1 INTRODUCTION

1.1 BACKGROUND AND APPLICATIONS

Polymer materials are suitable for numerous applications in a variety of fields due to their good processability, high durability, low price, and low weight. They are among the most adaptable materials and are utilized for diverse tasks. However, there are limits to polymer applications due to their crucial weak point: thermal conductivity.

With $\lambda = (0.1 \ldots 0.5)\ \mathrm{W\ m^{-1}\ K^{-1}}$ [1–4], this is far below that of metallic and ceramic materials. In micro and power electronic systems, heat loss often needs to be transferred to cooling systems or the environment across very small areas and with minimal temperature drops. By using highly thermally conductive materials in the heat path, the system temperature can be sustainably reduced and the service life of the system increased. To employ polymer materials in these applications, they must be modified with highly thermally conductive, granular fillers. Recent review articles report numerous use cases and requirements for thermally conductive filled polymers in electronic applications [2,4–6]. **Figure 1.1** illustrates typical applications of thermally conductive filled polymers in electronics and shows exemplary cross-sections through the material structure.

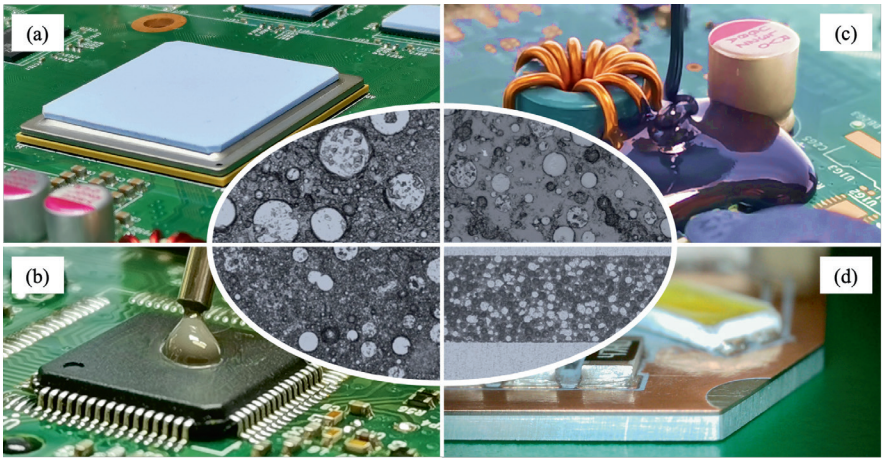

Figure 1.1. Thermally conductive filled polymer applications in electronics.
Thermal interface materials: Thermal pad (a) and thermal grease (b), potting compound (c), and insulated metal substrate (d). The inner illustrations show cross-sections of typical material compositions in the corresponding applications.

Thermal interface materials (TIMs), such as thermal pads (a) or thermal grease (b), are used to optimize thermal transfer between two solids in a heat path. For example, between a chip and a heat sink or, in the automotive sector, a battery module and a cooling unit. Surface roughness and manufacturing tolerances of the two contact partners lead to poor thermal contact and air inclusions. Soft and elastic thermal interface materials can displace this air and thus optimize thermal transfer. A review of materials, established technologies, applications, and recent advances is given in [5,7–11]. In part (c) of **Figure 1.1** a potting or encapsulant is shown. The main purpose of these materials is to protect the electronic assembly from environmental impact, while guaranteeing good heat dissipation. Shen and Feng [12] published an extensive review on the recent advances in encapsulants for light emitting diodes (LEDs) in 2023.

As a last example, an insulated metal substrate (IMS) is presented in part (d) of **Figure 1.1**. Electronic components with large power densities, such as LEDs, require a circuit board with good heat spreading characteristics. An IMS is a layered structure consisting of an aluminum or copper base plate, a thin dielectric intermediate layer, and a thin copper layer into which the circuit paths can be inserted. While copper and aluminum provide outstanding thermal conductivities, the dielectric layer in between is always the bottleneck for heat dissipation. The basis is usually an epoxy polymer, modified with ceramic filler particles. The layers are kept very thin, often less than $100\ \mu\mathrm{m}$, to ensure that the thermal resistance is as low as possible. The structure, requirements, applications, and current advances in IMS are described in [13–15].

