Chapter 6

On thermal relaxation of non-equilibrium electrons in the metal and the semiconductor nano-scale samples.

6.1 Abstract

In this Chapter we consider; (a) thermal relaxation of non-equilibrium electrons in the metal nano-scale samples (2D films and nanoparticles), (b) the energy relaxation between non-degenerate electrons and the phonons (electron-(multi)phonon interaction). The fundamental assumption[50] of the theory of hot electrons in metal nano-particles is that, when the particle size is of the order of electron mean free path, the main channel of hot electron energy loss is through surface-phonon generation, rather than bulk phonon generation. A calculation for the hot electron relaxation by the generation of surface-phonons is given, assuming that electrons and surface-phonons are described by their equilibrium fermi and bose distribution functions. The assumption is valid because time required to establish equilibrium in the electron gas is much less than the time for achieving equilibrium between the electrons and the surface-phonons(see
introduction). The expressions obtained for low temperature and high temperature regimes are inversely proportional to the radius of the particle. This shows that size dependency of electron surface-phonon energy exchange arises from the geometric effect.

6.2 Relaxation between electrons and surface phonons in nanoscale metal films.

Consider a degenerate electron distribution at temperature $T_e$ and a phonon distribution (in 2-D) at temperature $T$ ($T < T_e$). Our aim is to calculate how much energy is transferred/second/volume from the hot degenerate electron distribution to the relatively cold phonon gas. The equilibrium distributions for electrons and phonons are

$$N_k = \frac{1}{e^{\beta_e (\epsilon - \epsilon_0)} + 1}, \beta_e = \frac{1}{k_B T_e}$$

$$N_f = \frac{1}{e^{\beta \hbar \omega_f} - 1}, \beta = \frac{1}{k_B T}$$

(6.1)

Energy and momentum conservation conditions gives
On simplifying
\[ \frac{\hbar^2}{2m} [2k' \sin \theta \cos (\phi - \phi') - f] = h \omega. \] (6.3)

Where \( \phi \) is the angle between \( k_x \)-axis and plan of incidence, \( \phi' \) is the angle between scattered phonon direction and \( k_x \)-axis, and \( \theta \) between incident electron direction and \( k_z \) direction as shown in FIG.1.

The probability \( W \) per unit time that the electron in a state with wave vector \( k' \) will scatter to a state with wave vector \( k \) by emitting a phonon of wave vector \( f \) is:

\[ W(k' - f; k') = \alpha \delta (\varepsilon_{k'} - \varepsilon_k - h \omega), \quad \alpha = (\pi U_s^2/\rho VS_s^2). \]

With \( U_s \) as the electron surface-phonon interaction constant. Here \( \rho \), \( V \) and \( S_s \) is the metal density, unit cell volume and surface sound speed respectively. The change per unit time per unit volume in the number of surface-phonons with wave vector \( f \) and energy \( h \omega \) is (Bloch-Boltzmann-Peierls formula):

\[ \dot{N}_f = \int \alpha \omega_f \{(N_f + 1)N_{k'}(1 - N_k) - N_fN_k(1 - N_{k'})\} \delta (\varepsilon_{k'} - \varepsilon_k - h \omega)(2/(2\pi)^3) d^3k'. \] (6.4)

Using the energy and momentum conservation equations, the delta function can be written as \( \delta (\varepsilon_{k'} - \varepsilon_k - h \omega) = \frac{2m}{\hbar^2} \delta [(2k' \sin \theta \cos (\phi - \phi') - f) - \frac{2ms}{\hbar}], \) and for a metal, we have \( (f \sim 10^9 m^{-1}) \gg (\frac{2ms}{\hbar} \sim 10^7 m^{-1}). \) So the above equation i.e.,(Eq.5) is

\[ \dot{N}_f = \int \alpha \omega_f \{(N_f + 1)N_{k'}(1 - N_k) - N_fN_k(1 - N_{k'})\} \delta (2k' \sin \theta \cos (\phi - \phi') - f) \]
\[ \times \frac{4mk'^2}{2\pi^2 \hbar^2} \sin \theta d\theta d\phi dk'. \] (6.5)

