

## PAPER • OPEN ACCESS

# A theoretical model for double percolation in hybrid polymer nanocomposites reinforced with carbon nanotubes and aramid nanofibers

To cite this article: Eduard Lysenkov 2026 *Nano Ex.* **7** 035011

View the [article online](#) for updates and enhancements.

## You may also like

- [Modeling the electrical percolation behavior of hybrid nanocomposites based on carbon nanotubes and graphene nanoplatelets](#)  
O Maxian, D Pedrazzoli and I Manas-Zloczower
- [About the relevance of waviness, agglomeration, and strain on the electrical behavior of polymer composites filled with carbon nanotubes evaluated by a Monte-Carlo simulation](#)  
Sebastián Román, Fernando Lund, Javier Bustos et al.
- [Synergy effect in hybrid nanocomposites based on carbon nanotubes and graphene nanoplatelets](#)  
Audrey Gbaguidi, Sirish Namilae and Daewon Kim



## Millikelvin characterization for superconducting devices

### ■ L-TYPE RAPID

- < 4 hrs sample loading and cooldown to base
- 50 mK base temperature
- 30 min warm up and sample exchange

[Find out more](#) →





## PAPER

## OPEN ACCESS

RECEIVED  
12 June 2026

REVISED  
8 July 2026

ACCEPTED FOR PUBLICATION  
19 August 2026

PUBLISHED  
26 August 2026

Original content from  
this work may be used  
under the terms of the  
Creative Commons  
Attribution 4.0 licence.

Any further distribution  
of this work must  
maintain attribution to  
the author(s) and the title  
of the work, journal  
citation and DOI.



# A theoretical model for double percolation in hybrid polymer nanocomposites reinforced with carbon nanotubes and aramid nanofibers

Eduard Lysenkov\*

Petro Mohyla Black Sea National University, 68 Desantnykiv St., 10, Mykolaiv 54003, Ukraine

\* Author to whom any correspondence should be addressed.

E-mail: [ealysenkov@ukr.net](mailto:ealysenkov@ukr.net)

**Keywords:** carbon nanotubes, aramid nanofibers, hybrid polymer nanocomposites, double percolation, excluded volume theory, transport networks, theoretical modeling

## Abstract

A theoretical model of double percolation in hybrid polymer nanocomposites reinforced with carbon nanotubes (CNTs) and aramid nanofibers (ANFs) is proposed. The model is based on the excluded-volume concept and a mean-field description of network connectivity. An analytical expression describing the effective connectivity of the hybrid system was derived by considering CNT–CNT, ANF–ANF, and CNT–ANF interactions. The proposed approach demonstrates that the formation of a continuous transport network is governed not only by the individual percolation behavior of each filler type, but also by hybrid interactions between dissimilar nanostructures. The model predicts that ANFs can promote network formation at reduced CNT concentrations through the development of hybrid CNT–ANF contacts. Theoretical concentration maps, scaling dependences, and parametric analyses were constructed to investigate the influence of filler composition and hybrid interaction probability on network connectivity. The obtained results provide a theoretical framework for describing double-percolation phenomena and transport network formation in hybrid polymer nanocomposites.

## 1. Introduction

Polymer nanocomposites containing high-aspect-ratio nanofillers have attracted considerable attention over the past two decades because of their ability to significantly enhance the mechanical, electrical, and thermophysical properties of polymer matrices at relatively low filler loadings [1]. Among the wide range of nanomaterials, carbon nanotubes (CNTs) have attracted particular attention due to their extremely high mechanical, electrical, and thermophysical properties [2].

In modern research, hybrid nanocomposites containing two or more types of fillers are of increasing interest [3, 4]. The use of combinations of particles of different geometries or dimensions (e.g. 0D–1D, 1D–2D or 1D–fibrous structures) allows the formation of more complex conductive networks in the polymer matrix and often leads to the so-called synergistic effect, when the effective properties of the composite exceed the values expected for systems with a single filler. Similar effects have been reported, for example, for composites with hybrid systems of graphene nanoplatelets and carbon nanofibers, where the interaction of fillers of different morphologies contributes to the formation of a more effective conductive network and a decrease in the percolation threshold [5–7].

Despite significant progress in the development of hybrid polymer nanocomposites, the theoretical description of such hybrid systems remains insufficiently developed. Most classical models of thermal or electrical conductivity of composites, including the Lewis–Nielsen, Maxwell–Garnett, Agari, Nan or Lichtenecker models, were developed for systems with a single type of filler and do not take into account the possibility of simultaneous formation of multiple interacting percolation networks [8, 9]. These

approaches primarily predict the effective transport properties of composites with an already established microstructure rather than describing the evolution of conductive network formation during material design.

In hybrid systems, more complex structural phenomena may occur. In particular, each type of nanofiller is able to form its own percolation network, while the interaction between fillers can lead to the formation of additional bridges between individual clusters [10, 11]. As a consequence, an interpenetrating or dual percolation network can be formed, in which the macroscopic properties of the composite are determined not only by the concentrations of individual components, but also by their mutual ratio and the topology of the formed network. Such cooperative interactions cannot be adequately represented by models that treat different fillers independently or account for their interaction only through empirical correction factors [12,13].

Particularly promising are systems combining CNTs and aramid nanofibers (ANFs) [14,15]. ANFs are characterized by high mechanical strength, a significant specific surface area, and the ability to form three-dimensional fibrous networks in a polymer matrix [16], while CNTs can provide efficient electron or phonon transport channels [17]. Experimental studies show that the combination of these components can lead to the formation of lightweight, mechanically strong, and electrically conductive structures with a wide range of applications, in particular in functional films or aerogels [18].

Although numerous analytical, effective-medium, and semi-empirical models have been proposed for predicting the effective thermal conductivity of composite materials, very few of them explicitly describe the formation of hybrid percolation networks arising from interactions between different high-aspect-ratio nanofillers [19, 20]. Consequently, the evolution of network connectivity itself remains largely outside the scope of existing transport models. As a result, the problem of predicting the optimal ratio of fillers for the formation of an effective conductive network remains open.

Although the proposed connectivity framework is not restricted to a particular transport property, thermal conductivity was selected as an illustrative example because the development of thermally conductive hybrid polymer nanocomposites has attracted increasing attention in recent years [21].

In this regard, it is relevant to develop a physically based analytical model that would take into account the simultaneous formation of two interacting percolation networks and allow predicting the macroscopic properties of polymer nanocomposites depending on the concentrations of both types of fillers. In this work, a double percolation model is proposed for hybrid polymer–CNT–ANF systems, which allows describing the formation of an interconnected transport network and constructing theoretical property maps in the space of nanofiller concentrations. The present work addresses this gap by introducing a connectivity-based analytical framework that explicitly accounts for CNT–CNT, ANF–ANF, and CNT–ANF interactions within a unified mean-field description. Thermal conductivity is subsequently employed only as a representative transport property to demonstrate the predictive capability of the proposed connectivity model.

