SUPERDIFFUSIVE HEAT CONDUCTION IN SEMICONDUCTOR ALLOYS

I. Theoretical foundations

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Abstract

Semiconductor alloys exhibit a strong dependence of effective thermal conductivity on measurement frequency. So far this quasi-ballistic behaviour has only been interpreted phenomenologically, providing limited insight into the underlying thermal transport dynamics. Here, we show that quasi-ballistic heat conduction in semiconductor alloys is governed by Lévy superdiffusion. By solving the Boltzmann transport equation (BTE) with ab initio phonon dispersions and scattering rates, we reveal a transport regime during which the mean square displacement of thermal energy scales superlinearly with time: \(\sigma^2(t) \sim t^\beta\) (\(1 < \beta < 2\)). The time exponent is directly interconnected with the order \(n\) of the dominant phonon scattering mechanism \(\tau \sim \omega^{-n}\) (\(n > 3\)) and phonon relaxation time spectrum \(\kappa_\Sigma(\tau) \sim \tau^\gamma\) through simple relations \(\beta = 2 - 3/n = \gamma + 1\). The quasi-ballistic energy density inside alloys is no longer governed by Brownian motion, but instead obeys a Lévy process with fractal dimension \(\alpha = 3 - \beta\). This has important implications for the interpretation of thermoreflectance (TR) measurements with modified Fourier theory. Experimental \(\alpha\) values for InGaAs and SiGe, determined through TR analysis with a novel Lévy heat formalism, match ab initio BTE predictions within a few percent. Our findings lead to a deeper and more accurate quantitative understanding of the physics of nanosecond heat flow experiments.

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Introduction

Heat conduction in semiconductors is predominantly governed by collective lattice vibrations called phonons [1]. These describe the transport of thermal energy through the medium in terms of a wide variety of wave-like modes. Interactions with crystal impurities, electrons and other phonons cause phonons to scatter. This induces a finite thermal conductivity that acts as a basic measure of the material’s thermal transport capabilities. The scattering probabilities per unit time and unit length are expressed, respectively, by the inverses of the phonon mode relaxation time $\tau$ and mean free path (MFP) $\Lambda$. Macroscopically, the net collective effect of the phonon modes is observed as thermal diffusion described by the well known Fourier equation.

At short length and time scales, however, this classical model begins to fail [2]. Experimental observations in which thermal gradients are induced over microscale distances clearly deviate from standard Fourier predictions [3]–[7]. A notable and pioneering example consists of time domain thermoreflectance (TDTR) measurements on semiconductor alloys [3]. This technique performs thermal characterisation of test samples by measuring their response to a modulated pulse train of ultrashort laser pulses. Alloys including InGaAs and SiGe were found to exhibit a near 50% reduction in apparent Fourier thermal conductivity over the 1–10 MHz laser modulation frequency range. The effect can be attributed to phonons whose MFPs exceed the thermal penetration depth of the heat source. These so called quasi-ballistic modes are unlikely to experience scattering events within the thermal gradient. This violates the inherent assumption of the Fourier model, causing it to fail. The interpretation of quasi-ballistic heat flow in several other experimental configurations has also primarily focused on the overlap between phonon MFPs and the characteristic dimension of the heat source [4]–[8]. Far less attention was given to the transient aspects of the Fourier breakdown.

In this work, we take a deeper look at the underlying temporal dynamics of the anomalous transport regimes probed by thermoreflectance measurements. We derive analytical solutions of the Boltzmann transport equation (BTE) under the relaxation time approximation to study the transition from purely ballistic to purely diffusive transport in close detail. Our results reveal that the earlier mentioned reductions of apparent conductivity in semiconductor alloys are a direct manifestation of superdiffusive heat conduction. During
this regime, the mean square displacement of thermal energy grows with a stable, super-
linear time exponent $\beta$. The exponent’s value as well as the temporal extent of the regime
are closely related to the shape of the cumulative conductivity $\kappa_{\Sigma}(\tau^*)$. This function is
the conductivity that would be observed if only those phonon modes with scattering times
$\tau \leq \tau^*$ were present in the medium. In addition, we find that the superdiffusive transport
dynamics are non-Brownian but instead governed by a Lévy process with fractal dimen-
sion $\alpha = 3 - \beta$ that can be experimentally measured. The associated energy density is no
longer Gaussian, causing shortcomings of modified Fourier models conventionally used for
experimental analysis of quasi-ballistic heat flow.

