

Review

Theoretical Characterization of Thermal Conductivities for Polymers—A Review

Cornelia Bretkopf 

Chair of Thermodynamics, Institute of Power Engineering, TU Dresden, Helmholtzstr. 14, 01062 Dresden, Germany; cornelia.bretkopf@tu-dresden.de

Abstract: Polymer thermal conductivities play an important role for their potential use in industrial applications. Therefore, great efforts have been made to investigate fundamental structure–property relationships to understand and predict thermal conductivities for polymers and their composites. The review summarizes selected well-proven microscopic theoretical approaches to calculate thermal conductivities such as EMD, NEMD, EMT, and BTE, and cites examples to focus on different qualitative aspects of recent polymer theoretical research. Examples other than polymer materials are given as supplemental information to support the general discussion of heat transport phenomena in solid materials.

Keywords: thermal conductivity; theory; Green–Kubo; equilibrium molecular dynamics; non-equilibrium molecular dynamics; effective medium theory; Boltzmann transport equation; EOS

1. Introduction

Polymers are important materials for numerous industrial and everyday applications based on their wide range of properties, which can be tailored precisely to the intended use. The thermal conductivity of polymers is a very important feature that essentially influences future applications of polymer-based materials or composites. Pure polymers are mainly thermally resistant, having thermal conductivities κ around 0.1–0.5 W/m.K [1]. Those polymers may be applied preferably as thermal barrier coatings [2]. Figure 1 provides an overview about selected thermal conductivities κ for different characteristic polymers.

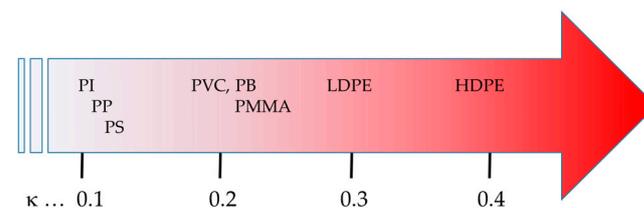


Figure 1. Thermal conductivities κ [W/m.K] for selected polymers (PI: polyimide, PVC: polyvinyl chloride, PB: polybutadiene, LDPE: low-density polyethylene, HDPE: high-density polyethylene, PP: polypropylene, PMMA: poly(methylmethacrylate), PS: polystyrene).

In recent decades, great research efforts have therefore been made to investigate structure–property relationships for polymers, e.g., the influence of molecular weight, chain interactions, or domain sizes, in order to increase their thermal conductivity and thus open up new fields of application [3,4]. Several review articles focusing on this aspect for polymers can be found here, where also quantitative comparisons of applied simulation methods can be found: Mehra et al. [5], Zhang B. et al. [6].

The basic theory to describe heat transport in solid materials dates back to the very early time of modern physics. Macroscopic approaches based on Fourier’s law of heat conduction dominated at first, where the conduction in solid materials is treated via a



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continuum approach (see textbooks of Nellis and Klein) [7]. A more atom-based view started with the development of statistical thermodynamics, and the successful expansion of scientific research into the microscopic range of polymers began. It is now generally recognized that future material developments require a systematic, atomistic approach to predict and describe the thermal properties of polymer materials.

This paper intends to give a short overview of common proven theoretical methods to calculate thermal conductivities for polymers. This applies above all to EMD, NEMD, EMT, and BTE. However, those methods may be also applicable to other solid materials as well. These methods are briefly supplemented by EOS and Einstein formula-based approaches to complete the qualitative overview. It should be emphasised that thermal conductivities represent only one of many transport properties. An approach which allows characterising the thermal transport within a solid system may also be adopted to receive other transport quantities, such as, for instance, mass or momentum transport. Table 1 summarizes all transport coefficients, which are available via common molecular approaches.

Table 1. Transport coefficients and analogies among energy, mass, and momentum transport.

Transport Coefficient	Type of Transport	Physical Law
Thermal conductivity κ	Thermal energy	Fourier
Diffusion coefficient D	Mass	Fick
Viscosity η	Momentum	Newton

The transport coefficients define the response of the system to a perturbation, which results in a gradient as a driving force. The gradient then starts an equalizing flux, which is proportional to the driving force characterized by its transport coefficient. The transport coefficient is a characteristic material property. Based on this general phenomenological approach, several theoretical methods for calculating material properties have been developed. By calculating thermal conductivities for polymer model systems of different domain sizes, variable chain compositions, crosslinking, etc., it is possible to derive structure–property relations, which support the experimental design of new materials with improved material properties. The review intends to highlight proven theoretical approaches by summarizing recent articles in polymer research without going into detail for aspects such as basics of force fields, phonon transport, etc.

2. Theoretical Methods for the Calculation of Thermal Conductivities

The chapter provides an overview about existing and successful calculations with microscopic-based methods for determining thermal conductivities based on different depths of a theoretical level. The focus is given here to the background of the methods itself without going into detail with respect to equations or basics of the physics of phonon transport. For the description of phonon transport theory, the reader is referred to the articles or textbooks in references [8–13]. Also, basic terms such as molecular mechanics or molecular dynamics including their force fields as well as ab initio methods are not explained separately here. The review summarizes general concepts without presenting basic equations. The reader is therefore invited to refer to the original papers, which are listed below.

2.1. Green–Kubo Method

The Green–Kubo approach represents a well-proven method to characterize properties of existing polymer materials as well as to predict properties of polymers [14]. Green–Kubo, as a theoretical method, bases on the fluctuation–dissipation theorem, and goes back to the linear response theory [15]. Kubo has transferred the linear response theory, originally developed for the description of transport of electrons in metals by Drude [16], to the transport phenomena in solid non-metallic systems. At the same time, Green [17] published his research in statistical mechanics regarding transport processes in fluids. Both approaches,

i.e., Green and Kubo, were combined into one method, which has since then been referred to as Green–Kubo method.