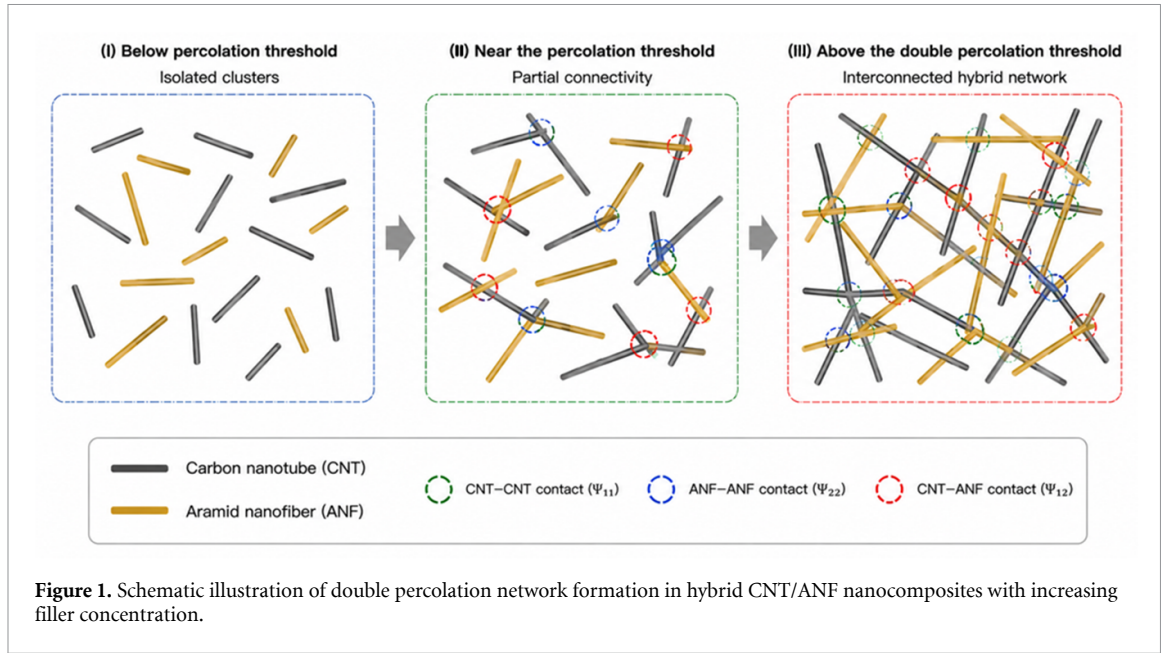
## 2. Theoretical part

### 2.1. Theoretical model of the formation of a double percolation network in polymer nanocomposites with two rod-shaped fillers

Consider a polymer nanocomposite consisting of a thermoplastic polymer matrix and two types of anisotropic rod-shaped fillers. Both types of particles have a high aspect ratio and are able to form spatial contact networks in the volume of the polymer matrix. In such a system, at a sufficient concentration of each of the fillers, a percolation network arises, which ensures the emergence of new macroscopic properties of the material—electrical conductivity, increased thermal conductivity or a sharp increase in the elastic modulus.

A feature of systems with two types of anisotropic fillers is the possibility of forming not only two independent networks (filler 1–filler 1 and filler 2–filler 2), but also hybrid contacts between different types of particles. It is these contacts that can significantly change the percolation conditions and lead to a synergistic effect, when the percolation threshold of the mixture turns out to be lower than for each filler separately (figure 1).

To describe the formation of the network, we will use the approach of percolation theory, which is widely used for systems of randomly oriented rod-like particles. According to this theory, percolation occurs when the average number of contacts per particle exceeds a certain critical value. Let the system contain two types of rods with lengths  $L_1$  and  $L_2$  and diameters  $D_1$  and  $D_2$ . The particle number concentrations are denoted by  $n_1$  and  $n_2$ .



The formation of a continuous transport network in such systems is associated with reaching a percolation threshold, which is determined by the statistics of contacts between particles. In the classical approach based on the concept of excluded volume, first proposed by Onsager [22] and adapted to percolation problems by Balberg [23], the critical percolation condition is written as:

$$nV_{\text{ex}} \sim \text{const}, \quad (1)$$

where  $n$  is the number concentration of particles, and  $V_{\text{ex}}$  is their excluded volume.

In multicomponent polymer systems, the formation of conductive networks is governed by several mechanisms, including percolation of individual phases and percolation of fillers within these phases [24]. These contributions can be considered as additive in terms of their influence on the overall connectivity of the system, which motivates the introduction of separate terms corresponding to different types of interparticle contacts. Therefore, for a two-component system, a natural generalization is to consider three types of contacts: between particles of the same type and between particles of different nature. Accordingly, the effective connectivity parameter of the system can be presented as the sum of the contributions:

$$\Psi = \Psi_1 + \Psi_2 + \Psi_{12}, \quad (2)$$

where  $\Psi_{12}$  characterizes the contribution of contacts of type 1–2 (figure 1).

Within the present framework, the mean-field approximation assumes that network connectivity is governed by statistically averaged interactions between fillers, while local structural fluctuations are neglected. This approach enables the derivation of analytical expressions describing the macroscopic evolution of hybrid network connectivity. The number of contacts between particles of different types can be estimated using a mean-field approach, where it is assumed to be proportional to the product of their number density and the excluded volume, which describes their geometric interaction. This assumption is consistent with the classical excluded volume percolation theory, where the connectivity of the system is determined by the product  $nV_{\text{ex}}$ . The contribution of contacts between different types of particles is determined by their statistics and is proportional to the product of the number concentrations and the excluded volume:

$$\Psi_{12} \sim n_1 n_2 V_{\text{ex}}^{12}. \quad (3)$$

The number concentrations of rods are related to their volume fractions by the ratio:

$$n_i = \frac{\varphi_i}{v_i} m, v_i = \frac{\pi D_i^2}{4} L_i, n_i = \frac{4\varphi_i}{\pi D_i^2 L_i}. \quad (4)$$

Using the excluded-volume expression derived by Onsager for cylinders [22, 25], the excluded volume for two long rods of lengths  $L_1$  and  $L_2$  with diameters  $D_1$  and  $D_2$ , averaged over the orientations, can be written as:

$$V_{\text{ex}}^{12} = \frac{\pi}{2} L_1 L_2 (D_1 + D_2). \quad (5)$$

Substitution yields:

$$\Psi_{12} \sim \varphi_1 \varphi_2 \frac{(D_1 + D_2)}{D_1^2 D_2^2}. \quad (6)$$

Similarly, for contacts of the same type [23]:

$$V_{\text{ex}}^{11} = \frac{\pi}{2} L_1^2 D_1, \quad V_{\text{ex}}^{22} = \frac{\pi}{2} L_2^2 D_2 \quad (7)$$

$$\Psi_{11} \sim \varphi_1 \frac{L_1}{D_1}, \quad \Psi_{22} \sim \varphi_2 \frac{L_2}{D_2} \quad (8)$$

which is consistent with the known result  $\varphi_c \sim \frac{D}{L}$  for rod percolation [26].

Combining all the contributions, we obtain an expression for the effective parameter:

$$\Psi \sim A\varphi_1 + B\varphi_2 + \Gamma_{\text{geom}}\varphi_1\varphi_2, \quad (9)$$

where the coefficients

$$A \sim \frac{L_1}{D_1}, \quad B \sim \frac{L_2}{D_2}, \quad (10)$$

characterize the individual ability of each filler to form a percolation network, and

$$\Gamma_{\text{geom}} \sim \frac{(D_1 + D_2)}{D_1^2 D_2^2} \quad (11)$$

is a geometric coefficient that determines the probability of contacts between particles of different nature.

The geometric contribution mentioned above describes only the probability of contact formation. However, for real transport properties (electrical conductivity, thermal conductivity) it is important to also consider the effectiveness of these contacts in forming continuous transport paths.

For this purpose, we introduce a dimensionless efficiency coefficient  $\eta$ , which may depend on the aspect ratios of the fillers:

$$\Gamma = \Gamma_{\text{geom}} \cdot \eta, \quad \eta = f\left(\frac{L_1}{D_1}, \frac{L_2}{D_2}\right). \quad (12)$$

Thus, the final expression takes the form:

$$\Psi \sim A\varphi_1 + B\varphi_2 + \Gamma\varphi_1\varphi_2. \quad (13)$$

The quantity  $\Psi$  represents the effective connectivity density of the hybrid network, which includes contributions from the three types of contacts.