**BTE modelling**

To identify key regimes of thermal transport inside the semiconductor as would occur
during thermoreflectance experiments, we solve the 1D BTE for cross-plane heat flow ($z$
direction). The temperature rise $\Delta T(z, t) = T(z, t) - T_0$ is typically small compared to the
reference temperature $T_0$. The single pulse response to a planar source located at $z = 0$
with unit strength can then be described by:

$$\frac{\partial g_k}{\partial t} + v_{q,k} \frac{\partial g_k}{\partial z} = -\frac{g_k - C_k \Delta T}{\tau_k} + \frac{C_k}{C} \delta(z) \delta(t)$$

(1)

$g_k$ denotes the deviational phonon energy distribution function, $v_{q,k} = \frac{\partial \omega}{\partial k_z}$ is the projection
of the phonon group velocity onto the thermal transport axis and $\tau_k$ is the phonon relaxation
time. We write the BTE in terms of spectral quantities, indicated by subscripts $k$, resolved
for phonon wavevector $\vec{k}$ rather than phonon frequency $\omega$. This enables us to utilise full
phonon dispersions obtained from ab initio calculations, thereby accounting for the actual
shape of the Brillouin zone (BZ) and potential crystal anisotropies. The scaling factor $\frac{C_k}{C}$ in
the source term expresses that the injected energy gets distributed across the various phonon
modes in proportionality with their contribution to the total heat capacity $C = \sum_k C_k$. The
mode specific heat is given by $C_k = \frac{E_k}{V} \frac{\partial f_{BE}}{\partial T}$ with $E_k = h\omega_k$ the phonon energy, $V$ the volume
of the supercell and $f_{BE}$ the Bose-Einstein distribution. After spatial Fourier ($z \leftrightarrow \xi$) and
temporal Laplace ($t \leftrightarrow s$) transformation of Eq. (1) we obtain

$$G_k(\xi, s) = \frac{C_k \left[ T(\xi, s) + \frac{\tau_k}{C} \right]}{1 + s\tau_k + j\xi A_{n,k}}$$

(2)
where \( j \) is the complex unit and \( \Lambda_{\mathbf{q}, k} = v_{\mathbf{q}, k} \cdot \tau_k \) denotes the projected phonon MFP. By inserting \( G_k \) into the conservation of energy,

\[
\sum_k \frac{1}{\tau_k} (G_k - C_k \Delta T) = 0 ,
\]

we can solve for \( \Delta T(\xi, s) \). In the above and following, we use summations \( \sum_k \) over a discrete wavevector grid as this is convenient for ab initio simulation data. Presented BTE expressions are readily applicable to analytical modelling as well by simply exchanging the summations with volume integrals \( \iiint_{BZ} \). Due to crystal symmetry with respect to the \( k_z = 0 \) plane, projected phonon MFPs occur in pairs with identical magnitude but opposite sign, and we obtain:

\[
P(\xi, s) = C \Delta T(\xi, s) = \frac{\sum_{k_z \geq 0} C_k \Psi_k(\xi, s)}{\sum_{k_z \geq 0} \frac{C_k}{\tau_k} [1 - \Psi_k(\xi, s)]}
\]

in which

\[
\Psi_k(\xi, s) = \frac{1 + s \tau_k}{(1 + s \tau_k)^2 + \xi^2 \Lambda_{\mathbf{q}, k}^2}
\]

Equation (4) provides a closed form expression in the Fourier-Laplace domain for the 1D energy density single pulse response in the semiconductor. One can easily verify fulfillment of the energy balance by observing that \( P(\xi \rightarrow 0, s) = 1/s \), signaling that \( \int_{-\infty}^{\infty} P(z, t)dz = 1 \) at all times \( t \). In stochastic terms, \( P(\xi, s) \) is the characteristic function of a properly normalised random walk process in which \( P(z, t)dz \) expresses the probability to find the injected source energy in location range \([z, z + dz]\) at time \( t \). The derivatives of \( P(\xi, s) \) with respect to \( \xi \) are continuous at \( \xi = 0 \), so the moments of \( P(z, t) \) exist and are finite. The vanishing of the first derivative \( \frac{\partial P(\xi, s)}{\partial \xi} \bigg|_{\xi=0} = 0 \) indicates zero mean, in accordance with spatial symmetry of the energy density around the heat source. The mean square displacement (MSD) of thermal energy now immediately follows

\[
\sigma^2(s) = -\frac{\partial^2 P(\xi, s)}{\partial \xi^2} \bigg|_{\xi=0} = \frac{2}{s^2} \cdot \frac{\sum_k \kappa_k}{\sum_k \frac{C_k}{1 + s \tau_k}}
\]

in which we introduced the spectral thermal conductivity \( \kappa_k = \Lambda_{\mathbf{q}, k} \cdot v_{\mathbf{q}, k} \cdot C_k \).