The Green–Kubo approach is, according to its theoretical basis, also called EMD approach, EMD = Equilibrium Molecular Dynamics [15,18]. EMD offers an important advantage compared to other theoretical approaches: it depends less on the size of the simulated systems [14]. Feng et al. [19] investigated such size effects intensively with EMD, and analysed recent size effects using new technical terms for heat transport such as propagons and diffusons (see Section 2.3).

Thermal conductivities are derived from Green–Kubo by analysing the heat flux auto correlation function in each direction. The general formula is written as follows, see Equation (1).

$$\kappa = \frac{V}{3 k_B T^2} \int_0^{t_c} \langle j_Q(t) j_Q(0) \rangle_{t_s} dt \quad (1)$$

where V is the volume of the framework of the model system, T the temperature of the system in Kelvin, k_B the Boltzmann constant, and j_Q are components of the heat current vectors providing the autocorrelation function. This function is evaluated via averages of all ensembles within a certain time (t_c is the finite correlation time in which the integration is done; t_s is the time frame for the average for obtaining the function). More details of the basic approach can be found in Alamfard et al. [20].

To calculate the heat flux vector, the total energy of the model structure needs to be determined. In general, the total energy of the model system resembles the kinetic and potential energy of all constituents. Based on the level of the chosen approach, this total energy may be evaluated via classical approaches as molecular mechanics, e.g., classical force field potentials [14,20], or using elevated approaches, e.g., quantum chemical potentials [21].

Because of the availability of modern high-performance computer systems, the calculation of the auto correlation function, which needs to evaluate in each step the total energy, is also possible for bigger model systems, such as polymer structures consisting of thousands of atoms with high molecular weights. For example, model systems reduced to single polymer chains can thus be compared to real polymer nanofibres or bulk polymer models having a 3D-structure with high molecular weights. Polyethylene as a single polymer chain, for example, has a much higher thermal conductivity compared to a polyethylen nanofibre or its bulk 3D structure [22]. The single chain polyethylene has an unusually high thermal conductivity, bigger than 100 W/m.K, whereas the nanofibre reaches 104 W/m.K, and the thermal conductivity κ for the bulk polymer lies around 0.1 W/m.K. Substantial scattering is discussed as a reason for this behaviour due to entanglements in the bulk polymer as well as highly disordered structures. Shen et al. [22] also reported that the chain orientation of the chosen polymer model along the fibre axis significantly influenced the thermal conductivity. Moreover, the fibre diameter has an influence on κ . Thinner diameters reduce the opportunity of scattering and thus enhance the phonon transport [5]. In addition, the transition from 1D to 3D structures increases phonon scattering and thus reduces thermal conductivity. This could be impressively shown for graphene, where the thermal conductivity was significantly reduced from 2800 to 1300 W/m.K when increasing the number of atomic planes from two to four [23]. The thermal conductivity of polyethylene was also shown to increase with its molecular weight. Hansen et al. [24,25] established a quantitative relationship stating that the thermal conductivity at low molecular weights depends on the square root of the molecular weight, while it is constant at high molecular weights. A comparison of branched and linear polymers with the same molecular weight showed smaller thermal conductivities for branched polymers, emphasizing again the influence of phonon scattering depending on the molecular structure.

In general, the Green–Kubo simulation procedure follows distinct steps, which include the calculation of different ensembles to equilibrate the model structure, to correct densities, and to derive ensemble averages. The reader is referred to detailed descriptions of Vasilev et. al. [26] or Alamfard et. al. [20], where the use of NPT and NVT ensembles is ex-

plained for determining thermal conductivities of model structures such as polyurethanes, rubbers, and silicone rubbers. Figure 2 illustrates the principal approach in such MD simulations to calculate the thermal conductivity via the Green–Kubo approach.

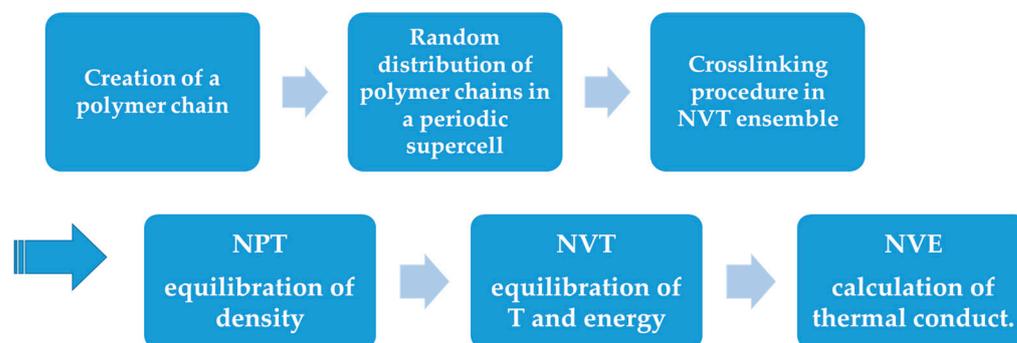


Figure 2. Approach to calculate thermal conductivities κ in molecular dynamics simulations using Green–Kubo.

Selected applications in polymer and elastomer research are summarized in the following in a compact way, highlighting different aspects of the cited research. A worked class example to calculate the thermal conductivity of argon via the Green–Kubo method can be found here [27], which may serve as a simple starting point to perform simulations on polymers. It may easily be adopted by more complex systems.

The orientation of the polymer chain and the segmental rotations are important aspects that are of interest for polymer characterizations. This was investigated for polymer nanofibers to highlight the fundamental linkage between molecular characteristics and the final macroscopic thermal property [28]. In general, it must be taken into account that an explicit simulation of all atoms in a polymer chain is always a compromise between the precision and the interpretability of the final result as well as the calculation time for the time steps within the molecular dynamics approach [29].