The percolation transition occurs when the critical value  $\Psi = \Psi_c$  is reached. In the concentration plane  $(\varphi_1, \varphi_2)$  this condition determines the curve

$$\varphi_2 = \frac{\Psi_c - A\varphi_1}{B + \Gamma\varphi_1} \quad (14)$$

which separates the region of non-percolating structures and the region of continuous mesh formation. Equation (14) defines the theoretical percolation boundary predicted by the present model and should be interpreted as a model-derived connectivity criterion rather than a universal percolation threshold.

Of particular importance is the regime in which the concentrations of both fillers are below their individual percolation thresholds, but the hybrid contacts ensure the formation of a continuous cluster. In this regime, the term  $\Gamma\varphi_1\varphi_2$  dominates, and the percolation condition approaches

$$\varphi_1\varphi_2 \approx \frac{\Psi_c}{\Gamma}. \quad (15)$$

This means that percolation is determined not by the individual concentrations of fillers, but by their product, i.e. the density of hybrid contacts becomes the main factor in the formation of the network.

After the formation of an infinite cluster, the macroscopic properties of the composite obey the power laws of the percolation theory [27]. In particular, for the property  $P$  we can write

$$P = P_0(\Psi - \Psi_c)^t, \quad (16)$$

where  $t$  is a critical parameter, the value of which depends on the nature of the physical property. In three-dimensional systems, typical values are  $t \approx 1.6$ – $2$  for electrical conductivity [28–30] and  $t \approx 0.2$ – $0.86$  for thermal conductivity [31].

In the mode of dominance of hybrid contacts, the scaling law takes the form

$$P \sim (\varphi_1 \varphi_2)^t, \quad (17)$$

which can be used as an experimental criterion for the existence of double percolation. If the dependence of the property on the product of the filler concentrations in logarithmic coordinates is described by a straight line, this indicates the determining role of hybrid contacts in the formation of the network. The proposed model allows describing both the structural parameters of the composite and its macroscopic properties. In particular, it can be used to determine the effective contact density between fillers, construct a percolation map in the concentration space, and estimate the optimal ratio of fillers that provides the maximum synergistic effect. In addition, the parameters  $A$ ,  $B$ , and  $\Gamma$  can be estimated independently from the geometric characteristics of the particles (length and diameter), which makes the model suitable for quantitative comparison with experimental data.

Thus, double percolation in systems with two types of rod-shaped nanofillers can be interpreted as the result of the formation of interconnected networks of rod-shaped particles, where the statistics of contacts between particles of different nature play a key role. The proposed approach allows us to move from the description of individual networks to a generalized characterization of the composite structure through a single parameter of effective connectivity  $\Psi$ , which determines both the conditions for the occurrence of percolation and the scaling of the physical properties of the material.

Unlike conventional thermal-conductivity models, the present approach focuses on the evolution of network connectivity rather than on heat-transfer mechanisms themselves.

## 2.2. Analytical form of the hybrid percolation model of thermal conductivity of a nanocomposite

Thermal conductivity is employed here as a representative transport property to demonstrate the applicability of the proposed connectivity model. For a more complete description of the thermal conductivity of polymer composites containing two different types of nanofillers, it is advisable to formulate an explicit analytical model that takes into account the possibility of the formation of a hybrid percolation network. In systems containing CNTs and ANFs, heat transfer can occur not only through contacts between particles of the same type, but also through contacts between different fillers [10]. As a result, the effective connectivity of the thermally conductive network is determined by three types of contacts: CNT–CNT, ANF–ANF, and CNT–ANF.

To describe such a system, an effective network connectivity parameter  $\Psi$  is introduced, which depends on the concentrations of both fillers (13). In this equation,  $\varphi_1$  is the volume fraction of CNTs,  $\varphi_2$  is the volume fraction of ANFs. The coefficients  $A$  and  $B$  characterize the efficiency of the formation of heat-conducting networks by individual fillers and are related to their individual percolation thresholds. The hybrid interaction coefficient  $\Gamma$  is introduced as an effective mean-field parameter describing the average contribution of CNT–ANF contacts to the overall network connectivity. It is not intended to represent the probability of individual contacts at the microscopic level but rather the collective effect of hybrid interactions within the representative volume of the composite. The first two terms in this equation correspond to the independent formation of percolation networks of each type of particle, while the third term reflects the formation of bridges between these networks. The formation of a continuous heat conduction path in the composite occurs when the critical value of the connectivity parameter is reached, i.e.  $\Psi = \Psi_c$ .

Although the proposed framework employs a single effective connectivity parameter, this parameter represents the combined evolution of three connectivity mechanisms: CNT–CNT, ANF–ANF and CNT–ANF interactions. Thus, the model describes the cooperative development of two interacting percolation subnetworks rather than two independent percolation transitions.

This equation defines a curve in the concentration plane  $\varphi_1$ – $\varphi_2$  that separates the region without percolation from the region where a continuous hybrid nanofiller network is formed. Below this limit, the thermal conductivity is mainly determined by the polymer matrix, while above it, a rapid increase

**Table 1.** Model parameters used for theoretical calculations.

| Parameter | $A$ | $B$ | $\Gamma$        | $\Psi_c$ | $k_m$                                               | $k_0$                                             | $t$ |
|-----------|-----|-----|-----------------|----------|-----------------------------------------------------|---------------------------------------------------|-----|
| Value     | 100 | 80  | $10^3$ – $10^5$ | 0.2      | $0.2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ | $2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ | 0.5 |

in thermal conductivity occurs due to the formation of heat-conducting paths. After the formation of the percolation network, the thermal conductivity of the composite can be described by the scaling law characteristic of percolation-type systems [32, 33]:

$$k = k_m + k_0(\Psi - \Psi_c)^t, \quad (18)$$

where  $k_m$  is the thermal conductivity of the polymer matrix,  $k_0$  is the scaling factor characterizing the efficiency of the thermally conductive network, and  $t$  is the critical percolation index. In this case, the classical power law of percolation is generalized by replacing the filler concentration with the effective cohesion parameter  $\Psi$ . The present formulation isolates the effect of network connectivity on thermal transport and does not explicitly account for other mechanisms such as interfacial thermal resistance, phonon scattering, or filler intrinsic anisotropy. The obtained analytical expression makes it possible to construct a continuous function of the thermal conductivity of the composite as a function of the concentrations of the two fillers:

$$k = k(\varphi_1, \varphi_2). \quad (19)$$

This dependence can be represented graphically as a three-dimensional surface in the parameter space  $(\varphi_1, \varphi_2, k)$ . Each point of this surface corresponds to the predicted value of thermal conductivity for a certain combination of nanotube and nanofiber concentrations. In the region of low concentrations of both fillers, the value of thermal conductivity remains close to the thermal conductivity of the polymer matrix. As the percolation limit is approached, there is a sharp increase in thermal conductivity. In the region of high concentrations of both fillers, the hybrid term  $\Gamma\varphi_1\varphi_2$  dominates, which leads to a synergistic strengthening of the thermally conductive network. The present model assumes a statistically homogeneous dispersion of fillers and therefore does not explicitly account for nanotube aggregation or bundle formation.

For illustration of the proposed model, representative parameter values corresponding to typical CNT/ANF hybrid systems were used. The selected values do not refer to a specific material system and were chosen to demonstrate the qualitative behavior of the model.