From Eq. (6) we readily recover two well established limit regimes of the thermal transport. When \( s \tau_\omega \gg 1 \), corresponding to transitions that occur quickly compared to the
phonon relaxation times, we have

\[ \sigma^2(s \to \infty) = \frac{2}{s^3} \bar{v}^2 \Rightarrow \sigma^2(t) = \bar{v}^2 t^2 \]  

(7)

in which

\[ \bar{v}^2 = \frac{\sum_k C_k \tau_k v_{i,k}^2}{\sum_k \tau_k} \]  

(8)

This can be interpreted as purely ballistic energy displacement at net ensemble group velocity \( \bar{v} \). At long time scales, \( s \tau_\omega \ll 1 \), on the other hand,

\[ \sigma^2(s \to 0) = \frac{2}{s^2} \sum_k \kappa_k \sum_k C_k \Rightarrow \sigma^2(t) = 2 \frac{\kappa}{C} t = 2Dt \]  

(9)

which is the standard diffusive regime. The remainder of the paper studies the transition between ballistic and diffusive limits in detail. We first outline our simulation procedures for obtaining the phonon properties which then serve as input for (4) and (6). We demonstrate the onset of a superdiffusive regime in semiconductor alloys, explain its physical origin, and point out significant differences between the associated transport dynamics and modified Fourier solutions.

**Ab initio methodology**

We start by considering the fully ordered semiconductors Si, Ge, InAs and GaAs. For each of them, we perform an unconstrained relaxation of their unit cell using the VASP DFT package [9] with projector-augmented-wave (PAW) pseudopotentials [10], the local density approximation to exchange and correlation [11], a \( 12 \times 12 \times 12 \) \( \vec{k} \)-point grid, and a plane-wave energy cutoff 30\% higher than the maximum value prescribed for each pseudopotential. We then generate a minimal set of displaced \( 6 \times 6 \times 6 \) supercells using Phonopy [12], compute the forces on atoms in those configurations using VASP, and obtain the harmonic force constants for each semiconductor. For the polar compounds InAs and GaAs, we employ density functional perturbation theory to compute a set of Born effective charges and the high-frequency dielectric tensor to account for Coulombic interactions [13]. Those ingredients allow us to obtain the compound’s phonon spectrum. A larger set of supercell calculations is used to compute the relevant third-order derivatives of the potential energy with respect to
atomic displacements. Finally, all elements are combined to obtain a relaxation time for each phonon mode, including both phonon-phonon processes and isotopic scattering. The last two steps are performed using open-source software developed by some of us and documented in full detail elsewhere [14]. For the supercells, Γ-point-only DFT runs are adequate. We include neighbors up to the fifth coordination shell in our third-order calculations and use a $32 \times 32 \times 32$ wavevector grid, which yields fully converged values of the thermal conductivity. Our method requires no experimental input and is fully parameter free. The first-principle lattice constants, phonon spectra and room-temperature thermal conductivities agree well with values from the literature.

For a disordered binary alloy $A_xB_{1-x}$ we operate under the virtual crystal approximation, which has been successfully tested in similar settings [15, 16]. Lattice constants, second- and third-order interatomic force constants and dielectric parameters are taken as weighted averages of their values for A and B, with weights $x$ and $1-x$. Mass disorder in the alloy is treated in the same way as isotopic disorder in pure compounds [17], as described in Ref. 14.

The materials considered in this paper are Si, In$_{0.53}$Ga$_{0.47}$As and Si$_{0.82}$Ge$_{0.18}$. The calculated bulk thermal parameters are listed in Table I.

**TABLE I.** Thermal properties obtained from ab initio phonon calculations.

| Material       | $\kappa$ [W/m-K] | $C$ [MJ/m$^3$-K] | $D = \kappa/C \ \bar{v}$ (Eq. 8) |
|---------------|------------------|------------------|-----------------------------------|
| Si            | 166              | 1.62             | 103                               |
| In$_{0.53}$Ga$_{0.47}$As | 8.56             | 1.56             | 5.49                               |
| Si$_{0.82}$Ge$_{0.18}$ | 10.7             | 1.66             | 6.46                               |

**Results**

First, we investigate the transient evolution of the thermal energy MSD. The ab initio calculations provide 196,608 phonon modes (six branches over a $32 \times 32 \times 32$ wavevector grid) whose properties are inserted into (6) to calculate the MSD. Time domain curves, obtained by transforming $\sigma^2(s)$ with a standard Gaver-Stehfest Laplace inversion scheme
are plotted in Fig. 1.