Molecular dynamics simulations may be performed via different model representations of the polymer of interest, and examples range from monomers as adequate representations to a complete polymer structure. The earliest idea of an effective potential was to treat one monomer as one single degree of freedom [30]. Nowadays, a variety of model approaches for molecular dynamics apply united atom approaches [20,26,31,32] or all atom approaches [33]. All of them show a very reliable quantitative agreement for the polymers or elastomers of interest and deliver reasonable precision with respect to the calculated thermal properties. Later examples show that an all-atom force-field such as PCFF has advantages in terms of accuracy for thermal conductivities.

The description of thermal properties actually requires an explicit consideration of all hydrogen atoms in the chain, e.g., with all individual degrees of freedom. The AIREBO potential in LAMMPS is one option to proceed molecular dynamics simulations, as it was used for polyethylene materials (see Henry and Chen) [33]. The model included all hydrogen atoms for the polyethylene structure, and it was shown that the specific heat was only one-third of that predicted by the classic potential employing a united-atom approach [33]. The recognition of all explicit hydrogen atoms and, consequently, also their motion, was reported to have an impact on properties such as glass transition temperature, thermal expansion, as well as the mechanical properties of polyethylene [34].

A similar discussion on the validity of simulation results can be found when referring to the dimensionality of the model structure, which can range from 1D to 3D model systems. Again, for polyethylene, a study was performed to investigate the changes in phonon scattering in lattices of polyethylene going from 1D to 3D model structures [15]. The transition from 1D to 3D was used to analyse the influence of phonon scattering processes depending on the dimensionality of the model system. The Green–Kubo method using the AIREBO potential in LAMMPS was applied. The AIREBO potential was chosen

because it includes Lennard–Jones terms to better represent the interaction of neighbouring chain molecules. Thus, the phonon–phonon scattering was enhanced. The authors aimed to distinguish weak intermolecular interactions versus strong intramolecular covalent forces. Results show that the anharmonic scattering induced by weak van der Waals forces causes significant attenuation of modes propagating along the stiff covalently bonded polymer chain backbone. Thermal conductivities of single chains were unusually high and decreased by 40%, when two chains were combined. In addition, a further 30% decrease in conductivity was observed for periodic conditions. Wang et al. [35] also focused on the thermal transport in single polymer chains compared to 3D-lattices. 1D-models often neglect cross-axial vibrations, and thus are still under discussion for their accuracy to describe those structures accurately. These studies revealed nice quantitative insights into heat conduction in lattices, which is important for designing and manufacturing low-cost polymers with high thermal conductivities [15] and demonstrated the efficiency of Green–Kubo approaches.

2.2. Non-Equilibrium Molecular Dynamics—NEMD

The investigation of the heat flux inside a model system is another important aspect of interest for a detailed characterization of heat transport in solid materials. This kind of investigation is accessible via non-equilibrium molecular dynamics (NEMD). NEMD simulations have different requirements compared to EMD. NEMD requires simulation dimensions much larger than the largest phonon mean free path length [35,36].

For NEMD, the system of interest is divided into slabs, where one cold and one hot end is defined. Those “ends” resemble hot and cold plates in an experimental setup, which thus correspond to the original macroscopic view of the Fourier equation [14]. The advantage of the NEMD is that it can be used to calculate nonlinear as well as linear transport coefficients. Transport coefficients can be calculated as a function of external field strength, frequency, or wave vector [37].

As calculations become very complex in order to reach a steady-state, different algorithms have been developed to derive steady-state conditions in NEMD. The first is called reverse non-equilibrium MD (RNEMD) [38], which imposes a periodic velocity exchange between atoms of different temperatures. The velocity change provokes a heat flux from hot to cold, leading to the quantities used in the Fourier macroscopic equation. The second algorithm [39] couples the slabs with heat baths, and starts an energy transfer between model system and bath. This system is then compared to a NVE ensemble without a coupled heat bath. The NEMD method to determine the final thermal conductivity is calculated in one direction, and is thus strongly dependent on the system size. Several polymers, such as polystyrene, stretched polystyrene, and mixtures of polystyrene and CO₂, have been successfully investigated by RNEMD [40].

NEMD is also referred to as a direct method [36]. It is called direct as the method is a non-equilibrium, steady-state technique in which a heat flux is applied to a simulation cell along the direction of interest. Using the imposed heat flux and the resulting steady-state temperature gradient, the Fourier law is directly applied to calculate the thermal conductivity. For many materials, it is computationally prohibitive to obtain sample size-independent thermal conductivity predictions using the direct method. For such cases, it becomes necessary to make thermal conductivity predictions for several sample lengths and then perform a postprocessing extrapolation procedure [36].

Amorphous as well as crystalline polymers with outstanding thermal conductivities have been studied with the NEMD approach. The study showed the fundamental linkage between the molecular structure of the polymers (crystalline or amorphous) and their final macroscopic thermal properties [41]. Figure 3 illustrates such regions with crystalline and amorphous parts within one polymer structure. Both regions have to be treated appropriately with respect to the molecular model. Further details can be found in Mehra et al. [5] and Zhang et al. [6].

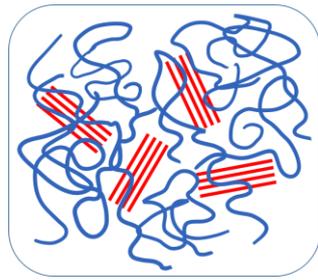


Figure 3. Crystalline (red) and amorphous (blue) regions within a polymer structure need appropriate model treatment.