The values of  $A$  and  $B$  were selected to represent high-aspect-ratio rod-like fillers with percolation thresholds typical for CNT- and ANF-filled polymer systems reported in the literature. The chosen range of  $\Gamma$  ( $10^3$ – $10^5$ ) was used to investigate the sensitivity of the model to the probability of hybrid contact formation. The parameter  $\Gamma$  may be extracted from fitting experimental conductivity data or estimated from microstructural characterization of the hybrid network. The values of  $\Psi_c$ ,  $k_m$  and  $k_0$  were selected as representative parameters allowing qualitative analysis of the double-percolation behavior rather than fitting a specific experimental system. In the calculations presented below,  $\eta$  was assumed constant to focus on the influence of filler concentrations and hybrid connectivity. So, the parameter values listed in table 1 were selected to represent physically realistic CNT/ANF systems and to illustrate the behavior of the proposed model. They should therefore be regarded as representative model parameters rather than a fit to a specific experimental dataset.

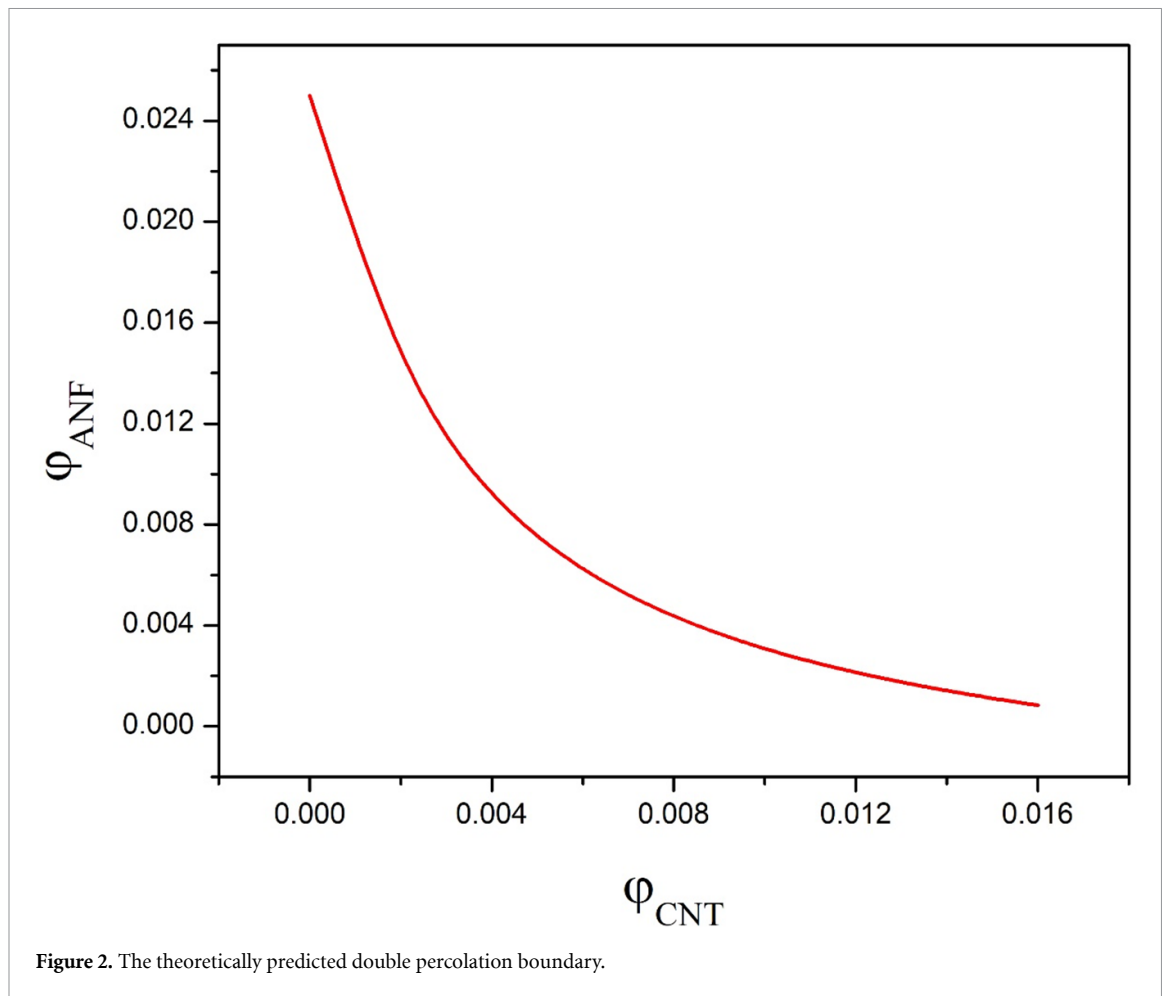
The same connectivity framework may be extended to other transport phenomena, including electrical conductivity, provided that the corresponding scaling relations are introduced.

### 3. Results and discussion

#### 3.1. Formation of a hybrid percolation network

Within the framework of the approach described in section 2, an effective structural parameter  $\Psi$  is introduced, which takes into account the contributions of individual fillers and their hybrid interaction. The formation of a continuous network occurs when the value of this parameter exceeds the critical value  $\Psi_c$ . Thus, the percolation condition simultaneously depends on the CNT and ANF concentrations (figure 1).

The calculated percolation limit in the space of filler concentrations, calculated according to equation (14), is presented in figure 2. This curve separates the region in which a continuous network



is formed and the region where the nanofillers remain structurally isolated and cannot provide effective transport channels.

As shown in figure 2, with increasing concentration of one type of filler, the concentration of the other required to achieve percolation decreases. This behavior suggests the presence of a hybrid percolation mechanism. In this case, contacts between different types of nanostructures also contribute to the formation of a continuous cluster. In other words, CNT–ANF connections can contribute to the formation of a transport network along with CNT–CNT or ANF–ANF contacts.