![Graph showing renormalised mean square displacement of thermal energy.](image)

**FIG. 1.** Renormalised mean square displacement of thermal energy obtained from BTE solution Eq. (6) with ab initio phonon dispersions and scattering rates at room temperature. The emergence of a superdiffusive regime with time exponent $\beta \approx 1.34$ is clearly apparent for the alloy materials.

Intuitively, one may expect the MSD time exponent to drop smoothly from 2 to 1 during the transition from purely ballistic ($\sigma^2 \sim t^2$) to purely diffusive ($\sigma^2 \sim t$) transport. Instead, for alloy materials we observe the emergence of a striking regime $\sigma^2 \sim t^{\beta}(1 < \beta < 2)$ where $\beta$ remains virtually stable during up to two orders of magnitude of time. Transport in which the MSD scales superlinearly with time is typically referred to as superdiffusive [20]. Least square fitting of the obtained MSD curves yields $\beta = 1.331$ (30 ps $\leq t \leq 700$ ps) for InGaAs and $\beta = 1.350$ (20 ps $\leq t \leq 2$ ns) in SiGe. These time windows overlap with the typical bandwidths of laser thermoreflectance measurements commonly employed to reconstruct phonon MFP spectra [21]. To better understand the physical dynamics of the superdiffusive regime and its implications on the interpretation of quasi-ballistic heat flow, we take a closer look at the shape of the energy density.

Ideally one wishes to look at the distribution $P(z, t)$ in real space-time domain, but numerical limitations prevent a stable and accurate direct inversion. However, we can identify key dynamics directly from the Fourier-Laplace entity [4]. Figure 2 shows the magnitude of $|P(\xi, s)|$ versus $|\xi|$ ($P$ is even in $\xi$) at various frequencies $s = j2\pi f$ for the three considered materials.
FIG. 2. Magnitude of the energy density distribution in Fourier-Laplace domain, $|P(\xi, s)|$, at various frequencies $s = j2\pi f$, calculated from (4) with ab initio phonon dispersions and scattering rates. Distinct regimes are visible that each can be described well with a simple analytic expression. The fittings over the intermediate frequency range indicate that quasi-ballistic thermal transport in alloys behaves as Lévy superdiffusion with fractal dimension $\alpha = 3 - \beta$.

In the diffusive limit, the BTE results recover classical Fourier solutions. Here, $P(z, t)$ is the familiar Gaussian with variance $2Dt$, which in transformed variables reads $P(\xi, s) = 1/(s + D\xi^2)$. In the ballistic limit, the distribution tends to a Lorentzian: $P(\xi, s) \to 1/(s + v_\infty |\xi|)$ hence $P(z, t) \to v_\infty t/(\pi(v_\infty^2 t^2 + z^2))$. We note that the actual ballistic distribution
will slightly deviate from this asymptotic limit since the phonon group velocities contain the energy within a finite $z$ interval that grows with time. At intermediate frequencies in alloys, we find $P(\xi, s) \to 1/(s + D_\alpha |\xi|^\alpha) \Leftrightarrow P(\xi, t) \to \exp(-D_\alpha t |\xi|^\alpha)$, where $1 < \alpha < 2$ and $D_\alpha$ is a fractional diffusivity constant. These solutions correspond to the characteristic function of a so called Lévy stable process \[22\], and immediately imply that the superdiffusive energy transport is stochastically equivalent to a random walk with fractal dimension $\alpha$ \[20\]. Lévy-type anomalous diffusion has been encountered across a wide variety of disciplines ranging from travel patterns of foraging animals \[23\], protein movements along DNA chains \[24\], tracer motion in turbulent fluids \[25\], and financial market fluctuations \[26\]. Lévy processes in which finite transition velocities are enforced, as would be appropriate in the context of phonon dynamics, are known to induce an MSD $\sigma^2(t) \sim t^{3-\alpha}$ \[27\]. This suggests the superdiffusive exponent and fractal dimension are directly interrelated as $\alpha = 3 - \beta$. Figure 2 confirms that for InGaAs and SiGe, whose MSDs exhibit $\beta \simeq 1.34$, the quasi-ballistic BTE energy density can indeed be fitted accurately using $\alpha \simeq 1.66$. Contrary to the Gaussian energy densities associated with Fourier diffusion, Lévy distributions have ‘fat tails’ that spatially decay as a power law $P(z \to \infty, t) \sim |z|^{-(1+\alpha)}$ while the response at the heat source takes the form $P_0(t) = P(z = 0, t) \sim t^{-1/\alpha} \Leftrightarrow P_0(s) \sim s^{1/\alpha-1}$. We have verified that the BTE solutions in alloys at the heat source, obtained numerically through

$$P_0(s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} P(\xi, s) d\xi,$$  \hspace{1cm} (10)

indeed exhibit those signature Lévy characteristics.

