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L2 – Light-matter interaction

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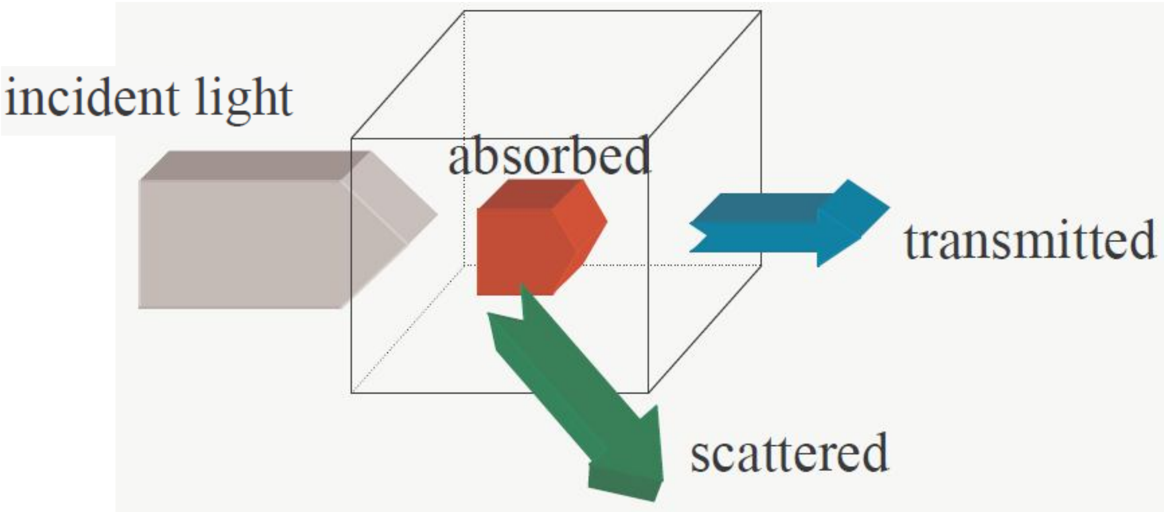
The interaction of light with matter can take many forms.

Consider a beam of light on a material

It can be
(a) scattered,
(b) absorbed, or
(c) transmitted



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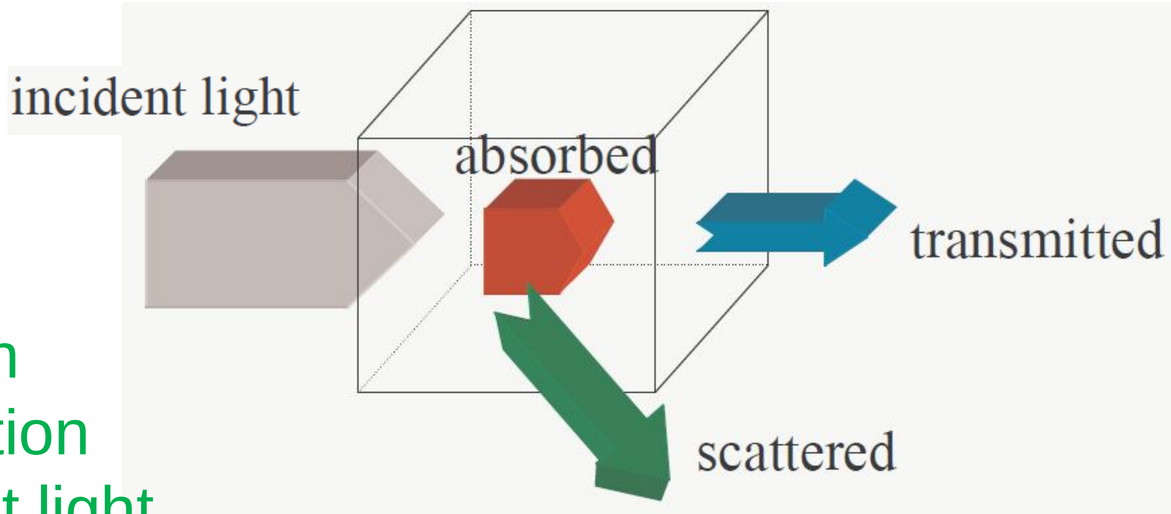