\[ \dot{N}_f = \left[ \frac{4m\alpha \hbar}{(2\pi \hbar)^3} \right] \int_{k_m}^{\infty} [(N_f + 1)N_{k'}(1 - N_k) - N_fN_k(1 - N_{k'})] k'^2 dk' \]
\[ \times \int_0^{\pi/2} \sin \theta d\theta \int_0^{2\pi} \delta [2k' \sin \theta \cos (\phi - \phi') - f] d\phi. \] (6.6)
The last integral in the above equation is

\[ \int_0^{2\pi} \delta[2k' \sin \theta \cos(\phi - \phi') - f] d\phi = \frac{1}{|2k' \sin \theta|} \]

\[ \times \left\{ \frac{1}{|\sin(\phi_1 - \phi')|} \right\}^{2\pi} \delta(\phi - \phi_1) d\phi + \frac{1}{|\sin(\phi_2 - \phi')|} \right\}^{2\pi} \delta(\phi_2 - \phi') d\phi \]

\[ - \frac{1}{k' \sin \theta \sqrt{(1 - f^2/(4k'^2 \sin^2 \theta))}} \]  

(6.7)

\[ \dot{N}_f = \left[ \frac{m\alpha_s}{(2\pi \hbar)^2} \right] \int_{k_m}^{\infty} [(N_f + 1)N_k'(1 - N_k) - N_f N_k(1 - N_k')] k' dk' \]  

(6.8)

The above mentioned process will always happen, as from energy and momentum conservation, \( \sin \theta \approx f/2k' \), which holds good in a metal as \( f < k' \). By inserting for \( N_e \) and \( N_f \) in equation (5.8) we get

\[ \dot{N}_f = \left[ \frac{m\alpha_s}{(2\pi \hbar)^2} \right] \left( \frac{e^\beta \hbar \omega_f - e^\beta \hbar \omega_f}{e^\beta \hbar \omega_f - 1} \right) \int_{k_m}^{\infty} \frac{e^\beta (\epsilon_k' - \hbar \omega_f - \epsilon_0)}{(e^\beta (\epsilon_k' - \hbar \omega_f - \epsilon_0) + 1)(e^\beta (\epsilon_k' - \hbar \omega_f - \epsilon_0) + 1)} \]  

(6.9)

Here, we will make an approximation to solve the integral in the above equation. The first approximation is that the phonon energy \( \hbar \omega_f (meV) \ll k_BT_e(eV) \), the electron energy. So, \( \beta \hbar \omega_f \sim 0 \). With this the integral in Eq.(5.9) is

\[ \frac{m}{\beta \hbar^2} \left[ \frac{1}{e^\beta (k_m) + 1} \right] , \ f(k_m) = \beta (\frac{\hbar^2 k_m^2}{2m} - \epsilon_0). \]

As \( \frac{\beta \hbar^2 k_m^2}{2m} \ll |\beta | \epsilon_0 | \), the quantity in the square brackets is order of unity. Finally, the integral in Eq.(5.9) is \( \frac{\hbar \omega_f}{\hbar} (1/\beta \hbar \omega_f) \sim \frac{\hbar \omega_f}{\hbar} (1/(e^\beta \hbar \omega_f - 1)) \). With all this Eq.(5.9) takes the form

\[ \dot{N}_f = \left[ \frac{m^2 \alpha \hbar \omega}{(2\pi \hbar^2)^2} \right] \left( \frac{e^{\beta \hbar \omega_f} - e^\beta \hbar \omega_f}{(e^{\beta \hbar \omega_f} - 1)(e^\beta \hbar \omega_f - 1)} \right). \]  

(6.10)

The energy transferred by the electrons to the surface-phonons per unit volume per unit time is

\[ U_{\text{surface}} = \frac{a^2}{(2\pi)^2} \int_0^{f_D} \dot{N}_f \hbar \omega_f 2\pi f df, \ a = \text{lattice constant}, \]  

(6.11)

where \( f_D \) is the Debye wave vector for the surface phonons. From Eq.(5.10) and Eq.(5.11) with relations \( \omega_D = S_s f_D \), \( \hbar \omega_D = k_BT_D \) and setting \( x = \hbar \omega_f/k_BT_e \), we
get

\[
U_{\text{surface}} = \left[ \frac{\pi U_e^2 m^2}{(2\pi)^3 \hbar^2 \rho \alpha S_b^3} \right] \left( \frac{k_B T_{Ds}}{\hbar} \right)^4 \left\{ \left( \frac{T_e}{T_{Ds}} \right)^4 \int_0^{T_{Ds}/T_e} \frac{x^3}{e^x - 1} dx - \left( \frac{T}{T_{Ds}} \right)^4 \int_0^{T_{Ds}/T} \frac{x^3}{e^x - 1} dx \right\}. \tag{6.12}
\]

