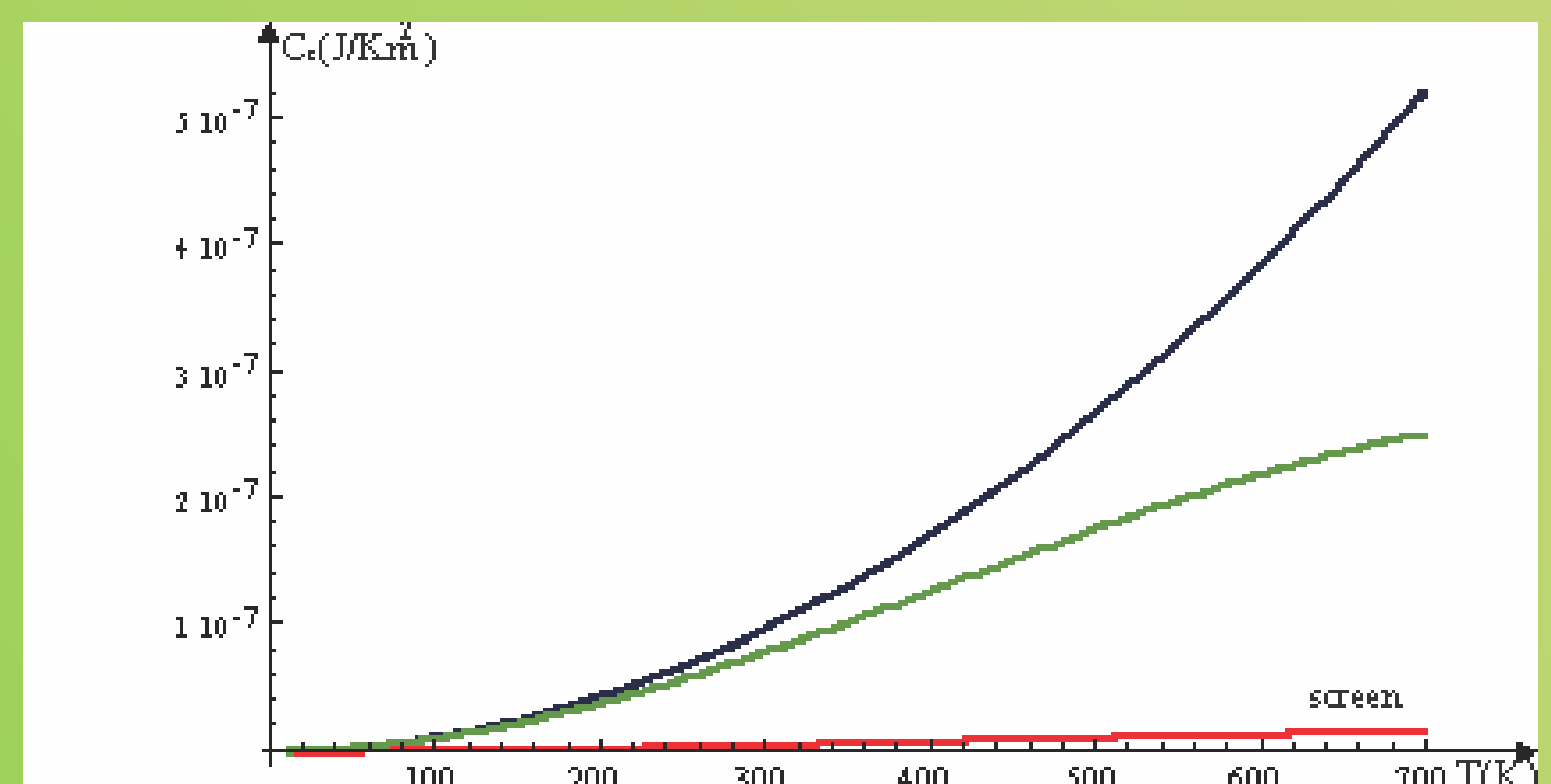


*Figure 4. Temperature dependence of graphene electronic specific heat up to 700 K, for temperature-independent μ (blue), temperature-dependent μ (green), and screening effect accounted (red).*

## CONCLUSION

Graphene phonon specific heat is calculated for all three acoustic branches (LA, TA, ZA), revealing greatest contribution of LA branch and lowest of ZA branch, with functional dependence in accoradnce with experimental data.

Graphene electronic specific heat is characterized by $T^2$ temperature law, it is greatest for temperature-independent chemical potential, and lowest when screening effect is accounted, in accordance with experimental data as well.