Thermally conductive fillers are not only used for polymers in the applications shown. Other examples are injection-molded casings or heat sinks [16–18], or thermally conductive adhesives [19].

The use of thermally conductive polymers in all those applications has been established for decades. Recent market research reports a large increase in market volume of thermally conductive filled polymers and predicts further significant growth until the beginning of the 2030s. This is primarily due to the increasing digitalization and simultaneous miniaturization of electronic systems [6]. For thermal interface materials a compound annual growth rate of $10.49\ \% - 21\ \%$ is predicted [20–23]. The market growth for pottings and IMS is assumed at an annual rate of $3.9\ \% - 6.15\ \%$ [24–27]. For thermally conductive compounds, an annual growth of $12.8\ \%$ is predicted [28].

1.2 OBJECTIVE AND METHODS

The targeted and efficient development of advanced, high-performance polymer composites requires a profound understanding of the heat transport processes in the materials. From afar, it seems to be obvious and is well known that thermal conductivity increases with the concentration of highly thermally conductive fillers and that in principle, more thermally conductive base materials enable higher effective thermal conductivities [29]. It follows that it is crucial how effectively the filler particles can form a thermally conductive network in the polymer matrix. This ability probably depends on many factors, such as particle shape, size distribution and dispersion. The exemplary cross-sections in **Figure 1.1** show the complexity and versatility of the material structures. For thermal interface materials, shown in part (a) and part (b), multi-scale filler blends with grain sizes in different orders of magnitude are used to achieve the highest possible filler volume fractions. The result is a highly complex microstructure with filler concentrations close to the maximum packing density. Pottings (c) require good flowability for processing, i.e., a low viscosity, thus the possible filler volume fraction is very limited. In these loose filler packings, agglomeration and sedimentation phenomena are favored. With IMS, the complexity of the microstructure increases because of the two contact surfaces of the metal layers above and below the dielectric layer. Often only a few particle layers are between the contact surfaces. This influences the overall packing structure.

Numerous recent review articles conclude that there are still many open questions and unexplored relationships, especially with regard to the microscopic filler packing structure [2,4,5,19,29,30]. The most concise conclusions were formulated by Burger et al. in 2016 [29],

> *"Nevertheless, it will be crucial to focus in future work on the structural and geometrical aspects of the materials, which are essential parameters to increase thermal conductivity."*

and Xu et al. in 2021 [5],

> *"For the critical thermal percolation [...], existing knowledge is still very limited and a universal picture about the threshold of the thermal percolation is still lacking. Open questions remain on how to form a more effective heat conduction network with less thermal resistances between fillers."*

There remain questions regarding whether there are pronounced percolation effects in thermally conductive filled polymers and how the formation of thermally conductive paths in the material can be favored [3,5,30]. Furthermore, Yang et al. [6] see a need to improve and expand existing approaches for calculation and simulation, as these have so far neglected many important parameters. In principle, however, detailed simulation and calculation approaches promise important insights into the microscopic heat transport processes

and can help answer the open questions. With this as a basis, the present work is intended to make a decisive contribution to the development of a detailed and comprehensive understanding of microscopic heat transport processes in filled polymers. The aim is a detailed investigation and quantification of the effects of filler properties, geometric packing structure, and interactions of different fillers in mixtures. The focus is on the effective thermal conductivity of the particle-filled polymer and filled polymer to substrate (FPS) transitions, which are of exceptional importance in IMS, for example. Both phenomena are investigated experimentally and using newly developed simulation methods.

Experimental techniques are mainly used to access macroscopic material properties. Since the spatial resolution of simulative approaches is unlimited in principle, these techniques allow analyses at the microscopic level which may then help explain macroscopic observations. Local heat transport processes inside the materials can be analyzed that are not experimentally accessible. Experimental, and simulative investigations combine to allow derivation of empirical theories on the impact of the geometric microstructure of filled polymers on their heat transport properties. This is a common strategy used also in particle physics, as the numerical reconstruction of processes can reach spatial and time scales for which there are no experimental techniques yet available.