In a large-scale molecular dynamics study [28], model polymer fibres such as polyethylene were compared to ten nanofibers with weak and strong inter-chain and intra-chain interactions. All simulations have been performed at temperatures higher than 300 K to also excite low-frequency acoustic modes, which are believed to be the main contributors to the thermal conductivity. An extensive morphology study to characterize quantitative structure–property relations was performed on polyethylene with suppression of its segmental rotation using the COMPASS potential and compared to polymers with stronger inter-chain interactions such as Nylon 6-6, Teflon, and polyketone. A phonon dispersion relation analysis for all investigated polymer nanofibers was performed, focusing on the π -conjugation in all polymers. The phonon velocity could be determined via Fourier transforms of backbone velocities from the simulations [28]. The analysis included only low-frequency acoustic phonons. For all π -conjugated polymers, phonon velocities above 7000 m/s have been found, which are significantly higher than for other polymers (see Table 3 in [28]). The reason discussed for this behaviour is that the π -conjugation suppresses segmental rotations and thus the phonon scattering. π -Conjugation in the molecule thus enforces the polymer backbone, and allows for higher phonon velocities. Polymers such as Teflon with intrinsic segmental rotations showed consequently lower thermal conductivities due to a higher disorder-phonon scattering. The study convincingly showed that the simulations and its interpretations provided a general rule to design thermally conductive polymer nanofibers with high-temperature stabilities [28]. The thermal properties improved significantly when a targeted selection of appropriate initial structures of molecules with intrinsically ordered backbones, strong backbone bonds, or strong dihedral angles was chosen. Therefore, π -conjugated polymers are suggested as a category of polymers that are ideal for fabricating nanofibers with high thermal conductivities for high-temperature application [28]. NEMD in detail was performed with several temperature gradients using the Langevin thermostat in LAMMPS with time steps of 0.25 fs combined with a 10 Å cut-off for the Lennard–Jones potential [28]. Values of the outstanding thermal conductivities were found to be for crystalline polyethylene at 100 W/m.K [15], whereas, going from amorphous to crystalline polyethylene, a change in κ from 0.3 to 50 W/m.K was described [28].

Polyethylene (PE) is a welcome easy-to-handle model polymer in all kinds of theoretical approaches. Its simple structure enables easy and cost-effective simulations [40]. Crystalline PE with different molecular weights ranging from 2800 to 22,400 g/mol have been investigated (see Brenner in Algear [40]). The thermal conductivity increased from 11.7 to 99.6 W/m.K with increasing chain length. The maximum experimental value for ultradrawn single-crystal PE mats was found around 40 W/m.K. Thus, the simulation was overestimating thermal conductivities for higher chain length. Authors claim impurities and defects in the real structure to be responsible for that difference as the model simulation is based on ideal crystal structures. Any kind of defect will decrease the thermal conductivity for real samples. PE was also used as a model to represent semi-crystalline materials using a united-atom force field [42]. The NEMD performed in LAMMPS was used to investigate light-weight and corrosion-resistant polymers for plastic heat sinks and thermal management in flexible electronics. The thermal conductivity was calculated

perpendicularly and parallel to the model chains. A correlation to a modified Takayanagi model for semi-crystalline polymers was found, whereas the Choy-Youngs's model did not predict the thermal conductivity of the semi-crystalline material [42]. Moreover, the authors compared their new NEMD calculations with the Effective Medium Theory EMT (see later here in Section 2.4). Their NEMD provided more accurate results for thermal conductivities of semi-crystalline polyethylene. Another NEMD study on polyethylene and other polymer nanofibers, such as nylon 6-6, Teflon, and polyamide, used the COMPASS potential. The authors described that a divergent thermal conductivity was seen with NEMD for one-dimensional systems due to simulation artefacts along the elastically soft direction in anisotropic crystals. Thermal conductivities from NEMD were found to increase linearly with the simulation system length [28]. EMD, BTE, and EOS (see later here in this article) are not affected by such size effects.

The thermal transport in elastomers, namely vulcanized polyisoprene, was also studied by molecular dynamics. The effect of deformation was studied in detail, and it was found that the thermal conductivity increased parallel to the direction of elongation [43].

It has to be emphasized again that all molecular dynamics results depend strongly on the choice of the classical potentials, e.g., the force field governs the accuracy. Especially in polymers, intra-chain and interchain interactions determine the method of phonon transport, as covalent bonds and van der Waals bonds are responsible for those interactions, respectively. Highly ordered structures lead to higher thermal conductivities [5]. Therefore, the potentials used in the chosen force field influence the final value [44]. From this, it also follows that force fields may be limited to one class of materials. Moreover, a restriction of its validity near or above the Debye temperature may be given, and thus concerns about simulations at room temperature exist.

In summary, a comparison of EMD and NEMD show essentially equivalent results for thermal conductivities of polymers [6]. Force fields such as the all-atom potential PCFF and COMPASS are usually more accurate compared to united-atom potentials such as OPLS-UA (also see Section 2.5). However, all force fields generally predicted thermal conductivities of polymers quite well with respect to experimental values. A summarizing table with thermal conductivities of various polymers and their simulation details, such as computational method, either EMD or NEMD; and the used potential functions, for instance AIREBO, PCFF, OPLS, COMPASS, OPLS-UA, can be found in Zhang et al. [6]. The NEMD approach is therefore also a reliable simulation method to investigate complex polymers structures in detail and to derive important transport coefficients such as thermal conductivity.

2.3. Applications of Green–Kubo Methods for Polymers Composites and Other Non-Polymer Solid Materials

Polymer composite materials with polyvinyl-alcohol and inorganic fillers based on boron have been investigated with respect to the phonon propagation in-plane and cross-plane of the model system. The thermal conductivity of in-plane materials was found to be higher compared to the cross-plane models [45]. Mehra et al. [5] also discussed the complexity for composite systems for polymer composites, where, depending on the system conditions and compositions, several factors may dominate the final thermal conductivity. In detail, the influence of fillers on the thermal conductivity is discussed as the sum of the filler properties, its geometry, the functionality of the composite, the interfaces, the cumulative effect of the filler–matrix system, and the purity of fillers such as CNTs [5].

