Auxiliary Material for the paper by A. N. Volkov and L. V. Zhigilei

"Scaling laws and mesoscopic modeling of thermal conductivity in carbon nanotube materials"

Derivation of Eqs. (1,2, and 4)

(A) Conductivity of 2D and 3D systems of spherocylinders, Eqs. (1,2)

The derivation of the theoretical equations for thermal conductivity is performed for a model material composed of straight nanofibers. Each nanofiber has a shape of soft-core spherocylinder (SC), i.e. a circular cylinder of length L_T and external radius R_T capped on its both ends by two hemispheres. The "soft-core" assumption implies that SCs can freely intersect with each other and the intersections are treated as thermal contacts between nanotubes. In real materials, the intersections would be accommodated by local bending of the interacting nanofibers. The analysis is performed under assumption that the intrinsic thermal conductivity of SCs is infinitely large and the conductivity of the material is governed by the inter-tube thermal contact resistance. As a consequence, every SC *i* in the sample is characterized by a single value of temperature T_i and the heat flux at a contact between SCs *i* and *j* is equal to $Q_{ij} = \sigma_c (T_j - T_i)$, where the inter-tube contact conductance, σ_c, is assumed to be the same for all contacts, $\sigma_c = \sigma_{c0}$.

To ensure transparent connection between the analytical equations and the results of the numerical calculations presented in the paper, we consider finite-size square (in 2D case) or cubic (in 3D case) systems with a size of L_S. The distribution of SCs within the systems is homogeneous and isotropic, with the total number of centers of SCs defined by the surface number density, n_S, and volume number density, n_V, in the 2D and 3D cases, respectively. It is assumed that a constant gradient of averaged temperature, ∇T_x, is maintained along the *x*-axis and periodic boundary conditions are applied in the other direction(s) in the system.

The heat flux through a cross sections of the systems at $x = 0$ can be calculated as $Q_x = -\sum\sum \delta_{ij(+)} Q_{ij}$, where $\delta_{ij(+)} = 1$ if SC *i* intersects axis $x = 0$ and the point of contact between SCs *i* and *j* is located to the right of the cross section, otherwise $\delta_{ij(+)} = 0$. The derivation of Eqs. (1-2) is based on representation of the ensemble averaged heat flux as

$$\langle Q_x \rangle = -\sigma_{c0} \left\langle \sum\sum \delta_{ij(+)} (T_j - T_i) \right\rangle = -\sigma_{c0} \langle N_x \rangle \langle N_J \rangle \langle \Delta T_{(+)} \rangle / 2, \qquad \text{(S1)}$$

where $\langle N_x \rangle$ is the averaged number of SCs crossing the plane $x = 0$, $\langle N_J \rangle$ is the averaged number of contacts for a SC, and $\langle \Delta T_{(+)} \rangle$ is the averaged temperature difference in contacts between SCs *i* and *j* with $\delta_{ij(+)} = 1$. From practical point of view, the ensemble averaging corresponds to the averaging over all possible random configuration of SCs. For dense systems of SCs, the temperature of a SC is defined mainly by the position of the nanotube center. Assuming that $T_i = T_0 + \nabla T_x x_{ci}$ (x_{ci} is the *x*-coordinate of the nanotube center and T_0 is the ensemble averaged temperature of the sample at $x = 0$), one can prove that $\langle \Delta T_{(+)} \rangle = \nabla T_x \langle \Delta x_{(+)} \rangle$, where $\langle \Delta x_{(+)} \rangle$ is the averaged difference between *x*-coordinates of centers of interacting SCs, for which the condition $\delta_{ij(+)} = 1$ is satisfied. For a pair of SCs *i* and *j*, the difference in *x*-coordinates is defined as $x_{cj} - x_{ci}$ (Fig. S1).

The values of $\langle N_x \rangle$, $\langle N_J \rangle$, and $\langle \Delta x_{(+)} \rangle$ can be calculated for both 2D and 3D systems of soft-core SCs as statistical means of the corresponding random variables. For calculation of $\langle N_J \rangle$ and $\langle \Delta x_{(+)} \rangle$ we use the concept of the excluded volume [15] (excluded area in the 2D case) and consider all possible types of junctions between a pair of SCs. For all types of junctions, the point of a junction, *J*, is assumed to be located in the middle of a line segment connecting the closest points on the axes of the cylindrical parts of the intersecting SCs, e.g. points J_i and J_j in Fig. S1. Then, for a random (homogeneous and isotropic) distribution of SCs of an arbitrary aspect ratio $\overline{R}_T = R_T / L_T$, the following expressions for $\langle N_x \rangle$, $\langle N_J \rangle$, and $\langle \Delta x_{(+)} \rangle$, can be derived:

$$\langle N_x \rangle = \frac{L_S}{L_T} \frac{2}{\pi} \overline{n}_S (1 + \pi \overline{R}_T), \tag{S2}$$

$$\langle N_J \rangle = \frac{2}{\pi} \overline{n}_S (1 + 4\pi \overline{R}_T + 2\pi^2 \overline{R}_T^2), \tag{S3}$$

$$\langle \Delta x_{(+)} \rangle = L_T \frac{\pi}{24} \frac{1 + 8\pi \overline{R}_T + (72 + 6\pi^2) \overline{R}_T^2 + 96\pi \overline{R}_T^3 + 24\pi^2 \overline{R}_T^4}{(1 + \pi \overline{R}_T)(1 + 4\pi \overline{R}_T + 2\pi^2 \overline{R}_T^2)} \tag{S4}$$

for the 2D system ($\overline{n}_S$ is the dimensionless density parameter defined as $\overline{n}_S = n_S L_T^2$), and