Light emerges in
a different direction
from the incident light

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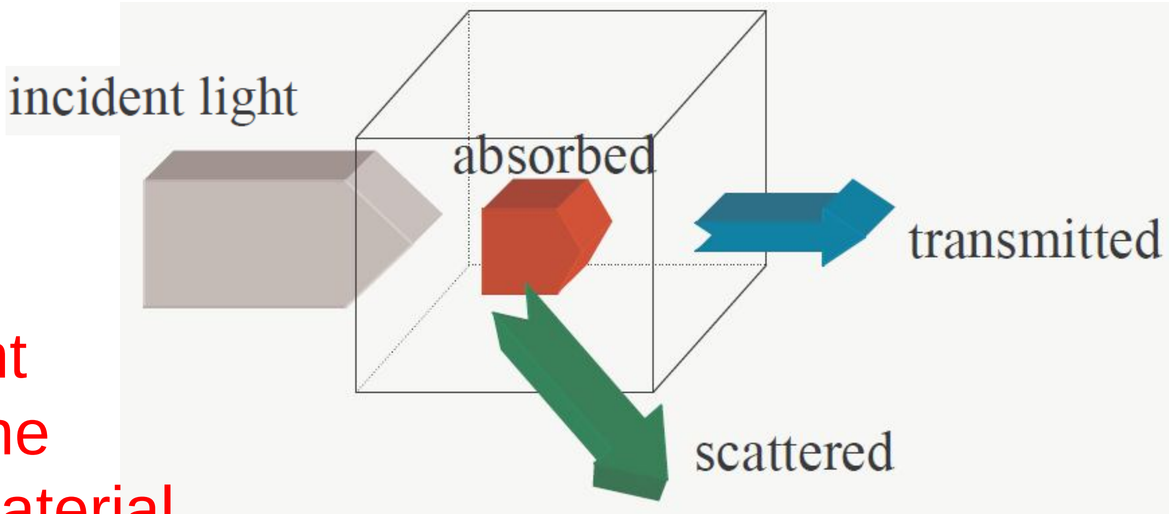

Energy from light is absorbed in the volume of the material

The interaction of light with matter can take many forms.

Consider a beam of light on a material

It can be
(a) scattered,
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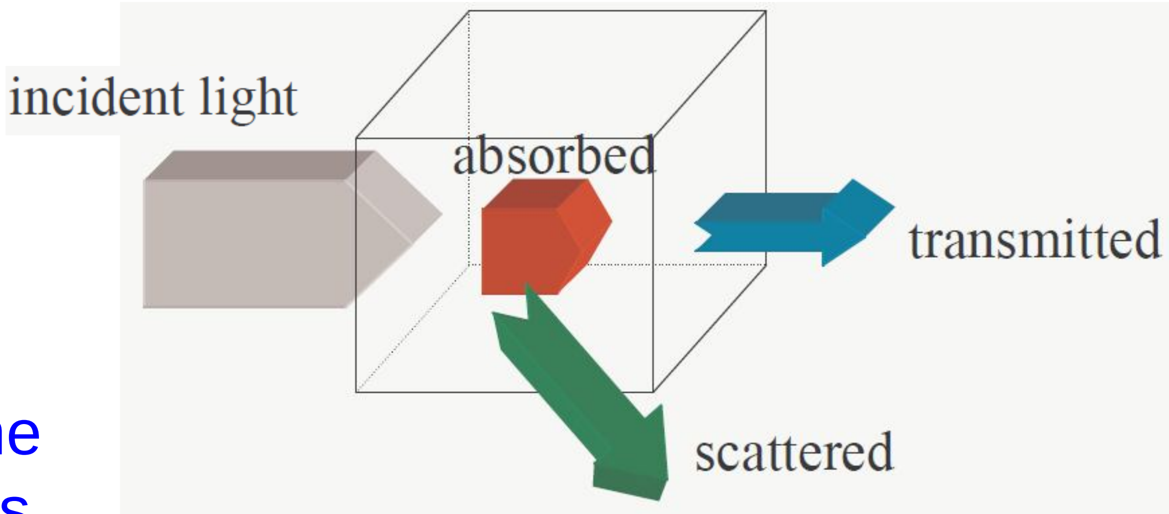
(c) transmitted

Light emerges propagating in the same direction as the incident light



Optical Excitation

⇓

Absorption

⇓

Excited State Relaxation

⇓

Temperature Change ⇔ *Density Change* ⇔ *Pressure Change*

(*Thermal Diffusion*) (*Acoustic Wave*)

⇓

Optical Probe ⇒ *Refractive Index Change* ⇒ *Photothermal Signal*

Optical radiation (light), usually from a laser or LED, is used to excite a sample. The sample absorbs some of this radiation.