**Physical origin of superdiffusion**

The question still remains why alloys exhibit a superdiffusive regime, and what physically determines the associated time exponent $\beta$. Here, we show that the quasi-ballistic dynamics of a material originate in its dominant phonon scattering mechanism. To simplify the analysis, we limit ourselves to a single phonon branch with constant group velocity $v_0$ in an ideal isotropic crystal with spherical BZ. We should expect this approach to capture the essential trends occurring in actual media, as a major fraction of thermal conduction is governed by acoustic phonons on quasi straight branch segments near the zone center. At room temperature, energies of the dominant acoustic phonons typically do not exceed $k_B T$. 


Under these circumstances, $\hbar\omega \frac{\partial f}{\partial T}$ varies by less than 8% across the modes, and we can simply assume a constant mode capacity ($C_k \equiv C_0$) with good approximation. We consider a single dominant phonon scattering mechanism of the form:

$$\tau \sim \omega^{-n} \Rightarrow \tau_k = \tau_{\text{min}} \left( \frac{ka}{\pi} \right)^{-n} \quad (11)$$

in which $n$ is order of the mechanism (not necessarily integer), $a$ is the lattice constant and $k = ||\vec{k}||$ the wavevector norm $0 \leq k \leq \frac{\pi}{a}$. First principle calculations in Si [28] have suggested that Umklapp processes, which dominate its bulk thermal conductivity at room temperature, are characterised by $n = 3$, although we note that other works have also inferred $n = 2$ [29] and $n = 4$ [30] relations. Mass impurity (Rayleigh) scattering, dominating alloy behaviour, ideally obeys $\tau \sim v^3 \omega - 4$ which corresponds to $n = 4$ under the assumed linear dispersion. Inserting the single branch relations into the BTE variance (6) and performing BZ volume integration in spherical coordinates yields

$$\sigma^2(s) = \frac{2}{3} v_0^2 \tau_{\text{min}} \int_0^1 \frac{\tilde{k}^{n+2}d\tilde{k}}{(\tilde{k}^{n+s\tau_{\text{min}}})^2}, \quad \tilde{k} = \frac{ak}{\pi} \quad (12)$$

For $s\tau_{\text{min}} \ll 1$, i.e. once a sufficient fraction of the phonon population have undergone scattering events to break up the purely ballistic regime, one finds $\sigma^2(s) \sim s^{-3+3/n}$ when $n > 3$. The time domain counterpart is a power law $\sigma^2(t) \sim t^{\beta_n}$ with superdiffusive exponent

$$\beta_n = 2 - \frac{3}{n}, \quad n > 3 \quad (13)$$

We point out that simple scattering relations of the form (11) produce arbitrarily large relaxation times near the zone center. Bulk thermal conductivity of the single branch model diverges for $n > 2$, and the regular diffusive transport regime is never recovered. In reality, scattering times are physically bounded to a finite range $\tau_{\text{min}} \leq \tau \leq \tau_{\text{max}}$ with $\tau_{\text{max}} \gg \tau_{\text{min}}$. As a result, a superdiffusive regime with $\beta \simeq \beta_n$ is only maintained over a finite time window in the actual medium, as observed earlier in Fig. 1.

We can additionally link $\beta$ and the temporal extent of the superdiffusive window to the shape of the cumulative conductivity function $\kappa_{\Sigma}(\tau) = \sum_{\tau_k \leq \tau} \kappa_k$. A single branch model with
scattering relation (11) provides

$$\kappa_\Sigma(\tau) \sim \int_{(\tau_{\text{min}}/\tau)^{1/n}}^{1} \frac{d\tilde{k}}{\tilde{k}^{n-2}}$$

(14)

from which we obtain

\begin{align*}
n = 2 : \kappa_\Sigma & \sim 1 - \sqrt{\frac{\tau_{\text{min}}}{\tau}} \\
n = 3 : \kappa_\Sigma & \sim \ln\left(\frac{\tau}{\tau_{\text{min}}}\right) \\
n > 3 \text{ (incl. Rayleigh)} : \kappa_\Sigma & \sim \left(\frac{\tau}{\tau_{\text{min}}}\right)^{\beta_n-1} - 1
\end{align*}

(15)

where we used (13) for the last case. The interconnections between the scattering relation \(\tau(\omega)\), the cumulative conductivity \(\kappa_\Sigma(\tau)\) and the superdiffusion exponent \(\beta\) we have derived for a single phonon branch with linear dispersion are preserved quite well in realistic media (Fig. 3).