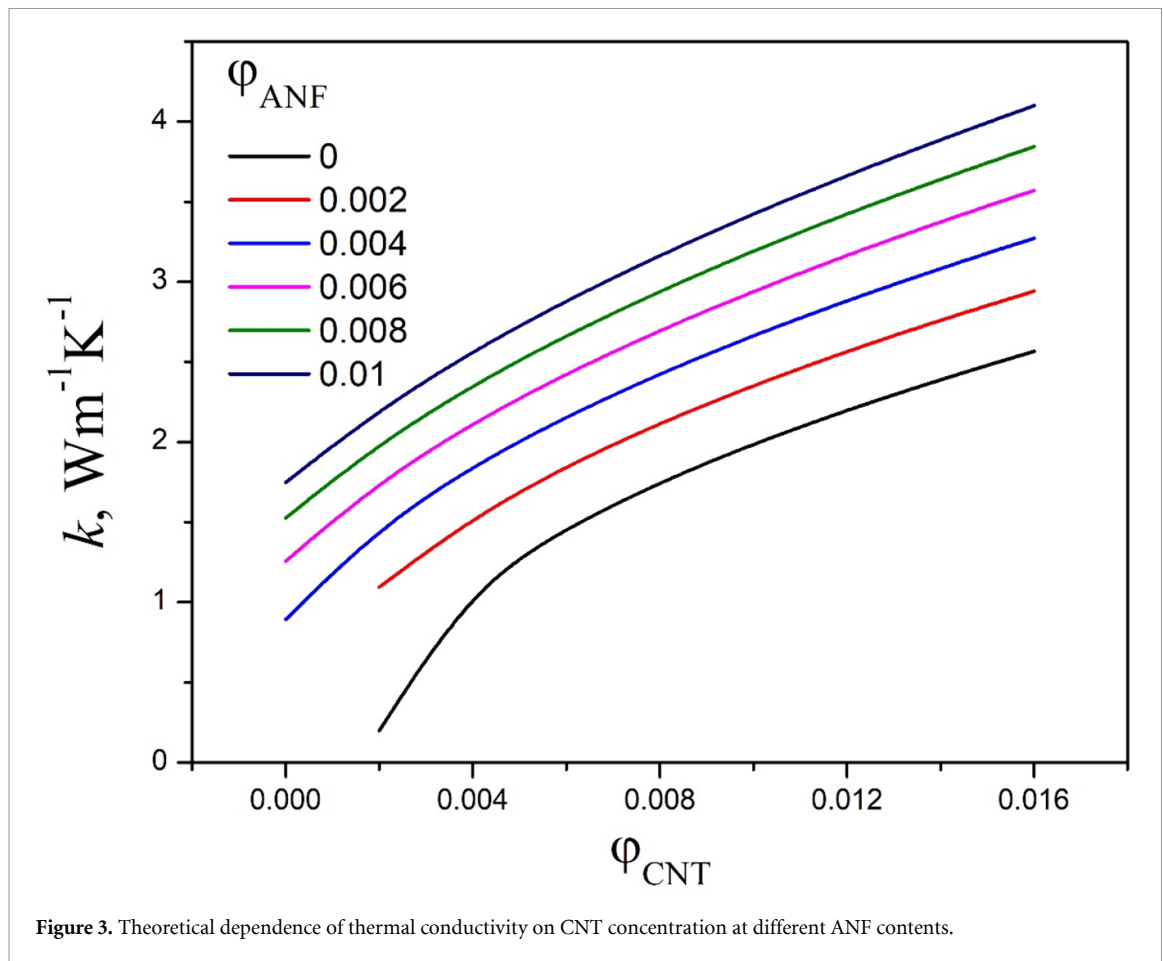
This effect is especially important for hybrid nanocomposites in which fillers perform different structural functions. CNTs can act as effective conductive bridges due to their large aspect ratio and high intrinsic electrical conductivity, while ANFs are able to form a mechanically stable fibrous framework that promotes the formation of contacts between nanotubes.

### 3.2. The effect of ANFs on the percolation threshold of carb CNTs on nanotubes

A more detailed analysis of the hybrid network formation can be obtained by considering the dependence of thermal conductivity on CNT concentration at different fixed ANF concentrations. Such dependences are shown in figure 3.

As shown in figure 3, an increase in CNT concentration leads to a monotonic increase in the predicted thermal conductivity for all investigated ANF contents. However, the shape and position of the calculated curves strongly depend on the concentration of ANFs. At low ANF contents, the increase in thermal conductivity occurs only after a relatively high CNT concentration is reached. In contrast, increasing the ANF concentration results in a systematic upward shift of the entire conductivity curve and promotes a more rapid development of the transport network.

A particularly important observation is that comparable values of thermal conductivity can be achieved at significantly lower CNT concentrations when the ANF content is increased. For example, thermal conductivity values exceeding approximately  $2 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  are obtained only at relatively high CNT contents in ANF-poor systems, whereas similar values are achieved at substantially lower CNT concentrations in composites containing larger amounts of ANFs. This behavior indicates that ANFs actively



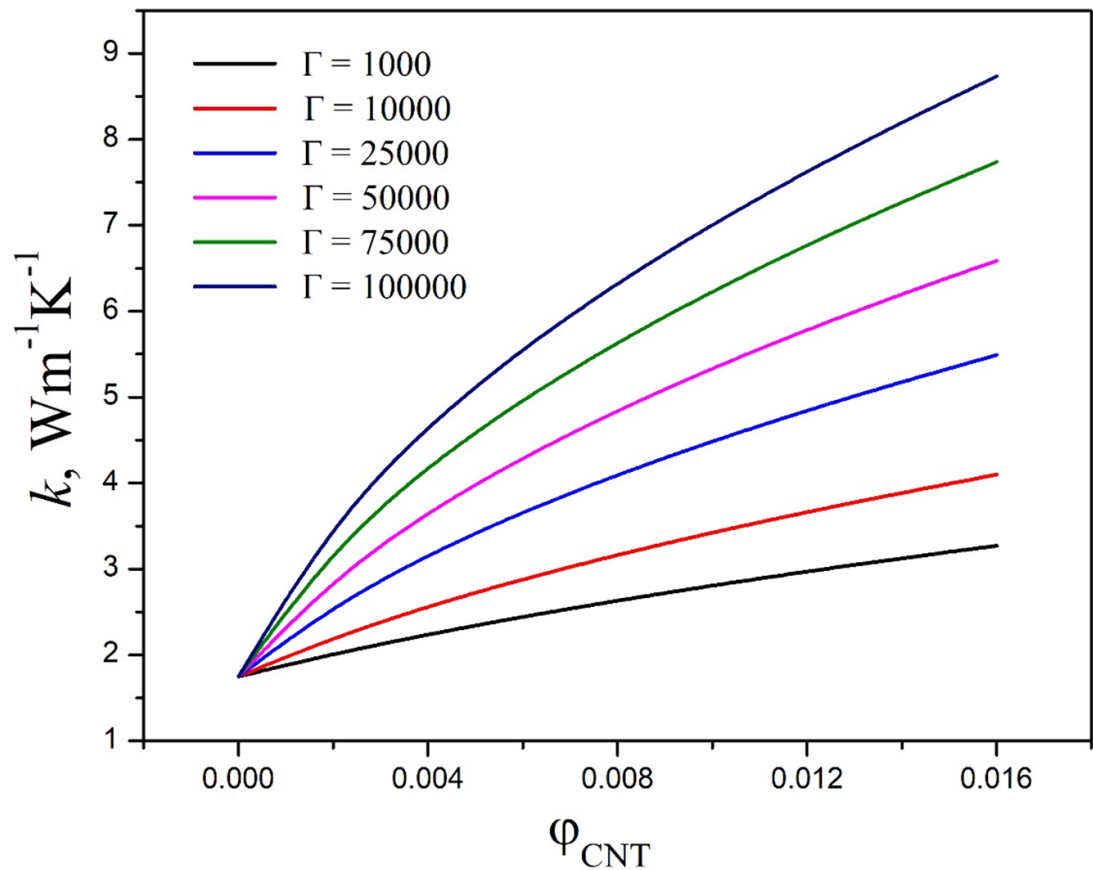
participate in the formation of the transport network and facilitate the establishment of long-range connectivity between nanotube clusters.

Within the framework of the proposed model, this effect originates from the hybrid connectivity term associated with CNT–ANF contacts. As the ANF concentration increases, the number of potential hybrid contacts grows, resulting in a larger contribution of the interaction term to the effective connectivity parameter. Consequently, the probability of forming a continuous transport pathway increases even when the concentration of CNTs remains relatively low. In physical terms, ANFs act as additional structural elements that enhance network connectivity and reduce the amount of nanotubes required to achieve a given level of transport performance.

The calculated dependences therefore suggest a reduction of the effective CNT percolation threshold in the presence of ANFs. Although the model does not define the percolation threshold through a sharp transition point, the progressive leftward displacement of the conductivity curves with increasing ANF content clearly demonstrates that the onset of efficient transport occurs at lower CNT concentrations. This behavior is consistent with the concept of double percolation, in which hybrid CNT–ANF contacts contribute to the formation of an interconnected network alongside CNT–CNT and ANF–ANF interactions. Therefore, the term double percolation is used here to emphasize the simultaneous evolution of two coupled filler networks rather than the existence of two separate critical transitions.