Optical Excitation

⇓

Absorption

⇓

Excited State Relaxation

⇓

Temperature Change ⇔ *Density Change* ⇔ *Pressure Change*

(*Thermal Diffusion*) (*Acoustic Wave*)

⇓

Optical Probe ⇒ *Refractive Index Change* ⇒ *Photothermal Signal*

Absorption of radiation form the excitation source followed by radiative and/or non-radiative excited state relaxation

Optical Excitation

⇓

Absorption

⇓

Excited State Relaxation

⇓

Temperature Change ⇔ *Density Change* ⇔ *Pressure Change*

(*Thermal Diffusion*) (*Acoustic Wave*)

⇓

Optical Probe ⇒ *Refractive Index Change* ⇒ *Photothermal Signal*

Non-radiative relaxation resulting in an increase in the internal energy. The increased internal energy results in a temperature, pressure, and density changes in the sample.

Optical Excitation

⇓

Absorption

⇓

Excited State Relaxation

⇓

Temperature Change ⇔ *Density Change* ⇔ *Pressure Change*

(*Thermal Diffusion*) (*Acoustic Wave*)

⇓

Optical Probe ⇒ *Refractive Index Change* ⇒ *Photothermal Signal*

The temperature changes will induce thermal diffusion process in the sample.

Optical Excitation

⇓

Absorption

⇓

Excited State Relaxation

⇓

Temperature Change ⇔ *Density Change* ⇔ *Pressure Change*

(*Thermal Diffusion*) (*Acoustic Wave*)

⇓

Optical Probe ⇒ *Refractive Index Change* ⇒ *Photothermal Signal*

The density change is primarily responsible for the refractive index change.

Optical Excitation

⇓

Absorption

⇓

Excited State Relaxation

⇓

Temperature Change ⇔ *Density Change* ⇔ *Pressure Change*

(*Thermal Diffusion*) (*Acoustic Wave*)

⇓

Optical Probe ⇒ *Refractive Index Change* ⇒ *Photothermal Signal*

The pressure change is primarily responsible for the acoustic wave generation.

Pulsed excitation sources produce transient signals. These signals are a maximum immediately following sample excitation and decay as the sample approached equilibrium through thermal diffusion. The transient signals last from a few microseconds in the gas phase to several milliseconds in condensed phases. The time duration is inversely proportional to the thermal conductivity of the media since thermal diffusion or conduction removes energy from the sample and more importantly, distributes the energy throughout the sample.