A wide range of models to calculate thermal conductivities for polymers and composites is given as tables in the recent article of Mehra et al. [5]. Numerous model approaches are compared and examples are given. An older review with a table for popular simulation methods at the micro- and nanoscale can be found in Anderson [46]. Another review summarizing model approaches is given by Bao et al. [47].

Molecular dynamics simulations investigated the thermal conductivity and especially the effect of an anomalous heat conduction [34]. These approaches go beyond the common approaches and mainly follow three different approaches: mode-coupling theory by

Lepri [48], the renormalization group theory by Narayan and Ramaswamy [49], and the Boltzmann equation which was basically used by Peierls [50] in its original basic work. The aim of the Henry [34] study was to calculate the longtime part of the heat flux auto-correlation function in the Green–Kubo formula to circumvent problems that arise from scattering, thus destroying the correlation function which is used for the calculation of κ . A discussion on advantages and disadvantages for all three above-mentioned approaches can be found in Henry [34], focusing on long-wavelength modes and the physical interpretation of results for 1D materials. Higher dimensional model systems have been also investigated with these elaborated methods. Henry et al. [15] found a decreasing thermal conductivity when increasing the dimensionality of the model material from 1D to 3D.

The Green–Kubo approach is applied both with using classical potentials, e.g., molecular mechanics, as well as using ab initio level, e.g., as ab initio molecular dynamics calculations. Ab initio Green–Kubo as first-principles formulation allowed the accurate assessment of the phonon thermal conductivity of solid semiconductors and insulators [51]. This approach is sophisticated and prevents limitations of the classical potentials in molecular dynamics as it accounts for anharmonicities to all orders. Accordingly, this approach is exact at temperatures at which nuclear quantum effects are negligible. This formalism was demonstrated and validated for the determination of the thermal conductivity of two solids with widely divergent thermal conductivities: firstly, Si in a certain solid crystal structure, which had an especially high thermal conductivity; and secondly, on tetragonal ZrO_2 , which had a very low thermal conductivity [51].

Quantitative comparisons of EMD and NEMD with respect to the same molecular structure are rare, especially for polymers. One study comparing both methods with respect to the determination of κ depending on domain size effects was performed for silicon compounds [52]. For EMD, the thermal conductivity of silicon increased with the domain size and converged finally. For NEMD, a domain size effect was found without a general trend for the investigated systems. The authors state that domain size effects for both methods are related with wavelength and mean free path accumulations of the thermal conductivity. Since phonon wavelength spans over a narrower range compared to the mean free path, EMD shows a less significant size effect than NEMD [52]. A benchmarking study for nanowire silicone compared EMD and NEMD, which showed rather similar quantitative results for both methods when an appropriate effective length in EMD is chosen [53]. NEMD was also reported to under-predict bulk thermal conductivities of Si-based systems compared to experimental values because of the length scales, which may differ several orders of magnitude [54]. It can be concluded that such effects also play a role in polymers.

Recently, new key terms have been used in the discussion of simulation results to improve the interpretation of heat transport in polymers. Amorphous polymers were investigated by Feng et al. [19]. Thermal conductivities were calculated by Green–Kubo and NEMD for comparison. For Green–Kubo, all calculated thermal conductivities were in the range between 0.15 to 0.47 W/m.K for polystyrene and polyethylene, respectively. All simulation results have been averaged from at least three runs, as large fluctuations in the calculated thermal conductivities in one MD run appeared due to flexible conformations in the chains. Thermal conductivities decreased with increasing dangling molecular weight, which was consistent with previous findings [19]. All EMD results agree well with experimental values for the investigated amorphous polymers. The results of their force field (PCFF) were found to be slightly better in agreement with experiments. In addition, the EMD was providing better results than the NEMD; however, the NEMD used was not affecting their further study. To improve the discussion, the authors suggested new terms to support their findings. The thermal conductivity is attributed generally to contributions from three parts: (i) propagons or phonons understood as κ are determined through the propagation of unlocalized atomic vibrational waves, (ii) diffusons understood as diffusion of unlocalized waves, and (iii) locons understood as the hopping of unlocalized waves [19]. The use of new key terms such as propagons, diffusons, and locons seems to replace the

common approach of Cahill, which assumed the thermal transport as dominated by a random walk of localized oscillators [19]. Moreover, size effects were not observable by the Cahill's model; thus, the new way of splitting single contributions may be beneficial to better understand heat transport in the nanoscale world.

In summary, NEMD is an often-used simulation method that provides thermal conductivities for complex polymers. The thermal conductivities reproduce experimental values and demonstrate the strength of the NEMD method.

2.4. Effective Medium Theory—EMT

The effective medium theory (EMT) is a quite common approach for determining thermal conductivities especially for polymer composites. Basic considerations of EMT date back to the early days of the theory of electricity [55–57]. Faraday (see in [58]) proposed already in 1837 one of the earliest models for a composite metal-insulator dielectric, and Maxwell [58] around 1870 and later Garnett [59] in 1904 developed models to describe a composite or a mixed material medium [60–63]. More details can be also found in the book by Choy [56].

Historically, Maxwell provided the first major contribution to the conductivity of heterogeneous solids. Originally, considerations have been made for electrical conductivity, but the same arguments hold true for the thermal conductivity [11,64]. One basic element within this approach is the sphere model, which was established to represent different volume fractions of the composite material.

EMT approach is based on dilute dispersed systems, where spherical particles are dispersed in a continuum matrix [65]. Limits of this approach, such as the missing interaction between fillers as well as the limit for the dispersed volume, are discussed in Mehra et al. [5].