Here, \( T_{Ds} \) is the surface Debye temperature. Now the equation (5.12) can be simplified in two special cases, first, for low electron and phonon temperatures as compared to Debye temperature, i.e., \( T, T_e \ll T_{Ds} \), Eq.(5.12) reduce to

\[
U_{\text{surface}} = \left[ \frac{\pi U_e^2 m^2}{3(2\pi)^3 \hbar^2 \rho \alpha S_b^3} \right] \left( \frac{k_B T_{Ds}}{\hbar} \right)^4 \left[ \left( \frac{T_e}{T_{Ds}} \right)^4 \int_0^{\infty} \frac{x^3}{e^x - 1} dx \right]. \tag{6.13}
\]

An important point to be noted in the above equation is that the electron to phonon energy transfer rate depends upon 4th power of electron and phonon temperatures as compared to the corresponding case in the bulk (there it is 5th power of electron and phonon temperatures[51]). In second special case, when \( T_e, T \gg T_{Ds} \), we get

\[
U_{\text{surface}} = \left[ \frac{\pi U_e^2 m^2}{3(2\pi)^3 \hbar^2 \rho \alpha S_b^3} \right] \left( \frac{k_B T_{Ds}}{\hbar} \right)^4 \left[ \frac{T_e}{T_{Ds}} \right] \int_0^{\infty} \frac{x^3}{e^x - 1} dx. \tag{6.14}
\]

The above equation (Eq.(5.14)) is the basics of what is called the two temperature model. Next, we calculate the surface Debye temperature \( T_{Ds} \). Clearly, for two acoustical modes per atom we have

\[
\frac{L^2}{(2\pi)^2} \int_0^{J_{Ds}} 2\pi f df = 2N_{\text{surface}}, \tag{6.15}
\]

which gives \( J_{Ds} = \sqrt{8\pi n^2/3} \), \( n \) is the number density per unit volume. Now, for the bulk case[51]

\[
U_{\text{bulk}} = \left[ \frac{\pi U_e^2 m^2}{2(2\pi)^3 \hbar^2 \rho \alpha S_b^4} \right] \left[ T_e - T \right]. \tag{6.16}
\]

From Eq.(5.14) and Eq.(5.16) we have

\[
\frac{U_{\text{surface}}}{U_{\text{bulk}}} = 2\pi (8\pi)^{3/2} \frac{U_e}{U_b} \frac{\rho S_b^4}{\omega_{Ds}^4} = \gamma_0 \left[ \frac{U_e}{U_b} \right]^2 \frac{1}{\alpha n^{1/3}}. \tag{6.17}
\]

83
6.2.0.1 results

For a gold metal film, assuming $U_s = U_b$, with $a = 4.1 \times 10^{-10} m$, $\rho = 19.3 \times 10^3 kg/m^3$, $n = 5.9 \times 10^{28} m^{-3}$, $T_D = 185 K$, $\omega_D = 2.42 \times 10^{13} rads/sec$, the above ratio is $\sim 0.088$ or about 9 percent of electron energy goes to surface phonon modes.

6.3 Hot electron relaxation in a metal nanoparticle: electron surface-phonon interaction.

With the advent of femtosecond lasers, it has become possible to investigate non-equilibrium phenomena in bulk metals [55, 56, 57, 58, 59, 60] and metal nanoparticles[61, 62, 63, 64]. The electrons can be preferentially excited keeping lattice at the same temperature due to their much smaller electronic heat capacity as compared to that of phonons. The pump-probe femtosecond spectroscopy permits a direct access to the internal thermalization of the electron gas. The experimental results are explained on the basis of classical two temperature model[60], in which the metal is treated as a system, composed of two coupled subsystems, one Fermi-Dirac distributed electronic subsystem at a high temperature $T_e$, and Bose-Einstein distributed phonon subsystem at a lower temperature $T$. The energy transfer takes place from electronic subsystem to phononic subsystem. But their distribution functions remain at their respective equilibrium values. The two temperature model holds good for the bulk metal case [51, 52]. But when this model is applied to metal nanoparticles one should consider the following points:

1) in quantum size regime when the particle size is less than 5nm, the band structure splits into discrete levels and the equilibrium partition function of electrons will not be the function for the bulk. The function depends upon evenness or oddness of the number of electrons in the particle [65];

2) Since electronic mean free path(several hundred angstroms in metals) is more than the particle size, even at high temperatures, the scattering events from the surface
of the particle will take place. If the time between two scattering events is less than the electronic internal thermalization time, one has to use non-equilibrium distribution functions to consider the problem of energy transfer from electrons to phonons[66];

(3)In quasi-continuum regime (particle size more than 10 nm) the main channel of electron energy loss is through electron surface interaction, but the energy spectrum of electronic translational motion will be quasi-continuous. It can lose energy to surface modes of vibration or to external vibrational modes to which it can possibly couple due to sudden change of ionic potential distributions at the boundary of the particle. The present calculation is done in quasi-continuum regime, considering point (3). The points (1) and (2) are not included in the present calculation. It is assumed that two temperature model holds good, but replacing bulk phonons by surface phonons. This will not be applicable for small time scales when the electron distribution function is not Fermi-Dirac. It is to be noted that, as the hot electrons lose their energy to the lattice, and after some time, the lattice will become very hot, this heating will reduce drastically the electron mean free path and cause the failure of the applicability of the model. But for the case of metal particles it takes about 2 psec-seconds to transfer the energy to the lattice bath, so the present model is applicable within this time scale. The dispersion relation used for the surface phonons is linear under Debye approximation and surface sound speed is determined in terms of elastic continuum theory assuming stress-free boundaries [67].

6.3.1 Electron surface-phonon interaction within two temperature model

Consider the case of homogeneously (no spatial diffusion) photo-excited metal nanoparticle, consisting of two inter-penetrating subsystems namely electronic (at temperature $T_e$) and surface-phononic (at temperature $T \ll T_e$). We calculate the energy transfer rate $U_{surface}$ from electronic subsystem to phononic subsystem at the surface considering one phononic process. The equilibrium distribution functions of electrons and
phonons are \(1/(e^{\beta e} - 1)\) respectively, here, \(\beta_e = 1/KT_e\) and \(\beta = 1/KT\).

We proceed on similar lines as in the previous section. We use the conservation of energy and momentum for one phonon scattering as shown in Fig. (2)). The change per unit time in the number of surface-phonons with wave vector \(f\) and energy \(\hbar \omega\) is

\[
\dot{N}_f = \int \alpha \omega_f \{(N_f + 1)N_{k'}(1 - N_k) - N_f N_k(1 - N_{k'})\} \delta(\varepsilon_{k'} - \varepsilon_k - \hbar \omega)(2V/(2\pi)^3)d\tau_{k'}.
\]  

We obtain the number of phonons generated per second

\[
\dot{N}_f = \left[\frac{m^2 \alpha s V \omega_f}{(2\pi \hbar)^2 \hbar}\right] \frac{e^{\beta_f \hbar \omega_f} - e^{\beta \hbar \omega_f}}{(e^{\beta \hbar \omega_f} - 1)(e^{\beta_f \hbar \omega_f} - 1)}.
\]  

Now, we calculate the energy transferred by electrons per unit volume per unit time to surface phonons. We use the elastic continuum theory assuming stress-free boundaries [67], for density of states on the particle surface, Clearly

\[
U_{\text{surface}} = \int_0^{\omega_{D_s}} \dot{N}_f \hbar \omega_f (D_s(\omega_f)/(4/3)(\pi R^3))d\omega_f
\]

\[
D_s(\omega_f) = \frac{\omega_f R^2}{2S_f^2},
\]  

Figure 6.2: Scattering of electrons from nanoparticle’s surface.
Where $\omega_{Ds}$ is the Debye frequency for the surface phonons and $D_s(\omega)$ is the surface phonon mode density[67].