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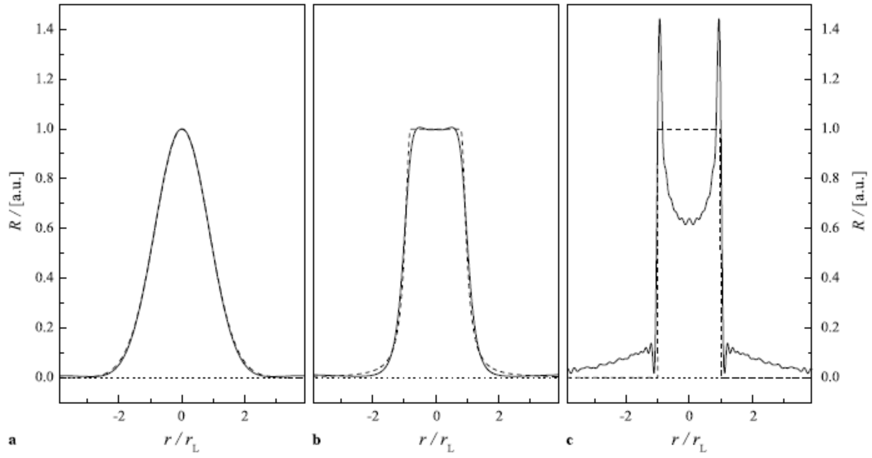
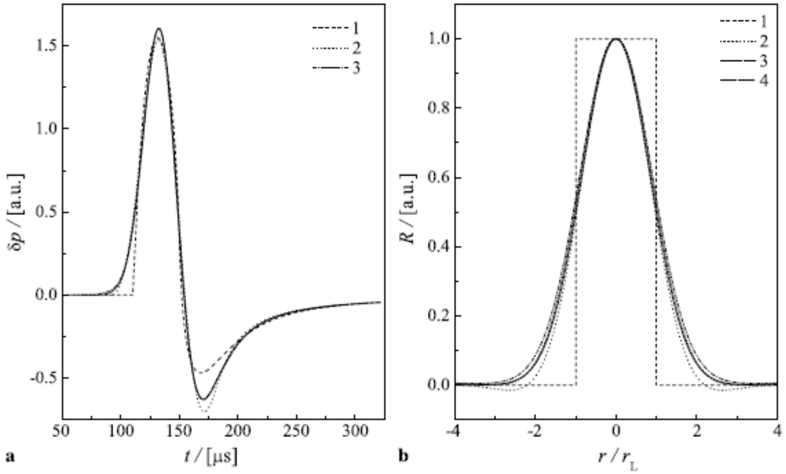
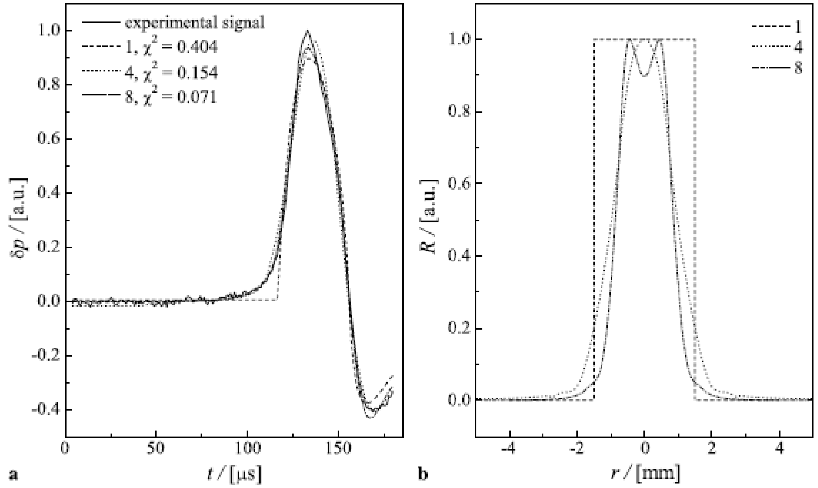
Time domain
pulsed photoacoustic

Test sample, 82 um







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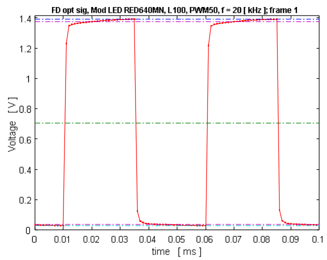
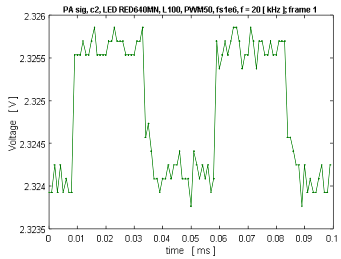
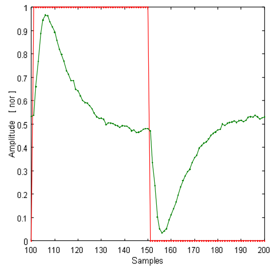
Excitation sources may also be modulated. Chopped or oscillatory excitation produces oscillating signals. The resulting signals can be processed using band pass filters or lock-in amplifiers. The magnitudes of the oscillating signals depend on sample absorbance, the frequency of excitation, and thermal conductivity of the medium.