Chapter 2 begins with a discussion of the physical principles of heat conduction in solids and composites. Thermal interfacial and thermal contact resistances are introduced and discussed regarding their significance for filled polymers. A comprehensive summary of the current knowledge and state of the art of thermally conductive filled polymer composites are presented. Chapter 3 provides an overview of the polymers and fillers used in the experimental investigations. Additionally presented is an overview of the two main measurement methods: the steady-state cylinder method and the newly developed micro thermography method. Chapter 4 includes numerical and experimental studies on the impact of filler properties and packing structures on the effective thermal conductivity of single scale filled polymers. The newly developed microscale modeling method used for these investigations is introduced at the beginning. Chapter 5 deals with the analysis of multiscale filled polymers with an emphasis on the interaction of different fillers at different scales. Once again, both experimental and numerical studies are presented. Chapter 6 focuses on FPS transitions and the contact resistances that occur using new experimental and simulative methods. Chapter 7 summarizes the findings and completes the comprehensive picture of heat conduction in particle-filled polymers.

2 PHYSICAL BASICS OF HEAT CONDUCTION

This introductory chapter provides an overview of the physical mechanism of heat conduction, first in solids and later in composites. In addition, it explains the phenomenon of thermal contact resistance and the resulting need for thermal interface materials. Thermal interface materials are a major area of application for the investigations and findings of this thesis. The chapter finishes with a brief overview of the current advances in the development of thermally conductive polymer composites.

2.1 HEAT CONDUCTION IN SOLIDS

In physics, there are various mechanisms of heat transport including: heat conduction through matter, heat transport through mass transport, and heat radiation. The basics of heat conduction in matter, and particularly in solids, are discussed below. Heat conduction is the transport of thermal energy through matter, mainly by diffusion of internal energy when a driving temperature gradient is imposed. In 1822, Fourier formulated the proportionality known today as Fourier's law [31]

$$\boldsymbol{q} = -\lambda \, \boldsymbol{\nabla} T \tag{2.1}$$

between the conducted heat flux $\boldsymbol{q}$ (vector) and the applied temperature gradient $\boldsymbol{\nabla} T$. According to the second law of thermodynamics, heat will always flow against the temperature gradient. The proportionality constant between heat flux and temperature gradient in Fourier's law is known as thermal conductivity. Thermal conductivity λ (second-order tensor in **Eq. (2.1)**) is an intrinsic thermophysical property of the heat conducting matter, nowadays specified with

$$[\lambda] = \mathrm{W\ m^{-1}\ K^{-1}}\ . \tag{2.2}$$

In general, it is a temperature dependent quantity [32,33], and can also depend on applied pressures, particularly for compressible matter [33]. The temperature dependence is often ignored when small temperature differences are applied [32]. Furthermore, thermal conductivity can be an anisotropic material property.

The theory of heat conduction in solids has been worked out in detail and is widely accepted. It is part of the basic repertoire of modern solid-state physics and is described in detail in numerous textbooks [34–37]. As the theory is very complex and multifaceted, there is additional specialized literature focusing solely on thermal conductivity [38–40]. Given here is a rough and simplified introduction to the topic for the purpose of assessing the differences in thermal conductivities of the polymer matrices and the metallic and nonmetallic fillers and evaluating the heat transfer across the interface from matrix to particle. Heat transfer through solids cannot be depicted using generally applicable models [41] and

there is no possibility for an exact prediction of thermal conductivity [40]. Nevertheless, a general impression and comprehension of the relationships can be acquired by discussing different basic approaches and models. To begin, a short introduction is given using the simple example of an ideal gas, before continuing with heat conduction in solids. A very helpful derivation can be performed, based on the theory of ideal gas molecular motion, following e.g., [33,35,41].

All particles of the gas are handled as point masses, perform a disordered thermal motion, and collide perfectly elastic with each other. The precondition for the validity of the following consideration is the existence of a sufficient number of individual particles for the thermodynamic equilibrium. The average time between two collisions of a particle is τ_r and the average absolute velocity of all particles is u. τ_r is sometimes referred to as relaxation time. The mean free path, the average distance a particle can travel freely, is [41]

$$l = u\tau_\mathrm{r} \ . \tag{2.3}$$

To induce one-dimensional heat conduction in the x direction, a temperature difference $\Delta T = T_2 - T_1$ with $T_1 > T_2$ is applied at the distance $\Delta x = x_2 - x_1$. On average, $1/3$ of all particles move in x direction and contribute to the heat conduction. The position $x_1 < x < x_2$ is considered. Particles that reach this position with positive velocity had their last collision at position $x - u\tau_\mathrm{r}$, and particles that reach this position with negative velocity had their last collision at position $x + u\tau_\mathrm{r}$. Let $U(T)$ be the temperature-dependent internal energy per particle. Then the particle with positive velocity brings the higher energy $U(T(x - u\tau_\mathrm{r}))$ and the particle with negative velocity brings the lower energy $U(T(x + u\tau_\mathrm{r}))$ to position x. To calculate the net heat flux q_x at the position x, the energies transferred by individual particles must be added together and multiplied by the mean particle velocity u and the number of particles n per Volume V.