$$U_{\text{surface}} = \eta \int_0^{\omega_{Ds}} \omega_f^3 \left( \frac{e^{\beta \omega_f} - e^{\beta \omega_f - 1}}{(e^{\beta \omega_f} - 1)(e^{\beta \omega_f - 1})} \right) \, d\omega_f. \tag{6.21}$$

$$\eta = \left[ \frac{3 \alpha m^2 V}{32 \pi^3 h^2 S_s R} \right]$$

The surface Debye frequency and surface Debye temperature will be,

$$\int_0^{\omega_{Ds}} D_s(\omega_f) \, d\omega_f = 2(4\pi R^2 a/V), \tag{6.22}$$

$$\omega_{Ds} = \sqrt{32 \pi a S_s^2 V} \text{ and } T_{Ds} = (\hbar S_s/k_B) \sqrt{32 \pi a/V} \text{ respectively.}$$

The above equation (5.23) can be simplified in two special cases, first, for low electron and phonon temperatures as compared to Debye temperature, i.e., $T, T_e \ll T_{Ds}$ , Eq.(5.23) reduce to

$$U_{\text{surface}} = \eta \left(\frac{k_B T_{Ds}}{\hbar}\right)^4 \left[ \frac{\left(\frac{T_e}{T_{Ds}}\right)^4 \int_0^{T_{Ds}/T_e} \frac{x^3}{e^x - 1} \, dx - \left(\frac{T}{T_{Ds}}\right)^4 \int_0^{T_{Ds}/T} \frac{x^3}{e^x - 1} \, dx}{T_{Ds}^4 - T^4} \right]. \tag{6.23}$$

The above equation (5.23) can be simplified in two special cases, first, for low electron and phonon temperatures as compared to Debye temperature, i.e., $T, T_e \ll T_{Ds}$ , Eq.(5.23) reduce to

$$U_{\text{surface}} = \eta \left(\frac{k_B T_{Ds}}{\hbar}\right)^4 \left[ \frac{T_e^4 - T^4}{T_{Ds}^4} \right] \int_0^{\infty} \frac{x^3}{e^x - 1} \, dx. \tag{6.24}$$

An important point to be noted in the above equation is that the electron to phonon energy transfer rate depends upon $4^{th}$ power of electron and phonon temperatures as compared to the corresponding case in the bulk (there it is $5^{th}$ power of electron and phonon temperatures[51]). In second special case, when $T_e, T \gg T_{Ds}$ , we get

$$U_{\text{surface}} = \eta \left(\frac{k_B T_{Ds}}{\hbar}\right)^4 \left[ \frac{T_e - T}{T_{Ds}} \right]. \tag{6.25}$$

The above equation (Eq.(5.25)) is the basics of what is called the two temperature model. The popular electron surface-phonon coupling coefficient in femtosecond pump-probe experiments for nano-particles is

$$\alpha_{\text{int}} = \left[ \frac{3(\sqrt{32\pi}) m^2 U^2_k B}{\pi h^3 \rho V} \right] \frac{1}{R}. \tag{6.26}$$
For a gold nanoparticle of radius $R = 10\text{nm}$, with $U_s = 10^{-19}\text{joule}$, $a = 4.1 \times 10^{-10}\text{m}$, $\rho = 19.3 \times 10^3\text{kg/m}^3$, $n = 5.9 \times 10^{28}\text{m}^{-3}$, $T_D = 185\text{K}$, $\omega_D = 2.42 \times 10^{13}\text{rads/sec}$,

$$\alpha_{\text{int}} \approx 7.1 \times 10^{13}\text{joule m}^{-3}\text{sec}^{-1}K^{-1}$$

(6.27)

Which agrees with experiments[68]. The electron-phonon coupling coefficient for the case of bulk is $\sim 5 \times 10^{16}\text{joule m}^{-3}\text{sec}^{-1}K^{-1}$(Anisimov et al. 1970). So, $\alpha_{\text{int(\text{surface})}}$ is less by a factor of $10^3$ from that of bulk, which indicates suppression of electron energy transfer to phonons in case of nano-particles. The present results show that the electron surface-phonon coupling constant will increase with the reduction of the particle size. So the hot electron thermalization time will reduce with decreasing size of the nanoparticle[61, 62]. The calculation does not include the effect of electron surface-phonon screening, but the fact that, due to electron wave function spill out and d- electron localization[69] in nanoparticles, the screening will be comparatively less as compared with the bulk. The question regarding the weight of the two factors, namely, surface to volume ratio (geometric factor), and reduction of electron phonon screening, in the thermalization of hot electron distribution is still open.