According to Henry [34], EMT is quite general in its application, and adequate for a two-component system with a filler of dispersed spheres. Many other theoretical models, some of them very special, have been developed for composites on the basis of the principal idea of the EMT approach. Main aspects of these enhancements have been the improved recognition of fillers (volume fractions, geometry, filler–matrix interaction, interaction between fillers and multicomponent mixtures, the recognition of the thermal interface resistance (TIR), and percolation. Some of them are reviewed in Henry [34] or one can find a summarizing table of thermal conductivity models for composites in Mehra et al. [5]. Some of them may not give accurate quantitative results; however, they deliver a qualitatively correct view on thermal conductivities for composites. For example, CNT-polymer composites showed experimentally lower values than predicted by EMT due to TIR [34]. Although CNT already has a high thermal conductivity >1000 W/m.K, CNT-composites could be shown as having thermal conductivities of >2000 W/m.K [34].

Semi-crystalline polymers with variable amounts of amorphous and crystalline parts have been intensively investigated via EMT by Maxwell and Garnett [66]. Amorphous regions generally showed lower thermal conductivities. Relations between κ for amorphous and crystalline parts, which contribute differently to κ , were given as a simple model (see following equation) [66].

$$\frac{\kappa}{\kappa_a} = \frac{(1-f)^2}{2 * X * \kappa_a * \left(\frac{R_b}{d}\right) + (1-f-X)} + f \quad (2)$$

where κ_a is the thermal conductivity of the amorphous region, f is the fractional area, X is the fractional crystallinity, R_b is a boundary resistance, d the thickness of the crystalline region.

Polymers often occur with different proportions of amorphous and crystalline components. The thermal conductivity of the bulk polymer strongly depends on the ratio of amorphous to crystalline parts. This was shown quantitatively by Choy [56,66] for polyoxymethylene, polypropylene, and low-density polyethylene LDPE. The thermal

conductivities at 300 K for polyethylene as a fully crystalline polymer were found to be 70 W/m.K, for a 50% crystalline structure to be 32 W/m.K, and for 100% amorphous polyethylene to be 15 W/m.K, adopted from a graph in Mehra et al. (page 26) [5]. In the paper by Lu et al. [42], EMT and NEMD have been compared quantitatively. Classical EMT underestimated the thermal conductivity of semi-crystalline polymers, when the polymer structures were highly drawn. Then, the interlamellar regions were treated as one amorphous region and EMT underestimated the role of chain topologies [42]. The authors provide a comprehensive quantitative comparison for the NEMD and EMT as well as their own approach [42].

In summary, it can be said that EMT is a widely applied method in materials science in general, which is a meaningful supplement to describe the thermal conductivity in polymers and elastomers. Due to the ability of EMT to recognise amorphous as well as crystalline regions in polymers, it provides a method to investigate the influence of the ration of amorphous-to-crystalline parts in detail quite easy.

2.5. First Principles Methods—Boltzmann Transport Equation

In recent years, a great deal of attention has been paid to synthesize high thermal conductivity polymers using evidence-based methods. Therefore, a separate subchapter is dedicated to the topic of high-level theoretical models on ab initio level. Basically, the idea of targeted modification of properties goes back to Choy et al. [67], who could show that mechanical stretching reduced entanglement of polymer chains, and thus the thermal conductivity increased.

Ab initio or first-principle methods are mainly lattice dynamics calculations of (thermal) transport coefficients, which base on the solution of the Boltzmann Transport Equation (BTE). The BTE is a complex non-linear integro-differential equation. The equation is used to consider the probability distribution for the position and momentum of a particle, e.g., phonon. Since there is a probabilistic approach behind it, the method is given the name Boltzmann, who first introduced this idea into thermodynamics. In general, the approach can be applied to any kinetic equation, which handles the change of a macroscopic quantity (energy, charge, or particle) in a thermodynamic system, thus giving either thermal conductivity, electrical conductivity, or viscosity. For details of the theory, the reader is referred to textbooks and review articles [10,35,68–70].

The main application field of BTE with respect to polymers are crystalline materials as the lattice periodicity provides a versatile starting point for model set-ups. Wang et al. [35] performed first-principles-based anharmonic lattice dynamics to calculate κ for bulk crystalline and single-chain polyethylene. The authors provide an overview about molecular dynamics simulations on different levels of complexity (for example, Green-Kubo, NEMD) for treating crystalline polyethylene, concluding that several disadvantages of classical approaches (empirical potentials, disadvantages of Green's function, validity near or above the Debye temperature, simulation times, size effects [15]) exist. The advantages of the first-principles BTE method, which is based on Kohn-Sham, concern the accuracy and the independence on fitting parameters for empirical potentials [71]. Using the BTE approach allows for the analysis of all modes of phonon transport and to distinguish main paths and describe scattering mechanisms [35]. It is possible to calculate the thermal transport mode with direct determination of single scattering mechanisms [35].

It was found that strong momentum-conserving phonon scattering of long-wavelength acoustic phonons contributed indirectly to the thermal resistance, which led to a convergent thermal conductivity. A single-chain polyethylene model system resulted in an impressive value for its thermal conductivity of 1400 W/m.K at 300 K. It was highlighted that the use of 1D- and 3D models in first-principles based methods may give different results. The VASP code was used to perform those calculations [35].

A comparative study investigated the hydrodynamic phonon transport in polymers as polyethylene, polyacene and polyacetylene, which differ in their bonding strengths in the chains going from single to triple bonds [72]. The BTE was used to determine the

lattice thermal conductivity along the axial direction. The AIREBO potential with long-range van der Waals interactions between polymer chains was used. Results show that the thermal transport can be clearly differentiated between ballistic, hydrodynamic and diffusive regimes for the phonon transport, which provides more deeper insights into single phonon transport processes compared to classical EMD. Moreover, scattering rates for so called normal processes, the Umklapp process, and boundary scattering were found [72]. As detailed results from BTE are not available from EMD, a quantitative comparison on this basis is not available. The BTE was able to distinguish single contributions from torsional motions and structural anisotropy for polyethylene.