Another notable feature of the calculated results is the nonlinear amplification of thermal conductivity at simultaneously high CNT and ANF concentrations. In this region, the spacing between neighboring curves increases, indicating that the influence of ANFs becomes progressively stronger as the CNT content rises. Such behavior is a direct consequence of the multiplicative nature of the hybrid interaction term and reflects the emergence of a synergistic effect associated with the formation of an interconnected hybrid network.

Overall, the obtained results demonstrate that ANFs play a dual role in the hybrid system. Besides contributing directly to network formation, they promote the connectivity of CNTs and effectively lower the CNT concentration required for the development of a continuous transport structure. This finding supports the central hypothesis of the proposed model describing double-percolation phenomena and



**Figure 4.** Predicted thermal conductivity of the hybrid CNT/ANF system as a function of CNT concentration at a fixed ANF content ( $\varphi_{\text{ANF}} = 0.06$ ) for different values of the effective hybrid interaction coefficient  $\Gamma$ . The calculations were performed using the proposed model describing double-percolation phenomena.

highlights the importance of hybrid filler interactions in determining the transport properties of multi-functional polymer nanocomposites.

### 3.3. Effect of the effective hybrid interaction coefficient on the predicted thermal conductivity

An important parameter of the proposed model is the coefficient  $\Gamma$ , which characterizes the contribution of hybrid CNT–ANF contacts to the overall connectivity of the transport network. Physically, this parameter reflects the probability of formation of effective interconnections between CNTs and ANFs and therefore determines the intensity of the synergistic interaction between the two nanofillers. Accordingly, variations of  $\Gamma$  should be interpreted as changes in the effective structural efficiency of hybrid network formation rather than direct changes in microscopic contact probability.

To evaluate the influence of  $\Gamma$  on the predicted transport behavior, thermal conductivity was calculated for a fixed ANF concentration of ( $\varphi_{\text{ANF}} = 0.06$ ) and different values of the hybrid interaction coefficient ranging from  $10^3$  to  $10^5$  (figure 4). The obtained results demonstrate a pronounced sensitivity of the model to this parameter. At zero CNT concentration, all curves converge to the same thermal conductivity value, indicating that the contribution of the hybrid term vanishes in the absence of one of the interacting components. However, as the CNT concentration increases, the effect of  $\Gamma$  becomes increasingly significant.

For example, at ( $\varphi_{\text{CNT}} = 0.002$ ), the predicted thermal conductivity increases from approximately 2.01–3.55 when  $\Gamma$  increases from  $10^3$  to  $10^5$ . At the highest investigated CNT concentration ( $\varphi_{\text{CNT}} = 0.016$ ), the corresponding values increase from 3.27 to 8.73. Thus, the difference between the extreme cases exceeds a factor of 2.5, indicating that the probability of hybrid contact formation becomes one of the dominant factors governing the transport properties of the system. The numerical value of  $\Gamma$  is system-dependent and reflects the combined influence of filler geometry, spatial distribution, and interfacial interactions. Therefore, it should be regarded as an effective structural parameter rather than a universal material constant.

Another important observation is that the influence of  $\Gamma$  is nonlinear. At low CNT contents, all calculated curves remain relatively close to each other, whereas at higher CNT concentrations the separation between the curves progressively increases. This behavior originates from the multiplicative form of the hybrid interaction term, which scales with the product of the concentrations of the two fillers. Consequently, the number of CNT–ANF contacts increases not only due to a larger value of  $\Gamma$ , but also due to the increasing availability of nanotubes participating in the formation of the hybrid network.

From a physical viewpoint, increasing  $\Gamma$  corresponds to a greater probability that CNTs and ANFs become incorporated into a common transport framework. Such a situation may arise when the spatial distribution of fillers promotes interparticle interactions, when nanotubes are localized near the nanofiber surface, or when the geometric characteristics of the fillers facilitate the formation of bridge contacts. As a result, the connectivity of the hybrid network increases, leading to the emergence of more efficient transport pathways throughout the system. Physically,  $\Gamma$  is expected to remain positive, since increasing the efficiency of hybrid contacts can only enhance the overall network connectivity within the assumptions of the present model. The magnitude of  $\Gamma$  is expected to depend on the morphology of both fillers, including their aspect ratio, waviness, orientation, and spatial dispersion, since these factors directly influence the probability of forming effective CNT–ANF bridge contacts.

These results indicate that the parameter  $\Gamma$  plays a crucial role in determining the magnitude of the synergistic effect predicted by the model. In practical terms, it can be regarded as a generalized descriptor of the structural efficiency of the hybrid network. Consequently, optimization of the CNT–ANF interaction probability may be as important as increasing the filler concentration itself for achieving enhanced transport properties in hybrid polymer nanocomposites.

### 3.4. Predicted evolution of hybrid network connectivity

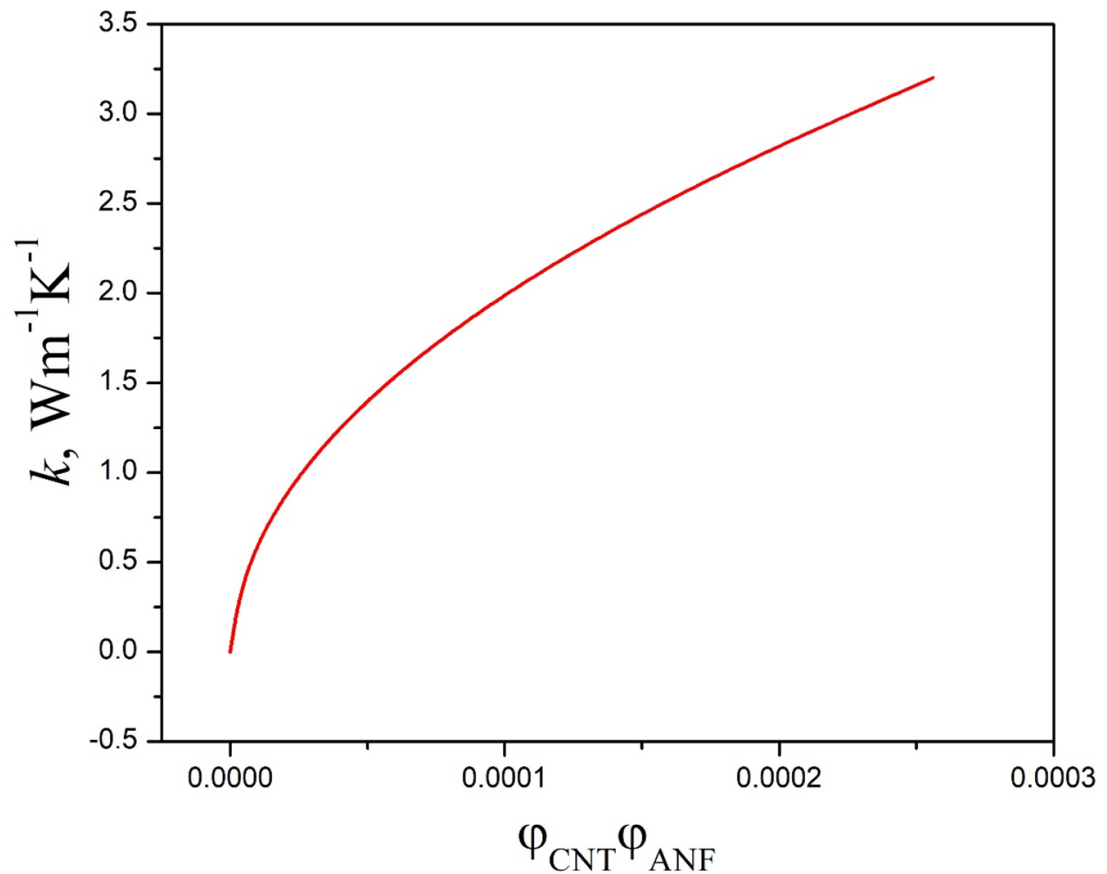
An important consequence of the proposed framework for double-percolation network formation is the emergence of a scaling relationship between the effective transport properties of the composite and the concentration product of the two nanofillers. According to the developed theoretical framework, the contribution of hybrid CNT–ANF contacts is determined by the interaction term proportional to  $\varphi_{\text{CNT}}\varphi_{\text{ANF}}$ . Therefore, analysis of the transport behavior as a function of this parameter provides insight into the fundamental mechanisms governing the formation of the hybrid network.