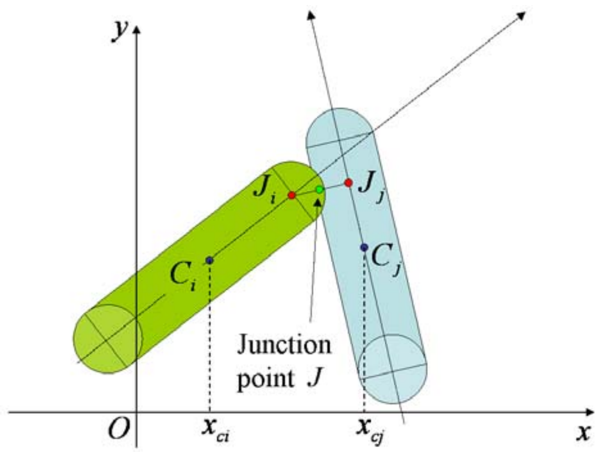

Figure S1. Schematic representation of a junction between two SCs, *i* and *j*. The junction point *J* is located in the middle of a line segment connecting the closest points J_i and J_j on the axes of the cylindrical parts of the SCs. Points C_i and C_j show the centers of the SCs.

$$\langle N_x \rangle = \frac{L_S^2}{L_T R_T} \frac{\overline{n}_V}{2} \left(1 + 4\overline{R}_T\right), \tag{S5}$$

$$\langle N_J \rangle = \pi \overline{n}_V (1 + 8\overline{R}_T + (32/3)\overline{R}_T^2), \tag{S6}$$

$$\langle \Delta x_{(+)} \rangle = \frac{L_T}{9} \frac{1 + 16\overline{R}_T + 80\overline{R}_T^2 + 192\overline{R}_T^3 + 153.6\overline{R}_T^4}{(1 + 4\overline{R}_T)(1 + 8\overline{R}_T + (32/3)\overline{R}_T^2)} \tag{S7}$$

for the 3D system ($\overline{n}_V$ is the dimensionless density parameter defined as $\overline{n}_V = n_V L_T^2 R_T$).

The thermal conductivity of the 2D system, k_{2D}, can be determined from the Fourier law adopted for the 2D case, $\langle Q_x \rangle = -k_{2D} \nabla T_x L_S$. Using the expression for the heat flux given by Eq. (S1), k_{2D} can be expressed as

$$k_{2D} = \sigma_{c0} (L_T / L_S) \langle N_x \rangle \langle N_J \rangle \langle \Delta T_{(+)} / (\nabla T_x L_T) \rangle / 2 . \tag{S8}$$

By inserting Eqs. (S2-S4) into Eq. (S8), the theoretical solution for the thermal conductivity of a dense 2D system given by Eq. (1) is obtained.

Similarly, the thermal conductivity of the 3D system, k_{3D}, can be determined from the Fourier law, $\langle Q_x \rangle = -k_{3D} \nabla T_x L_S^2$. Using the expression for the heat flux given by Eq. (S1), we obtain

$$k_{3D} = \sigma_{c0} (L_T / L_S^2) \langle N_x \rangle \langle N_J \rangle \langle \Delta T_{(+)} / (\nabla T_x L_T) \rangle / 2 . \tag{S9}$$

By inserting Eqs. (S5-S7) into Eq. (S9), the theoretical solution for the thermal conductivity of a dense 3D system given by Eq. (2) is obtained.

(B) Out-of plane conductivity of a quasi-2D film, Eq. (4)

The out-of-plane thermal conductivity of a film composed of 2D layers of SCs stacked on top of each other with interlayer distance Δz, k_{zz}^{film}, is calculated assuming that all SCs in a 2D layer have the same temperature. The averaged heat flux through any junction between SCs from neighboring layers is then equal to $\left\langle Q_{ij} \right\rangle = -\sigma_{c0} \nabla T_z \Delta z$, where $\nabla T_z \Delta z$ is the averaged temperature difference between adjacent layers and ∇T_z is the temperature gradient maintained in the sample in the *z*-direction that is normal to the 2D layer. The averaged heat flux in *z*-direction can be represented in the form $\left\langle Q_z \right\rangle = L_S^2 \left\langle n_J \right\rangle \left\langle Q_{ij} \right\rangle = -\sigma_{c0} L_S^2 \left\langle n_J \right\rangle \nabla T_z \Delta z$, where $\left\langle n_J \right\rangle$ is the total number of junctions between pairs of SCs from different adjacent layers per unit area of a layer. For high-aspect-ratio SCs ($\overline{R}_T << 1$), and assuming homogeneous and isotropic distribution of SCs in the 2D layers, one can find

$$\left\langle n_J \right\rangle = \frac{2}{\pi} n_S^2 L_T^2 . \qquad \text{(S10)}$$

The out-of-plane conductivity can then be expressed from the Fourier law $\left\langle Q_z \right\rangle = -k_{zz}^{film} \nabla T_z \, L_S^2$, which gives

$$k_{zz}^{film} = \sigma_{c0} \left\langle n_J \right\rangle \Delta z . \qquad \text{(S11)}$$

By inserting Eq. (S10) into Eq. (S11), the out-of-plane conductivity of the film given by Eq. (4) is obtained.