Although crystalline polymers can be studied fairly easily using solid-state techniques, the investigation of amorphous polymers is rather limited due to the lack of periodic symmetry. Several approaches appeared to overcome this problem. One of these solutions is the development of a reduced state quantum master equation approach based on the Merrifield exciton formalism [73]. The exciton transport in conjugated polymers and its dependence on morphology and temperature was studied. The exciton dynamics consists of a thermalization process, whose features depend on the relative strength of thermal energy, electronic couplings, and disorder, resulting in remarkably different transport regimes. The method was applied to poly(p-phenylene vinylene) and amorphous-derived structures. The structural changes were made to respect the physics of characteristic femtosecond to nanosecond time scales of exciton dynamics. New insights into the role of temperature and disorder on localisation and the experimental accessibility of thermal equilibrium states of excitons in amorphous polymers were found [73].

A combination of a classical and an ab initio approach is also promising. An all-atom polymer consistent force field (PCFF) was used to investigate polyethylene, PVC, EVOH, PP, and PS [19]. Starting with α -PS with the lowest thermal conductivity, structural variations such as dangling groups have been introduced to all polymers consisting of ethylene chains only. Contributions of diffusons, locons, and propagons to the thermal conductivity as well as the mean free path of propagons have been determined by calculation. The authors found size effects for the thermal conductivity, and used the BTE for interpreting the single contributions of pathway to the thermal conductivity. Size effects in the amorphous regime have been related to propagons, e.g., phonons, while diffusons and locons did not show any size effects. For polymers, one quantitative comparison of BTE and the Green–Kubo approach can be found in Henry [34].

In general, nanoscale heat transport is investigated by the BTE in many solid materials other than polymer materials. However, similar problems, such as the impact of amorphous regions on κ , can be observed here too. A review was published by Wingert et al. [74] stating that for amorphous materials, the concept of extended phonon waves is not well defined. Special care has to be taken with respect to the chosen boundary conditions, as periodic boundary conditions, as usually used, may impose an artificial length scale on the material [74].

New insights for characterizing heat transfer in polymers may also be derived from other solid materials. Heat transport is critical in thermoelectrics for energy harvesting, nanoparticle-mediated thermal therapies, nanoenhanced photovoltaics, and thermal management in integrated circuits [75]. In materials such as nickel nanowires, the dimension of the heat source and mean free path are not equally related in a way, that the diffusion equation is still valid. A new regime of nanoscale thermal transport was described, where, counterintuitively, nanoscale heat sources cooled more quickly, when placed close together compared to those, which were widely separated. The increased cooling efficiency is possible when the separation between nanoscale heat sources was comparable to the average mean free paths of the dominant heat-carrying phonons. This finding suggests new approaches for addressing the significant challenge of thermal management in nanosystems, with design implications for integrated circuits, thermoelectric devices, nanoparticle-mediated thermal therapies, and nanoenhanced photovoltaics for improving clean-energy technologies [75].

Thermal transport in semiconductors involve contributions of phonons having a wide range of mean free paths. Survey about those paths can be found in Zeng et al. [76]. Based on a new spectroscopic method, a diffusion heat transfer model was developed, which bases on an analytical solution of the heat equation using the transfer matrix method. Measurements were made under pump-probe conditions and are time-resolved. The new method on the nanoscale model allows the study of mean free paths distributions in optically absorbing materials.

BTE was compared quantitatively to NEMD for silicon materials [77]. The authors suggest a combination of both methods which may allow to enhance simulation quality for solid materials by overcoming unaffordable first-principles NEMD with computationally less expensive BTE [77]. It was shown, that a quantitative agreement between NEMD and phonon BTE was achieved. Values for thermal conductivities of Tersoff silicon reached similar values for two different sample length. For instance 13 nm systems showed values of 12.0 to 12.9 W/m.K for NEMD and BTE, respectively. A sample size of 56 nm gave 39.2 up to 44.8 W/m.K, respectively. The approach is intended to open new simulations in future and may guide practical heat flow manipulation.

BTE is compared to EMD and NEMD a more complex simulation approach, which preferably enables to investigate other temperature regions due to the physical basis. It is more applicable to crystalline solids with weak anharmonicities. The determined thermal conductivities are within the experimental range.

2.6. Other Theoretical Approaches—BGK-Model, EOS and Einstein Formula

Numerous approaches combine different aspects of the aforementioned models (Sections 2.1–2.5) and are aimed to prevent some of the disadvantages or try to extend the application range of these models with respect to the material class. Only a few comments are given here as the number of applications is lower compared to EMD, NEMD and BTE.

The Bhatnagar, Gross and Krook (BGK) model is one of these few approaches. The BGK uses the Boltzmann-equation with a modified collision term [78]. In the referenced paper, this model is further compared in its validity to continuum approaches but not to EMD or NEMD. The resulting thermal conductivity in BGK is proportional to the square root of the temperature, and resembles in that to the hard sphere approach for molecules [79], which is visible from Equation (3):

$$\kappa = \frac{5}{2} \frac{k}{m} \frac{nkt}{W} \sim \sqrt{T} \quad (3)$$

Within its theoretical limits, the BGK provides an additional method to derive thermal conductivities for polymer solids.

A rather rarely used approach to investigate polymer properties is the use of Equations of state (EOS) [80]. However, the focus of EOS is primarily different to EMD etc. as phase transformations and mixing processes are primarily of interest. For instance, the formation mechanisms of mesoscale structures for copolymers during manufacturing was studied by using EOS to describe changes in the flow field, temperature gradient, and external field. The EOS approach is a so-called off-lattice method [81]. In the review of Gubbins [82] numerous basic references are summarized. Blends of polystyrene and polybutadiene with different weight-average molecular weights have been investigated with the EOS approach, and detailed phase diagrams have been obtained and compared to experimental data showing very good agreements even close to the critical composition region. Similarly working fluids, where EOS is generally standard, have been investigated to receive transport coefficients from EMD simulations [83].