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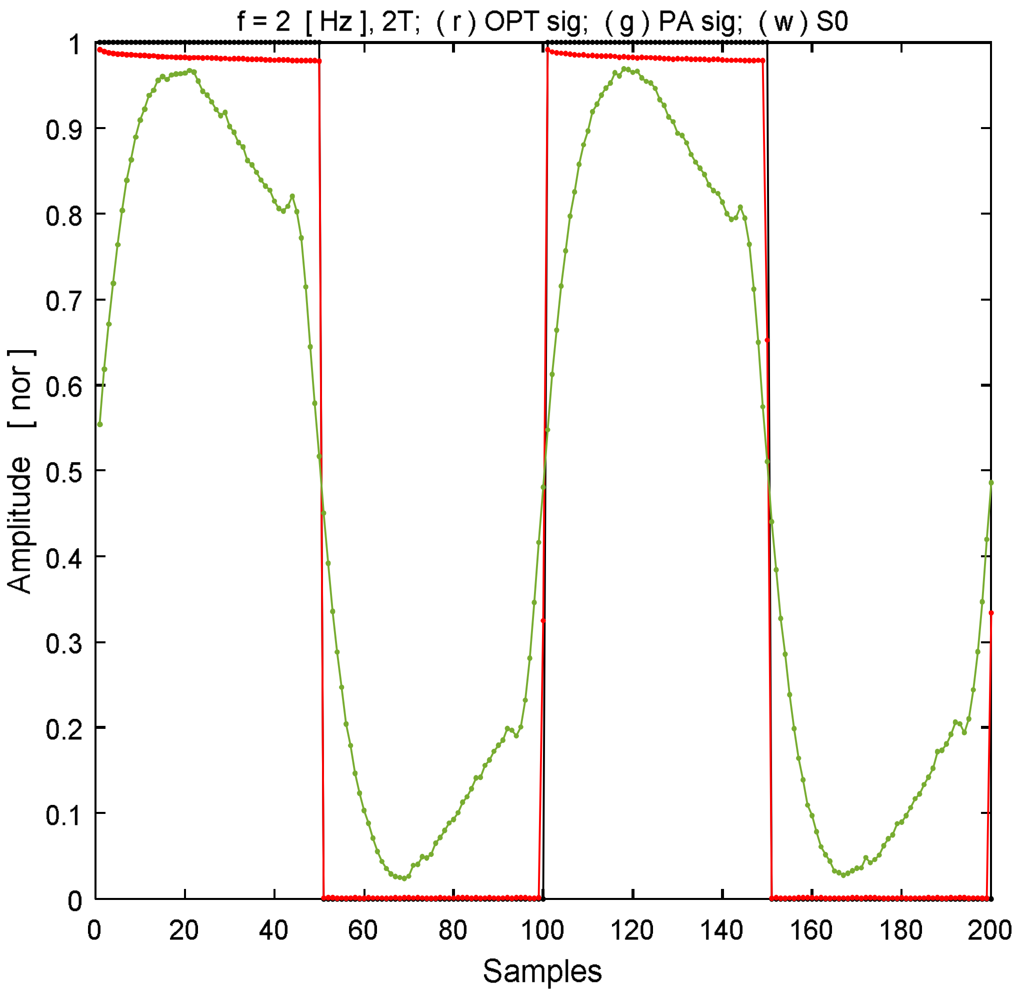
Time domain
modulated photoacoustic

Test sample, 82 um

Optical excitation signal

Photoacoustic signal



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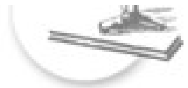

With modulated excitation, signal magnitudes are proportional to sample absorbance but decrease with increasing frequency. In addition to the signal amplitude information, phase-sensitive lock-in analyzers also produce signal-to-excitation phase-shift information. The frequency dependent phase-shift information is essentially equivalent to that contained in the time-dependent signal transients obtained using pulsed excitation.