$$q_x = -\frac{1}{6}\frac{n}{V}u[U\big(T(x + u\tau_\mathrm{r})\big) - U\big(T(x - u\tau_\mathrm{r})\big)] \ . \tag{2.4}$$

The sign determines the direction of the heat flow and the pre-factor $1/6$ considers that on average $1/3$ of all particles move in the x direction. $1/2$ each in the positive and negative x direction. If τ_r and thus l are small, q_x can be written as in [35]

$$q_x = -\frac{1}{6}\frac{n}{V}u\frac{\mathrm{d}U}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}x}2u\tau_\mathrm{r} \ . \tag{2.5}$$

$\frac{n}{V}\frac{\mathrm{d}U}{\mathrm{d}T} = C_\mathrm{V}$ is the heat capacity per unit volume and $\mathrm{d}T/\mathrm{d}x$ the local temperature gradient in x direction. After substitution and rearrangement, the equation becomes

$$q_x = -\frac{1}{3}C_\mathrm{V}u^2\tau_\mathrm{r}\frac{\mathrm{d}T}{\mathrm{d}x} \ . \tag{2.6}$$

A comparison with Fourier's law in one-dimensional notation

$$q_x = -\lambda \frac{\mathrm{d}T}{\mathrm{d}x} \,, \tag{2.7}$$

results in a thermal conductivity [33,35,41]

$$\lambda = \frac{1}{3} C_\mathrm{V} u^2 \tau_\mathrm{r} \,. \tag{2.8}$$

Finally, $u\tau_\mathrm{r}$ can be replaced with **Eq. (2.3)**, resulting in

$$\lambda = \frac{1}{3} C_\mathrm{V} u l \,, \tag{2.9}$$

as a general model for the thermal conductivity of an ideal gas, when considering the free gas molecules as the carriers of heat.

In solids, different carriers contribute to heat conduction. The main carriers are lattice waves and electrons. Less dominant carriers are magnetic excitations, spin waves, and radiation [40,42,43]. In non-metallic solids without any free electrons, the lattice waves dominate and are often the only noticed carriers [33,38,40,42,44]. In metallic solids, the electron contribution to heat conduction can predominate [33,40,42,44]. The total thermal conductivity can be generally expressed as the sum

$$\lambda = \frac{1}{3} \sum_i C_{\mathrm{V},i} u_i l_i \tag{2.10}$$

of all contributions, adapted from **Eq. (2.9)**. The subscript i stands for the respective carrier (electrons, lattice waves, …). $C_{\mathrm{V},i}$ is the heat capacity per unit volume due to the carrier i, u_i is the velocity of the carrier, and l_i its mean free path. At least velocity and mean free path for the different carriers are not as clearly defined as for gases. Models must be found to approximate them. In the following section, the thermal conductivity of non-metallic solids, metallic solids, and the special case of polymers are discussed.

2.1.1 NON-METALLIC SOLIDS

In contrast to the atoms of a gas, the atoms of a solid do not move freely but have a fixed equilibrium position. Many solids have a crystalline structure with a regular lattice [36]. The atoms perform thermal oscillations around their equilibrium position. As the temperature rises, the internal energy and thus the vibrational energy of the solid increases. Since the atoms are closely coupled, a temperature increase on one side of the solid and thus an increase in vibrational energy is transported further in the body by lattice waves. Lattice waves are primarily structure-borne sound waves that propagate through the solid body. In 1932, Frenkel introduced the term "phonons" for the energy quanta transported by these waves [45]. To simplify, the phonons can be imagined as free gas particles. They move

through the lattice, transporting a certain thermal energy at a specific velocity and over a certain mean path. This idea supports the use of the **Eq. (2.9)** or **(2.10)** to describe the lattice contribution λ_{ph} to the overall thermal conductivity. The objective quantities of the following discussion are therefore the heat capacity of the lattice waves, their propagation velocity, and their mean free path. Comprehensive descriptions of the theoretical foundations and models developed over the decades can be found in [38–41,43,46]. Brief summaries of the key aspects are presented in [42,44,47]. Such a description is also provided here for introductory purposes.