The calculated dependence presented in figure 5 demonstrates a monotonic increase in the effective transport property with increasing values of  $\varphi_{\text{CNT}}\varphi_{\text{ANF}}$ . The obtained curve exhibits a smooth nonlinear character and indicates that the connectivity of the hybrid network is strongly influenced by the simultaneous presence of both filler types. In contrast to conventional single-filler systems, where network formation is controlled primarily by the concentration of one component, the present model predicts that the transport performance is governed by the combined contribution of CNTs and ANFs.

An important feature of the calculated dependence is that the transport property increases continuously with increasing  $\varphi_{\text{CNT}}\varphi_{\text{ANF}}$ , demonstrating the growing contribution of hybrid contacts to the overall connectivity of the system. Since the concentration product represents the probability of interaction between CNTs and ANFs within the composite volume, larger values of  $\varphi_{\text{CNT}}\varphi_{\text{ANF}}$  correspond to a greater number of potential bridge connections linking individual filler clusters. As a result, the transport network becomes progressively more interconnected, leading to enhanced transport efficiency throughout the material. Although the scaling behavior originates from the analytical form of equation (17), the obtained dependence illustrates the expected evolution of network connectivity in hybrid CNT/ANF systems.

From a physical perspective, the observed scaling behavior supports the central assumption of the proposed model that CNT–ANF contacts constitute an independent contribution to network formation. The results suggest that the transport properties of hybrid nanocomposites cannot be described solely through the individual concentrations of CNTs or ANFs. Instead, the interaction between the two filler populations plays a crucial role and gives rise to an additional connectivity mechanism that becomes increasingly important as the density of hybrid contacts increases.

The observed dependence is consistent with the concept of double percolation, in which the transport pathways are formed not only through CNT–CNT and ANF–ANF interactions but also through CNT–ANF bridge contacts. Consequently, the concentration product  $\varphi_{\text{CNT}}\varphi_{\text{ANF}}$  may be regarded as a structural descriptor of hybrid network development. The existence of a well-defined scaling relationship between the transport property and this parameter indicates that the formation of the hybrid percolation network follows predictable connectivity laws and can therefore be described within a unified theoretical framework.



**Figure 5.** Scaling dependence of the effective transport property on the concentration product  $\varphi_{\text{CNT}}\varphi_{\text{ANF}}$  predicted by the proposed double-percolation model.

Overall, the results demonstrate that the concentration product of the two nanofillers is a key parameter controlling the evolution of the hybrid transport network. The identified scaling behavior provides additional support for the proposed framework for double-percolation network formation and highlights the fundamental role of hybrid CNT–ANF interactions in determining the macroscopic properties of multifunctional polymer nanocomposites.

### 3.5. Limitations of the model

The proposed model is based on a mean-field description of network connectivity and considers the nanofillers as randomly distributed rod-like objects in a three-dimensional isotropic system. In this framework, the formation of the hybrid transport network is described through averaged geometric interactions and excluded-volume concepts. Therefore, the model does not explicitly account for local heterogeneities of filler distribution, agglomeration effects, anisotropic orientation of nanostructures, or the influence of processing conditions on the spatial organization of the network. In addition, the interfacial thermal resistance and detailed molecular interactions between the fillers and the polymer matrix are not considered explicitly and are incorporated only implicitly through effective connectivity parameters. Consequently, the predicted percolation boundary should be regarded as a theoretical approximation whose quantitative validity requires experimental verification for specific CNT/ANF systems. A rigorous derivation of  $\Gamma$  from particle-scale geometry is beyond the scope of the present mean-field model and remains a subject for future multiscale investigations. Establishing quantitative relationships between  $\Gamma$  and measurable morphological characteristics requires dedicated experimental studies or particle-scale simulations and is beyond the scope of the present work.

It should also be noted that the present approach is primarily intended for qualitative and semi-quantitative analysis of double percolation phenomena in hybrid polymer nanocomposites. The derived analytical expressions describe the general scaling behavior and synergistic effects associated with the formation of interconnected CNT–ANF networks; however, accurate prediction of the absolute values of transport properties may require additional numerical simulations or experimental calibration for specific material systems. In real CNT or ANF-containing systems, partial nanotube or nanofiber

aggregation and bundle formation may reduce the effective aspect ratio and modify network connectivity. Consequently, the present model is expected to provide the most accurate predictions for well-dispersed nanocomposites or systems in which aggregation remains limited. Accordingly, the proposed model should be regarded as a connectivity-based theoretical framework rather than a comprehensive description of all heat-transfer mechanisms operating in polymer nanocomposites.

To the best of our knowledge, no comprehensive experimental thermal-conductivity datasets for CNT/ANF hybrid polymer nanocomposites are currently available in the open literature for direct quantitative validation of the proposed framework. Therefore, the present work is intended as a theoretical framework that may guide future experimental investigations of hybrid CNT/ANF nanocomposites.

Despite these limitations, the proposed model provides a physically consistent framework for describing hybrid percolation processes in multicomponent nanostructured polymer systems.

## 4. Conclusions

The proposed theoretical model demonstrates that the formation of transport networks in hybrid polymer nanocomposites cannot be adequately described solely in terms of the individual percolation thresholds of the constituent fillers. The connectivity of the system is governed by the combined effect of filler concentrations and hybrid interactions between CNTs and ANFs.

The developed analytical framework predicts that CNT–ANF contacts contribute to the formation of an interconnected transport network alongside CNT–CNT and ANF–ANF interactions. As a result, the effective onset of network formation may occur at lower CNT concentrations in the presence of ANFs, which is consistent with the concept of double percolation.

The obtained concentration maps and scaling dependences reveal that the transport behavior of the hybrid system is controlled not only by the individual filler contents but also by the concentration product of the two nanofillers. This observation indicates that hybrid contacts represent an independent mechanism governing network development and transport efficiency.

The proposed model also demonstrates the important role of the effective hybrid interaction coefficient, which determines the contribution of CNT–ANF interactions to the overall network connectivity. The analysis suggests that optimization of hybrid contacts may be as important as increasing filler concentration for achieving enhanced transport properties. From a practical perspective, the model provides a theoretical tool for identifying concentration regions favorable for hybrid network formation prior to experimental optimization.

Overall, the developed approach provides a theoretical framework for describing double-percolation phenomena and for predicting the influence of filler composition and hybrid interactions on the transport behavior of multifunctional polymer nanocomposites. Beyond predicting transport behavior, the model provides physical insight into the cooperative role of hybrid filler interactions during network formation.

## Acknowledgments

This work was funded by the Ministry of Education and Science of Ukraine within the framework of the research project ‘Creation of multifunctional polymer nanocomposite materials reinforced with para-aramid fibers and carbon nanotubes’ (state registration number is 0124U001739).