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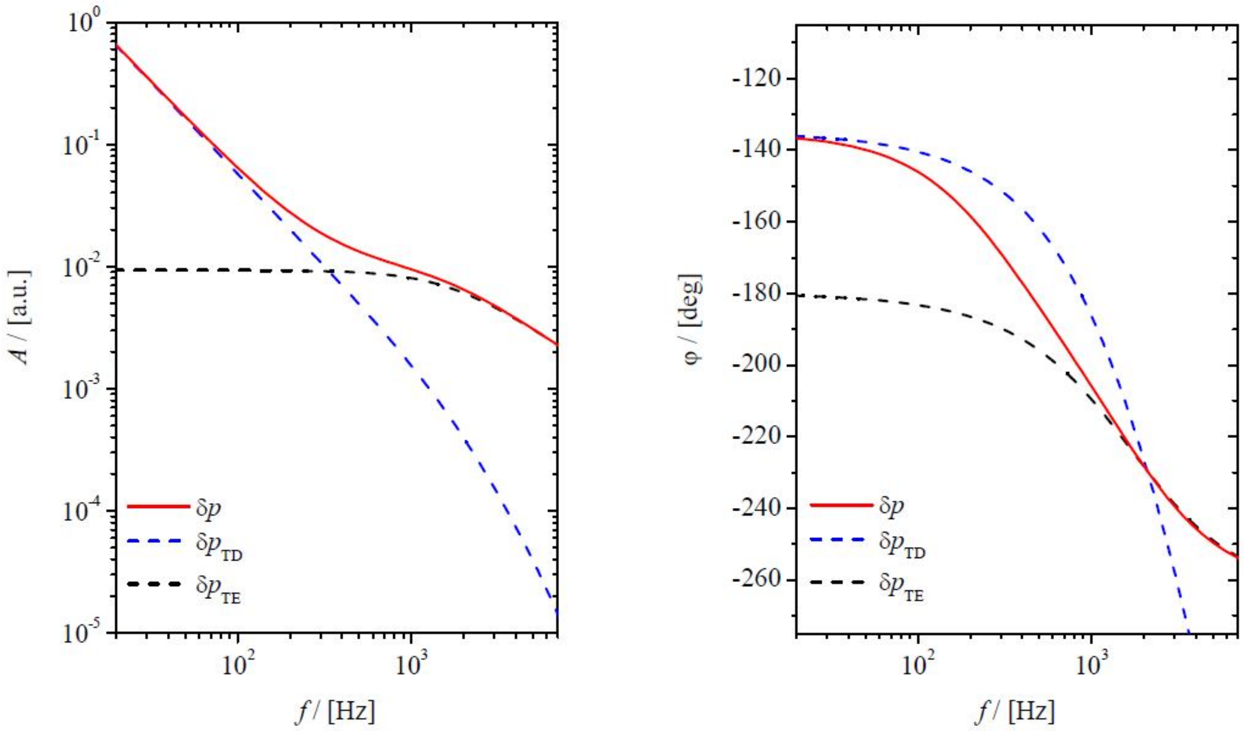
Frequency domain modulated photoacoustics



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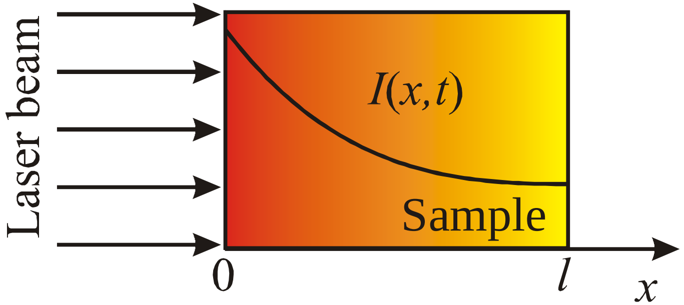
$$j_Q(x,t) = -k\frac{\partial T}{\partial x}$$

$$\frac{\partial j_Q}{\partial x} + \rho c\frac{\partial T}{\partial t} = 0$$

$$\frac{\partial T}{\partial t} = D_T\frac{\partial^2 T}{\partial x^2}$$

$$D_T = \frac{k}{\rho c}$$

Sample Heating



$$I = I_0 \,\mathrm{Re}\left(1 + e^{i\omega t}\right)$$

Modulated

$$T(x,t) = T_{dc}(x) + \mathrm{Re}\left(T(x)e^{i\omega t}\right)$$

Steady state

$$\frac{\partial^2 T_{dc}}{\partial x^2} = 0$$

$$\frac{\partial^2 T}{\partial x^2} - \frac{i\omega}{D_T}T = 0$$

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Temperature Distributions – Surface Absorbers

$$T_{dc} = ax + b$$

Steady state component

$$T(x) = Ae^{\sigma x} + Be^{-\sigma x}$$

Modulated component

$$\sigma = \sqrt{\frac{i\omega}{D_T}} = \frac{1+i}{\mu}$$

Thermal wave vector

$$\mu = \sqrt{\frac{2D_T}{\omega}}$$

Diffusion length

Total temperature

$$T(x,t) = ax + b + \mathrm{Re}\left(Ae^{i(\sigma x + \omega t)} + Be^{-i(\sigma x - \omega t)} \right)$$

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Temperature Distributions – Surface Absorbers
Modulated Component Calculation

$$T(x,t) = A_1 e^{\sigma_i x + i\,\omega t} + A_2 e^{-\sigma_i x + i\,\omega t}$$

$$\text{a)}\; -k \frac{\mathrm{d}T(x,t)}{\mathrm{d}x}\bigg|_{x=0} = I_0 e^{i\,\omega t} \qquad \text{b)}\; -k \frac{\mathrm{d}T(x,t)}{\mathrm{d}x}\bigg|_{x=l} = 0$$

$$T(x,t) = \frac{I_0 \cosh[\sigma(x-l)]}{k\sigma \sinh(\sigma l)} e^{i\,\omega t}$$