For Si, we find that our ab initio scattering rates can be fitted quite well by a scattering relation \(\tau \sim \omega^{-3}\). The upper portions of the cumulative conductivity curve show a clear logarithmic dependence on scattering time, as predicted by the ideal \(n = 3\) case. Initial parts of the \(\kappa_\Sigma\) curve are governed by higher energy modes with small velocity, and therefore do not obey the simple linear dispersion model, as could be expected. As far as alloys are concerned, single branch expressions (13) and (15) suggest that the SiGe superdiffusion exponent \(\beta = 1.35\) theoretically corresponds to \(n = 4.61\) and \(\kappa_\Sigma \sim \tau^{0.35}\). Both relations provide good fits to the actual phonon data as shown in Fig. 3. Similar observations hold for InGaAs. It is noteworthy that the relaxation time range over which \(\kappa_\Sigma\) closely follows a power law has a near one-to-one correspondence to the superdiffusive time window in the MSD observed earlier in Fig. 1. As a rule of thumb, we can say that thermal transport in a material whose cumulative conductivity curve \(\kappa_\Sigma(\tau)\) has a stable slope \(\gamma\) in double logarithmic scale for \(\tau_1 \leq \tau \leq \tau_2\) will exhibit Lévy superdiffusion with MSD time exponent \(\beta = \gamma + 1\) and fractal dimension \(\alpha = 2 - \gamma\) during times \(\tau_1 \lesssim t \lesssim \tau_2\).
FIG. 3. Interconnection between dominant scattering order $\tau \sim \omega^{-n}$, cumulative conductivity $\kappa(\tau) \sim \tau^\gamma$ and superdiffusive MSD $\sigma^2(t) \sim t^\beta$. Ab initio results (circles) agree well with single branch model predictions (lines) $\beta = 2 - \frac{3}{n} \leftrightarrow n = \frac{3}{2-\beta}$ and $\gamma = \beta - 1$.

Implications for transient laser thermoreflectometry

Regular diffusive transport is well known to correspond to Brownian motion [31], a stochastic process with fractal dimension 2. Many observations of quasi-ballistic heat flow are interpreted using so called modified Fourier theory [3–5, 7], which explains the anomalous heat conduction phenomenologically in terms of a reduced effective thermal conductivity. Such an approach still inherently maintains the assumption of purely diffusive
transport dynamics. The results we have presented here, however, demonstrate that the quasi-ballistic regime in alloys is characterised by superdiffusive Lévy motion with fractal dimension $\alpha < 2$. The associated energy density distributions, $P(\xi, s) \simeq 1/(s + D_\alpha |\xi|^\alpha)$, are decidedly non-Gaussian in space domain, and cannot be described by a modified Fourier solution $P(\xi, s) = 1/(s + D_{\text{eff}} \xi^2)$ due to fundamental mismatch of the $\xi$ exponent. The resulting shortcomings of modified Fourier analyses of thermoreflectance experiments are illustrated in detail in part II of the paper [32].

Hua and Minnich have recently shown that transient thermal grating (TTG) experiments probe a so called weakly quasi-ballistic regime in which the use of a modified Fourier approach is formally justified by the BTE [33]. As we have shown above, this is clearly not the case for time/frequency domain thermoreflectance (TR) measurements. The different behaviour can be attributed to important distinctions in experimental configuration and boundary conditions. TTG studies the transient decay of a spatially periodic temperature input directly at the semiconductor surface. The thermal gradients are predominantly in-plane and stretch across the grating wavelength $\lambda$, which typically measures several hundreds of nanometers or more. To a first order, this measurement configuration essentially probes the energy density distribution at a single spatial Fourier variable $\xi = \lambda^{-1}$. As a result, the recorded thermal decay can be fitted quite well by a Fourier solution with suitably chosen effective diffusivity. TR experiments, on the other hand, capture the response to temporally periodic energy impulses. For typical laser spot sizes, the predominant thermal gradient occurs cross-plane over the thermal penetration depth inside the semiconductor. In a crucial difference with the TTG configuration, the thermal field is not spatially periodic in the dominant thermal transport direction. As a result, the semiconductor surface response under cross-plane heat flow is governed by a wide spectrum of $\xi$ values, as symbolised formally by Eq. [10]. The thermal transients observed by TR experiments therefore preserve characteristic Lévy features, enabling this technique to actively probe the superdiffusive regime.
Experimental validation