The lattice waves occur in a broad frequency spectrum. The wavelength of the occurring vibration modes starts at atomic dimensions and extends to long waves comparable to the external dimensions [42]. Of particular interest are the propagating modes. To consider the specific contribution of the individual angular frequencies ω, the basic **Eqs. (2.9)** or **(2.10)** can be generalized to [42]

$$\lambda_{\mathrm{ph}} = \frac{1}{3}\int_0^{\omega_{\mathrm{D}}} C_{\mathrm{V,ph}}(\omega) u_{\mathrm{ph}} l_{\mathrm{ph}}(\omega)\,\mathrm{d}\omega \tag{2.11}$$

using the Debye theory [48] in good approximation. Strictly taken, a differentiation of the polarization should also be taken into account [46]. For a general discussion of the relationships, however, **Eq. (2.11)** will suffice. Frequencies up to a cutoff value ω_{D}, called Debye frequency, are considered [37,41,42,46]. It is selected to include $3N$ modes, with N being the number of atoms per unit volume. In the simplest form, u_{ph} is the velocity of sound averaged over the transverse and longitudinal velocities [41]. $C_{\mathrm{V,ph}}(\omega)\ \mathrm{d}\omega$ is the specific heat contribution of the corresponding frequency interval with [42,49]

$$C_{\mathrm{V,ph}}(\omega)\ \mathrm{d}\omega = 9Nk_{\mathrm{B}}\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^3 \frac{x^4 e^x}{(e^x-1)^2}\ \mathrm{d}\omega\ , \tag{2.12}$$

where k_{B} is the Boltzmann constant, T the absolute temperature, Θ_{D} the Debye temperature of the solid, and $x = \hbar\omega/k_{\mathrm{B}}T$, with $\hbar$ being the Planck constant divided by 2π. The Debye temperature is [37]

$$\Theta_{\mathrm{D}} = \frac{\hbar\omega_{\mathrm{D}}}{k_{\mathrm{B}}} = \frac{\hbar u_{\mathrm{ph}}}{k_{\mathrm{B}}}\sqrt[3]{\frac{6\pi^2 N}{V}} \tag{2.13}$$

for a crystal with N oscillators (atoms) in the volume V. Even though the Debye model for specific heat only provides a rough approximation, it is regularly used, as the influence of the uncertainties in the determination of the mean free path is much greater [42,46]. If there were infinite ideal crystals, with perfectly regular structures and harmonic interatomic forces, the mean free path and thus the thermal conductivity would be infinite [46]. In real solids, there are barriers that limit the mean free path and thus limit heat transport. There

is scattering caused by the collisions of phonons with impurities, crystal defects, grain boundaries, and external boundaries [41]. The phonons are scattered from one mode into another [46]. Anharmonicity in real crystal lattices additionally causes phonon-phonon collisions. However phonon-phonon collisions do not necessarily contribute to limiting the mean free path [36]. If a normal process (N-process) occurs, neither momentum nor energy flow is affected. In 1929, Peierls [50] showed that, in addition to N-processes, there are also Umklapp-processes (U-processes) that lead to an intrinsic resistance, since the direction of the energy flow changes after the phonon-phonon collision (German: umklappen, English: to flip over). The lattice absorbs momentum [36]. As given in **Eq. (2.11)**, the limited mean free path is a function of the frequency and generally also of the temperature $l_{\mathrm{ph}}(\omega, T)$ [36,38,40,46]. Thus, the specific heat $C_{\mathrm{V,ph}}$ and the mean free path l_{ph} are temperature-dependent, resulting in a strongly temperature-dependent lattice component of thermal conductivity $\lambda_{\mathrm{ph}}(T)$.