## Data availability statement

No new data were created or analysed in this study.

## ORCID iD

Eduard Lysenkov  0000-0002-1369-4609

## References

- [1] Ishizuka F, Jin Kim H, Kuchel R P, Yao Y, Chatani S, Niino H and Zetterlund P B 2022 Polymeric nanocomposites based on high aspect ratio polymer fillers: simultaneous improvement in tensile strength and stretchability *Eur. Polym. J.* **169** 111134
- [2] Vaka M, Walvekar R and Yanamadala S 2021 Carbon nanotubes and their composites: from synthesis to applications *Contemporary Nanomaterials in Material Engineering Applications. Engineering Materials* eds N M Mubarak, M Khalid, R Walvekar and A Numan (Springer) pp 37–67
- [3] Ren J *et al* 2026 Strengthened epoxy nanocomposites with binary fillers of magnetite@polyaniline and carbon nanofiber for high-performance thermal stability electromagnetic wave absorption *J. Mater. Sci. Technol.* **243** 139–48
- [4] Barani Z, Mohammadzadeh A, Geremew A, Huang C-Y, Coleman D, Mangolini L, Kargar F and Balandin A A 2020 Thermal properties of the binary-filler hybrid composites with graphene and copper nanoparticles *Adv. Funct. Mater.* **30** 1904008
- [5] Yao X, Raine T P, Liu M, Zakaria M, Kinloch I A and Bissett M A 2021 Effect of graphene nanoplatelets on the mechanical and gas barrier properties of woven carbon fibre/epoxy composites *J. Mater. Sci.* **56** 19538–51
- [6] Mishra K and Singh A 2024 Effect of graphene nano-platelets coating on carbon fibers on the hygrothermal ageing driven degradation of carbon-fiber epoxy laminates *Composites B* **269** 111106
- [7] Buketov A V, Smetankin S A, Lysenkov E A, Yurenin K, Akimov O, Yakushchenko S and Lysenkova I 2020 Electrophysical properties of epoxy composite materials filled with carbon black nanopowder *Adv. Mater. Sci. Eng.* **2020** 6361485
- [8] Nejad S J J 2012 A review on modeling of the thermal conductivity of polymeric nanocomposites *e-Polym.* **12** 025
- [9] Lysenkov E A and Dinzhos R V 2019 Theoretical analysis of thermal conductivity of polymer systems filled with carbon nanotubes *J. Nano Electron. Phys.* **11** 04004
- [10] Jang J-U, Lee S H, Kim J, Kim S Y and Kim S H 2021 Nano-bridge effect on thermal conductivity of hybrid polymer composites incorporating 1D and 2D nanocarbon fillers *Composites B* **222** 109072
- [11] Lysenkov E A, Striutskiy O V, Demchenko V L and Lazarenko M M 2026 The effect of ultra-low concentrations of aramid nanofibers on the structural and thermal characteristics of polylactic acid-based nanocomposites *J. Compos. Mater.* **60** 2071
- [12] Ngo I L and Truong V A 2019 An investigation on effective thermal conductivity of hybrid-filler polymer composites under effects of random particle distribution, particle size and thermal contact resistance *Int. J. Heat Mass Transfer* **144** 118605
- [13] Xiao Y-J, Wang W-Y, Chen X-J, Lin T, Zhang Y-T, Yang J-H, Wang Y and Zhou Z-W 2016 Hybrid network structure and thermal conductive properties in poly(vinylidene fluoride) composites based on carbon nanotubes and graphene nanoplatelets *Compos. A* **90** 614–25
- [14] Suresha B, Indushekhara N M, Varun C A, Sachin D and Pranao K 2021 Effect of carbon nanotubes reinforcement on mechanical properties of aramid/epoxy hybrid composites *Mater. Today Proc.* **43** 1478–84
- [15] Zhu J, Cao W, Yue M, Hou Y, Han J and Yang M 2015 Strong and stiff aramid nanofiber/carbon nanotube nanocomposites *ACS Nano* **9** 2489–501
- [16] Lysenkov E A, Sytnyk I O, Lysenkova I P and Demchenko V L 2025 Microstructure and mechanical properties of polymer nanocomposites based on polylactic acid and carbon nanotubes *Mater. Sci.* **61** 628–35
- [17] Xu B, Yin J and Liu Z 2013 Phonon scattering and electron transport in single wall carbon nanotube *Physical and Chemical Properties of Carbon Nanotubes* ed S Suzuki (IntechOpen)
- [18] Wei H, Lei T, Ma L and Li W 2024 Aramid nanofiber-reinforced carbon nanotubes@cobalt ferrite nanoparticles aerogel films achieve excellent electromagnetic interference shielding, photothermal and joule heating performance *Ceram. Int.* **50** 50388–96
- [19] Zha J-W, Wang F and Wan B 2025 Polymer composites with high thermal conductivity: theory, simulation, structure and interfacial regulation *Prog. Mater. Sci.* **148** 101362
- [20] Lysenkov E A 2019 Simulation of thermal conductivity of polymer nanocomposites, using models based on thermal-electrical analogy *Nanosistemi, Nanomateriali, Nanotehnologii* **17** 761–72
- [21] Vairagade S, Kumar N and Singh R P 2024 Recent advancements and applications in thermally conductive polymer nanocomposites *Polym.-Plast. Technol. Mater.* **63** 1371–420
- [22] Onsager L 1949 The effects of shape on the interaction of colloidal particles *Ann. N. Y. Acad. Sci.* **51** 627–59
- [23] Balberg I, Anderson C H, Alexander S and Wagner N 1984 Excluded volume and its relation to the onset of percolation *Phys. Rev. B* **30** 3933–43
- [24] Otero-navas I, Arjmand M and Sundararaj U 2017 Carbon nanotube induced double percolation in polymer blends: morphology, rheology and broadband dielectric properties *Polymer* **114** 122–34
- [25] Rawal A 2021 Excluded volume and its relation to the theory of fiber-fiber contacts *Mech. Mater.* **160** 103901
- [26] Bauhofer W and Kovacs J Z 2009 A review and analysis of electrical percolation in carbon nanotube polymer composites *Compos. Sci. Technol.* **69** 1486–98
- [27] Stauffer D and Sahimi M 2020 Scaling theory of percolation clusters *Encyclopedia of Complexity and Systems Science* ed R A Meyers (Springer) pp 1–12
- [28] Efros A L and Shklovskii B I 1976 Critical behaviour of conductivity and dielectric constant near the metal-non-metal transition threshold *Phys. Status Solidi B* **76** 475–85
- [29] Bergman D J and Stroud D 1992 Physical properties of macroscopically inhomogeneous media ehrenreich H, Turnbull D, eds *Solid State Phys.* **46** 147–269
- [30] Klepko V V and Lysenkov E A 2015 Features of percolation transition in systems on the basis of oligoglycols and carbon nanotubes *Ukr. J. Phys.* **60** 944–9
- [31] McLachlan D S 2021 The percolation exponents for electrical and thermal conductivities and the permittivity and permeability of binary composites *Physica B* **606** 412658
- [32] Sun K, Zhang Z D, Qian L, Dang F, Zhang X H and Fan R H 2016 Dual percolation behaviors of electrical and thermal conductivity in metal-ceramic composites *Appl. Phys. Lett.* **108** 061903
- [33] Jang J-U, Nam H E, So S O, Lee H, Kim G S, Kim S Y and Kim S H 2022 Thermal percolation behavior in thermal conductivity of polymer nanocomposite with lateral size of graphene nanoplatelet *Polymers* **14** 323