As mentioned in the Introduction, modified Fourier interpretation of TR measurements on semiconductor alloys produces effective conductivities that drop significantly with increasing laser modulation frequency [3]. Interestingly, in retrospect this behaviour is a direct manifestation of Lévy superdiffusion. The essence of the connection can be easily understood in terms of the dynamics at the semiconductor surface. In pure Lévy regime, the frequency domain response at \( z = 0 \) reads

\[
P_0(s) = \left[ \alpha \sin\left(\frac{\pi}{\alpha}\right) D_\alpha^{1/\alpha} s^{1-1/\alpha} \right]^{-1}.
\]

Interpreting this functionality with a modified Fourier solution \( P_0(s) = [2D_{\text{eff}}^{1/2} s^{1/2}]^{-1} \) suggests that \( D_{\text{eff}}(s) \sim s^{1-2/\alpha} \), and more specifically

\[
\kappa_{\text{eff}} = 2\pi C \cdot \left(\frac{\alpha}{2}\right)^2 \cdot \sin^2\left(\frac{\pi}{\alpha}\right) \cdot \left(\frac{D_{\alpha}}{2\pi}\right)^{2/\alpha} \cdot f_{\text{mod}}^{1-2/\alpha}
\]  

(16)

Based on the BTE results obtained above, we would therefore expect the effective conductivity in InGaAs and SiGe to drop by roughly 40% over the 1–10 MHz modulation range \( \frac{\kappa_{\text{eff}}(10 \text{ MHz})}{\kappa_{\text{eff}}(1 \text{ MHz})} = 10^{1-2/1.66} \approx 0.62 \), which is quite similar to the actual reduction observed experimentally. A closer look at our own TDTR measurements shows that the effective conductivity of semiconductor alloys can be fitted quite accurately by a power law (Fig. 4).

FIG. 4. The frequency dependence of effective thermal conductivity, observed in time domain thermoreflectance experiments on semiconductor alloys, is a direct manifestation Lévy superdiffusion. A power law fit, suggested by basic 1D model prediction (16), provides accurate estimates of the fractal metrics of the quasi-ballistic transport.

Comparing the fits to (16) produces \( \alpha = 1.67 \) for InGaAs and \( \alpha = 1.71 \) for SiGe, in
good agreement with the ab initio predictions found earlier (1.67 and 1.65). In addition, the extracted fractional diffusivities $D_\alpha$ are both within ±45% of the theoretical values from Fig. 2. This too can be considered a very reasonable agreement, given that the measured bulk thermal conductivity deviates from BTE predictions by similar amounts.

The intricacies of TR experiments are obviously far more involved than simple 1D model expressions. Rigorous analysis of raw measurement data is desirable to determine the fractal dimension directly, and establish a definitive experimental confirmation of superdiffusive Lévy behaviour. Unfortunately, 1D BTE solutions as derived here to illuminate essential trends are not easily suitable for this purpose. Crystal impurities in real samples cause perturbations in the phonon spectra, while the effects of heat source nonuniformity (Gaussian shaped laser beam) and lateral heat spreading can only be accounted for by 3D modelling. To achieve this, we have developed a phenomenological approach based on truncated Lévy theory [34]. Our method captures the essential physics of the BTE solutions yet offers sufficient flexibility for full 3D analysis of experimental data. The methodology and performance of the formalism are presented in full detail in part II of the paper [32]. Here, we just mention that our truncated Lévy model provides accurate fits to raw measurement data across the entire 1–20 MHz modulation range without requiring any frequency dependent ‘effective’ thermal parameters. This identification produced $\alpha = 1.67$ for InGaAs and $\alpha = 1.69$ for SiGe, once again in close agreement with previously derived values.

Conclusions

In summary, we investigated the fundamental dynamics of 1D quasi-ballistic heat conduction. Analytical solutions of the BTE with ab initio phonon properties reveal the distinct emergence of Lévy superdiffusion in semiconductor alloys. Simple algebraic expressions capture the intricate relationships between the superdiffusive time exponent, order of the dominant phonon scattering mechanism, cumulative conductivity function and fractal dimension of the Lévy transport. These interconnections illustrate the rich information that is contained within phonon relaxation time spectra, in complement to the traditionally used MFP counterparts. Our findings lend fundamental physical support to a novel truncated Lévy heat formalism we have developed, enabling direct experimental measurements of the
fractal dimension and fractional diffusivity of the quasi-ballistic thermal transport.