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Temperature Distributions – Volume Absorbers
Modulated Component Calculation

$$D_T \frac{\partial^2 T}{\partial x^2} - \frac{\partial T}{\partial t} = -\frac{D_T}{k} \beta I_0 e^{-\beta x + i\,\omega t},$$

$$\text{a)} \; -k \left.\frac{\partial T}{\partial x}\right|_{x=0} = 0 \qquad \text{b)} \; -k \left.\frac{\partial T}{\partial x}\right|_{x=l} = 0$$

$$T_{\text{therm}}(x) = \frac{I_0}{k} \frac{\varepsilon\text{-}\varepsilon_g}{\varepsilon} \frac{\beta}{\beta^2 - \sigma_i^2} \left[b \frac{e^{\sigma_i (x-l)} + e^{-\sigma_i (x-l)} - e^{-\beta l}\left(e^{\sigma_i x} + e^{-\sigma_i x}\right)}{e^{\sigma_i l} - e^{-\sigma_i l}} - e^{-\beta x} \right]$$

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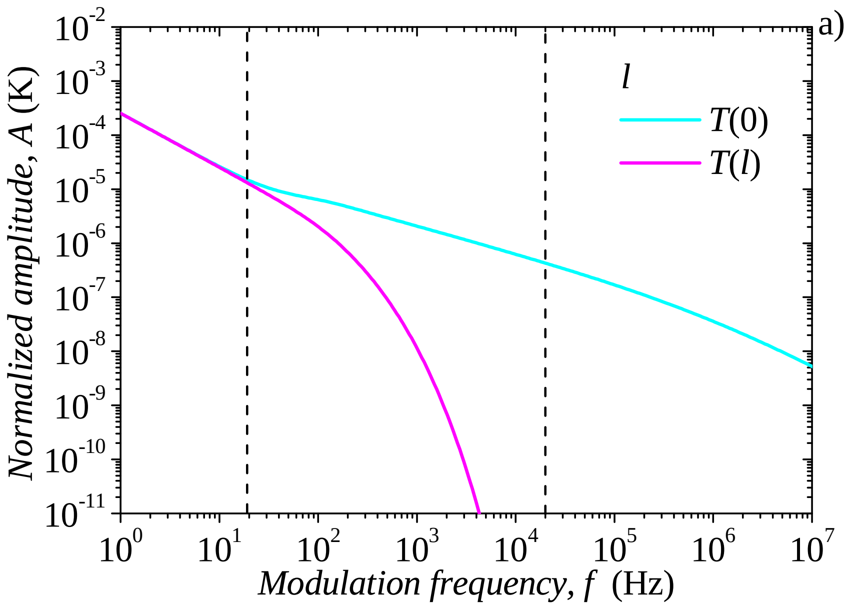
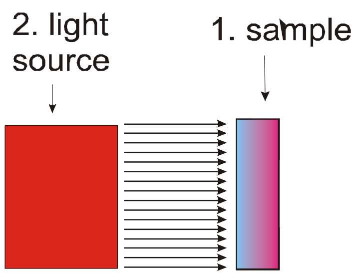
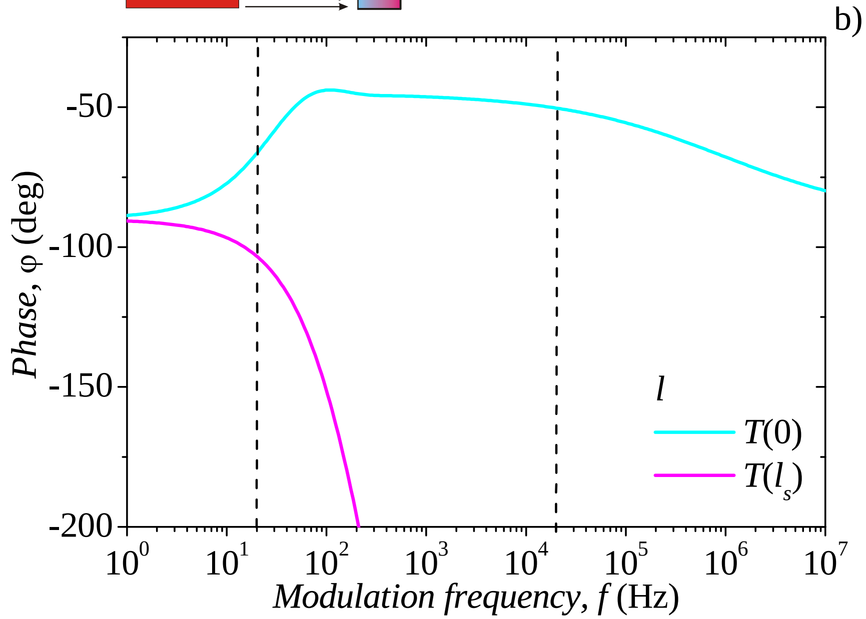
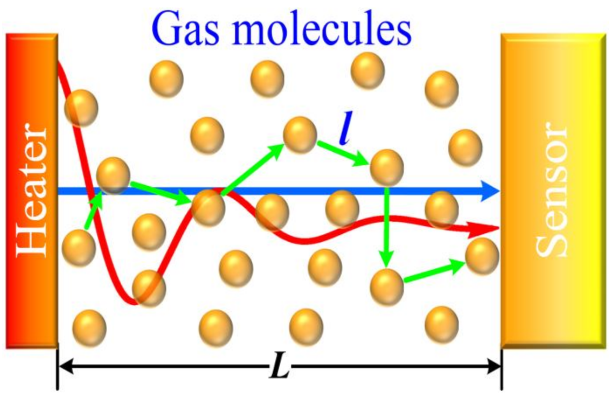
Temperature Distributions – at front (0) and back (*l*)