The influence of temperature on the specific heat is particularly evident at very low temperatures ($T < \Theta_{\mathrm{D}}/3$) in a T^3 dependency. At high temperatures ($T > \Theta_{\mathrm{D}}$), the heat capacity is approximately constant. At low temperatures, the influence of boundary collisions increases as the low frequencies become more dominant [44]. The mean free path can be limited by the dimensions of the sample [36,42]. As the effects of low temperatures are strongly pronounced, this range is in focus of certain specialized work [51,52]. In general, the thermal conductivity in this range increases with temperature. The thermal conductivity then reaches its maximum in the intermediate temperature range before decreasing again due to the growing influence of defect and impurity scattering [38,41,43]. The mean free path decreases stronger than the heat capacity increases. Further increasing temperatures increase the probability of phonon-phonon collisions and cause the thermal conductivity to drop further, approximately proportional to T^{-1} in the high temperature range [41,42].

The discussion thus far has been limited to crystalline solids with long-range order in structure. However, glasses and many polymers do not have long-range order. Section 2.1.3 is explicitly dedicated to polymers. For the sake of completeness, however, a few general connections will be made here.

Amorphous structures tend to have lower thermal conductivities than crystals [39,41]. Theories for predicting the thermal conductivity of amorphous solids emerged long after the fundamental theories for crystalline solids [33,42]. However, it was established early that the assumption of a constant, temperature-independent mean free path is sufficiently good, at least in the range of ordinary (e.g., room temperature) and high temperatures [41,42]. The mean free path in amorphous solids is closely linked to the structural length units of the solids [38,41]. In polymers, these are the building blocks of the polymer chains.

2.1.2 METALLIC SOLIDS

In metallic solids, heat can also be transported via lattice waves as in the non-metallic solids mentioned previously, however the contribution from free electrons as carriers of heat is just as important. In the case of pure metals, the contribution of the electrons λ_{el} can significantly exceed the contribution of the lattice waves λ_{ph}. Alloy thermal conductivity always depends on which elements are added and in what quantities, as well as the conductivity of the parent material. At ordinary and high temperatures, the contribution of the lattice becomes more important the worse the parent material conducts electricity [53].

We can model free electrons in metals as a free electron gas [36]. Again, we can adapt the general formulation from **Eq. (2.10)** [33,36,38,41,53]

$$\lambda_{\mathrm{el}} = \frac{1}{3} C_{\mathrm{V,el}} u_{\mathrm{el}} l_{\mathrm{el}} \ , \tag{2.14}$$

and consider the specific heat of the gas particles $C_{\mathrm{V,el}}$, their velocity u_{el}, and the mean free path l_{el} they can travel between two collisions. While the electrons are much faster than the phonons $u_{\mathrm{el}} \gg u_{\mathrm{ph}}$, typically two or three orders of magnitude faster, the electron specific heat is smaller than the lattice contribution to specific heat [41]. Considering a Fermi gas, the specific heat of the electrons is [38,41]

$$C_{\mathrm{V,el}} = \frac{\pi^2}{2} \frac{k_{\mathrm{B}}^2 T}{E_{\mathrm{F}}} n_{\mathrm{el}} \ , \tag{2.15}$$

where n_{el} is the electron density and E_{F} is the Fermi energy. If

$$u_{\mathrm{el}} = \sqrt{\frac{2E_{\mathrm{F}}}{m_{\mathrm{el}}}} \tag{2.16}$$

with m_{el} being the electron mass, is then set for the velocity of the electrons in a Fermi gas [38,41], the only unknown is again the mean free path l_{el}. The same factors must be considered as with phonons. Collisions between electrons or collisions with phonons, as well as scattering at grain boundaries, imperfections, and defects limit the mean free path [43,53]. The contribution of the electrons to the thermal conductivity also depends on the temperature. Zhang et al. [33] describe a linear increase with temperature in the low temperature range, a constant contribution in the intermediate range and a slight decrease with temperature at high absolute temperatures. If first **Eq. (2.3)** and then **Eqs. (2.15)** and **(2.16)** are put into **Eq. (2.14)**, the thermal conductivity of an electron gas is obtained as a function of the relaxation time $\tau_{\mathrm{r,el}}$ [41]

$$\lambda_{\mathrm{el}} = \frac{\pi^2}{3} \frac{k_{\mathrm{B}}^2}{m_{\mathrm{el}}} n_{\mathrm{el}} T \tau_{\mathrm{r,el}} \ . \tag{2.17}$$