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[1] Z.J. Ziman, Electrons & Phonons: The Theory of Transport Phenomena in Solids. (Oxford University Press, USA, 2001).
[2] A.J. Minnich, G. Chen, S. Mansoor, and B.S. Yilbas, Phys. Rev. B 84, 235207 (2011).
[3] Y.K. Koh and D.G. Cahill, Phys. Rev. B 76, 075207 (2007).
[4] M.E. Siemens, Q. Li, R. Yang, K.A. Nelson, E.H. Anderson, M.M. Murnane, and H. C. Kapteyn, Nature Mater. 9, 26 (2010).
[5] A.J. Minnich, J.A. Johnson, A.J. Schmidt, K. Esfarjani, K. M.S. Dresselhaus, and G. Chen, Phys. Rev. Lett. 107, 095901 (2011).
[6] J.A. Johnson, A.A. Maznev, J. Cuffe, J.K. Eliason, A.J. Minnich, T. Kehoe, C.M. Sotomayor Torres, G. Chen, and K.A. Nelson, Phys. Rev. Lett. 110, 025901 (2013).
[7] K.T. Regner, D.P. Sellan, Z. Su, C.H. Amon, A.J.H. McGaughey, and J.A. Malen, Nat. Commun. 4, 1640 (2013).
[8] K.C. Collins, A.A. Maznev, Z. Tian, K. Esfarjani, K.A. Nelson, and G. Chen, J. Appl. Phys. 114, 104302 (2013).
[9] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[10] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
[11] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
[12] A. Togo, F. Oba, and I. Tanaka, Phys. Rev. B 78, 134106 (2008).
[13] Y. Wang, J. J. Wang, W. Y. Wang, Z. G. Mei, S. L. Shang, L. Q. Chen, and Z. K. Liu, J. Phys.: Condens. Matter 22, 202201 (2010).
[14] W. Li, J. Carrete, N. A. Katcho, and N. Mingo, Comp. Phys. Commun. 185, 17471758 (2014)
[15] W. Li, L. Lindsay, D. A. Broido, D. A. Stewart, and N. Mingo, Phys. Rev. B 86, 174307 (2012).

[16] N. A. Katcho, N. Mingo, and D. A. Broido, Phys. Rev. B 85, 115208 (2012).

[17] S.-I. Tamura, Phys. Rev. B 27, 858 (1983).

[18] D.P. Gaver, Operations Research 14, 444 (1966).

[19] H. Stehfest, Commun. ACM 13, 47 (1970).

[20] R. Metzler and J. Klafter, Phys. Rep. 339, 1 (2000).

[21] A.J. Minnich, Phys. Rev. Lett. 109, 205901 (2012).

[22] G. Trefan, E. Floriani, B.J. West, and P. Grigolini, Phys. Rev. E 50, 2564 (1994).

[23] G.M. Viswanathan, S.V. Buldyrev, S. Havlin, M.G. E. da Luz, E.P. Raposo, and H.E. Stanley, Nature 401, 911 (1999).

[24] M.A. Lomholt, T. Ambjörnsson, and R. Metzler, Phys. Rev. Lett. 95, 260603 (2005).

[25] D. del Castillo-Negrete, Phys. Fluids 10, 576 (1998).

[26] R.N. Mantegna and H.E. Stanley, Nature 376, 46 (1995).

[27] J. Klafter, M.F. Shlesinger, and G. Zumofen, Physics Today 49, 33 (1996).

[28] K. Esfarjani, G. Chen, and H.T. Stokes, Phys. Rev. B 84, 085204 (2011).

[29] M.G. Holland, Phys. Rev. 132, 2461 (1963).

[30] A. Ward and D.A. Broido, Phys. Rev. B 81, 085205 (2010).

[31] M.F. Shlesinger, J. Klafter, and G. Zumofen, Am. J. Phys. 67, 1253 (1999).

[32] B. Vermeersch, A.M.S. Mohammed, G. Pernot, Y. Koh, and A. Shakouri, Superdiffusive heat conduction in semiconductor alloys – II. Truncated Lévy formalism for experimental analysis. Submitted to Phys. Rev. B. Preprint available online at.

[33] C. Hua and A.J. Minnich, Phys. Rev. B 89, 094302 (2014).

[34] I. Koponen, Phys. Rev. E 52, 1197 (1995).