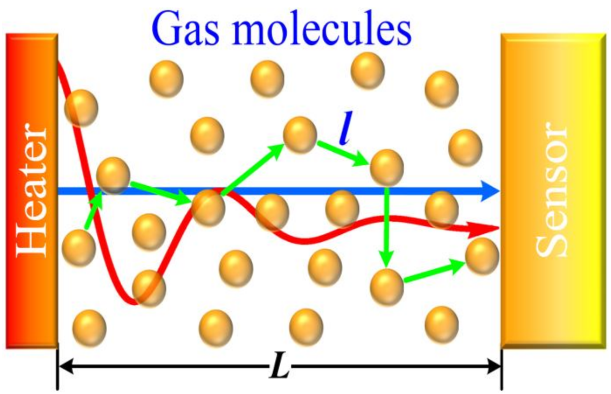




Fourier law of heat conduction has provided extensive and successful results in the study of heat conduction and is supported by a great amount of experimental data for most of the analyzed experimental conditions. However, when very short times scales, high heat fluxes and very low temperatures are involved, the validity of Fourier approach has been questioned.



Its main drawback comes from the fact that Fourier law predicts an infinite speed of heat propagation, such that a thermal disturbance in any part of a medium results in an instantaneous perturbation anywhere else in the sample. This fundamental problem is due to the fact that Fourier law establishes explicitly that both the temperature gradient and heat flux start instantaneously when one of them is imposed over a medium.



In this way, the heat flux and the temperature gradient are simultaneous and therefore there is no difference between the cause and the effect of the heat flow. Considering that heat transport is due to microscopic motion and collisions of electrons, phonons, atoms and molecules; it is clear that the condition on the velocity of heat transport under Fourier law is physically not admissible. These facts indicate that Fourier law may be the asymptotic limit of a more general law.

Fourier law

$$j_Q(x,t) = -k\frac{\partial T}{\partial x}$$

$$\frac{\partial j_Q}{\partial x} + \rho c\frac{\partial T}{\partial t} = 0$$

$$\boxed{\frac{\partial T}{\partial t} = D_T\frac{\partial^2 T}{\partial x^2}}$$

predicts an infinite speed (or velocity) of heat transfer (propagation)

Modified Fourier law

$$\tau\frac{\partial j_Q}{\partial t} + j_Q = -k\frac{\partial T}{\partial x},$$

τ is the thermal relaxation time

$$\tau\frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = D_T\frac{\partial^2 T}{\partial x^2},$$

$$\boxed{\frac{1}{v_T^2}\frac{\partial^2 T}{\partial t^2} + \frac{1}{D_T}\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2},}$$

gives the finite value of the heat transfer speed $\boxed{v_T = \sqrt{D/\tau}}$

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It can be observed that for low frequencies ($2\pi f\tau \ll 1$), the behavior of the spectra predicted by the Fourier and modified Fourier approach are similar, in contrast for higher frequencies ($2\pi f\tau \gg 1$), where the modified Fourier effects are dominant.