In addition, pressure–volume–temperature relations for polymer melts based on EOS and an artificial neural network have been suggested by Yousefi and Karimi [84]. Second virial coefficients, effective van der Waals volumes as well as correction factors were derived for several common polymers. The specific volumes at compresses state of polypropylene glycol, polypropylene, poly(1-butene), polyethylene have been determined for different

temperatures. Data show very good agreement with experimental values. The new method opens the opportunity to predict physical properties from just two scaling constants, the temperature and the liquid density at the melting point. The new Tao–Mason EOS was found to be superior to the previous ISM-EOS, see [84].

Another approach delivering adequate and similar results as Green–Kubo for polymers is given by the Einstein formula. This formula provides a relation between the thermal conductivity and the mean square displacement of the actual internal energy from the initial value of the internal energy in a given time [83]. Raabe [83] gives the following Equations (4)–(6).

$$2 t \kappa = \langle [A(t) - A(0)]^2 \rangle \quad (4)$$

$$2 t \kappa = \frac{V}{k_b T^2} \langle [\delta u_i(t) - \delta u_i(0)]^2 \rangle \quad (5)$$

$$\delta u_i = \frac{1}{V} \sum_i r_i (u_i - \langle u_i \rangle) \quad (6)$$

with A as flux at a certain time and at $t = 0$, u is the internal energy, r distances. Details can be found in Raabe [83].

Benchmarking of those models are generally more available for inorganic crystalline and glassy solid systems such as silicon dioxide or magnesium dioxide. A summary can be found at Ercole et al. [85]. Solid-argon- and silica-based systems have been benchmarked for the Green–Kubo approach against another EMD model, based on the Einstein relation [86], which is not as prominent as the Green–Kubo approach. The Einstein relation with an improved analytical form for the heat current was shown to yield similar results as from the heat autocorrelation function by Green–Kubo.

In summary, several theoretical approaches beyond EMD, NEMD, and BTE to determine thermal conductivities exist. They open the opportunity to tune the theoretical backbone of approaches and are focused mainly on special applications, which limits their general applicability.

3. Summary

The review summarizes common theoretical approaches as Green–Kubo-EMD, NEMD and BTE to characterize heat transport in polymer materials. All methods provide adequate results for thermal conductivities within their theoretical framework. The results must always be discussed within the limits of the respective method. In general, experimental values for thermal conductivities are reproduced by the methods in a very precise manner, thus qualifying them to be appropriate for predicting thermal conductivities of solid polymer materials. Additionally, examples for solids other than polymers have been added to this review as they may widen the view to new theoretical approaches, general application aspects as well as interpretation of heat transport in solids.

Table 2 summarizes key advantages and disadvantages of the most popular methods for polymers, e.g., the molecular dynamics-based ones and the Boltzmann Transport Equation method.

The main advantage of MD simulations in contrast to BTE is that they permit the simulation of large molecular model systems. Therefore, polymer structures with high molecular weights are accessible with an acceptable computational cost. Further, EMD and NEMD are essentially equivalent in terms of describing thermal conductivities with respect to experimental values. In addition, MD simulations may involve all anharmonicities of lattice vibrations due to the use of mostly classical potentials, which do not need much simulation time. For polymer structures with others than carbon, oxygen or hydrogen atoms in the model structure, classical force field potentials may be easily fitted and introduced into the force field for additional atoms or atom groups.

Table 2. Comparison of microscopic theoretical methods MD and BTE for the calculation of thermal conductivities in polymer solids.

Method	Advantages	Disadvantages
Molecular Dynamics simulations—MD	<ul style="list-style-type: none"> - Investigation of large systems possible (thousands of atoms; high molecular weights) - All anharmonicities of structures may be included - Choice of force fields according to the molecular structure (special force constants can be fitted) - Amorphous and crystalline structures possible to describe 	<ul style="list-style-type: none"> - Ignore quantum effects - Accuracy of chosen force field may influence the result - Limited temperature range; preferably at moderate high temperatures
Boltzmann Transport Equation—BTE	<ul style="list-style-type: none"> - Quantum distribution of phonons - First principle ab initio calculations without empirical functions - More appropriate for crystalline solids with weak anharmonicities - Lower Temperatures are accessible 	<ul style="list-style-type: none"> - High computational effort - System size may be smaller - Amorphous structures not represented - Complex discussion of couple phonon transport processes

Disadvantages of EMD and NEMD compared to BTE are the neglect of quantum effects and their dependence on the accuracy of the potential energy function, which is given by the choice of the force field. With respect to the temperature, the main application range of MD simulations is more limited compared to BTE. MD is valid for systems at moderately high temperatures as phonons in MD are considered to have a Boltzmann distribution, which is invalid at low temperatures [6]. In contrast to molecular dynamics, the BTE provides different features such as phonons obeying quantum distributions or the possible coupling to first-principle calculations. BTE is used for crystalline materials with weak anharmonicities. Importantly, the temperature range of BTE is not limited to moderate high temperatures and may applied to lower temperatures.

Further methods such as EMT and EOS extend the portfolio of EMD, NEMD and BTE and enable investigations that are more special. EMT, for example, has its primary use in describing semi-crystalline polymers. EOS is especially used to describe mixtures and blends and helps to elucidate phase diagrams.

In summary, a large number of theoretical approaches are available to describe transport properties such as the thermal conductivity. The atom-based view allows detailed insights into structure relationships and guides the design of new applications.

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