6.4 A model for electron-(multi)phonon relaxation in a regime where two temperature model is not applicable

A model calculation is given for the energy relaxation of a non-equilibrium distribution of hot electrons prepared in the conduction band of a polar indirect band-gap semiconductor, which has been subjected to homogeneous photo-excitation by a femtosecond laser pulse. The model assumes that the photoexcitation creates two interpenetrating electron and hole subsystems, initially comprising a non-degenerate hot electron subsystem in the conduction band and a similar hole subsystem in the valence band.
The relaxation process is taken to be dominated by the electron (multi)phonon interaction resulting in a quasi-continuous electron energy loss to the phonon bath. Due to this electron - (multi)phonon interaction, electrons after losing their energy, tend to accumulate at the conduction band minimum. Similarly holes tend to accumulate below the valence band maximum. The final relaxation (recombination) involves, a relatively slow, phonon-assisted radiative interband transition across the indirect gap. This leads to a peaking of the calculated hot electron distribution at the bottom of conduction band, and similarly for the holes in the valence band. This feature, as also the entire evolution of the hot electron distribution, may be time resolved by a pump-probe study. The model is particularly applicable to a divided (nano-metric) polar indirect band-gap semiconductor system with a low electron concentration, strong electron-phonon coupling, where the usual two temperature model[71, 72, 73, ?] may not be appropriate.

### 6.4.1 The model

Consider the kinetic evolution of a photoexcited non-equilibrium system of electrons in the conduction band of a polar, indirect band-gap semiconductor with a low electron density, strong electron-phonon coupling, and having high anharmonicity, such that, $\tau_{e-e} >> \tau_{e-p} >> \tau_{p-p}$. Here,$\tau_{e-e}, \tau_{e-p}$ , and $\tau_{p-p}$ are the electron-electron, electron-phonon and the phonon-phonon relaxation time scales respectively. This is the regime, in which the usual two-temperature model is not applicable[71, 72, 73, ?].

The femtosecond photoexcited non-degenerate hot electron distribution then evolves predominately through the non-radiative electron-phonon processes. Due to this electron - (multi)phonon interaction, electrons after losing their energy, tend to accumulate at the conduction band minimum. Similarly, holes tend to accumulate at the valence band maximum. The final relaxation (recombination) involves, a relatively slow, phonon-assisted, radiative interband transition across the indirect gap. There is then a pile up of the hot electrons/holes at the bottom/top of the conduction/valence
band. Thus, the entire relaxation process proceeds on two timescales, namely, the initial, fast time scale involving the non-degenerate intraband electron-phonon interaction, and the final, slow time scale involving the phonon-assisted radiative interband transition across the indirect gap. We have derived an analytical expression for the entire time evolution of the non-equilibrium hot-electron distribution, following the initial preparation by the femtosecond laser pulse. These two, the fast and the slow relaxation processes, can, in principle be time resolved using pump-probe experimental technique. Here, we are not considering the process of hole energy relaxation in the valence band.

Consider the sample is photoexcited homogeneously (i.e., no spatial diffusion) by a laser pulse. This generates a gas of electrons in the conduction band with the non-equilibrium distribution function $f_e(\epsilon, t)$. This non-degenerate, classical gas of electrons will relax predominantly through the non-radiative process in which the hot electrons undergo a quasi-continuous energy loss through multi-phonon processes (phonon friction). In the present work, two models of phonon friction are considered. A linear model in which the +phonon friction is taken to be linear in velocity of the hot electrons, and the other, in which the phonon friction is non-linear in electron velocity. The nonlinearity considered here is a power-law type. In the following, we drive analytical
expressions for the time-dependent non-equilibrium hot-electron distribution for the two models of electron-phonon friction.

6.4.1.1 The phonon friction is proportional to the electron velocity \( V \):

linear model

The kinetic equation is:

\[
\frac{\partial f_e(\epsilon, t)}{\partial t} + \epsilon \frac{\partial f_e(\epsilon, t)}{\partial \epsilon} = -\frac{\partial f_e(\epsilon, t)}{\tau_r} \tag{6.28}
\]

Here, \( \dot{\epsilon} = (m\dot{v}^2)/2 = -\gamma_p v^2 = -\epsilon/\tau_p \), where \( \tau_r \) and \( \tau_p \) are the radiative (photon) and the non-radiative (phonon) relaxation times, and \( \tau = t/\tau_p \) and \( \alpha_{r-p} = \tau_r/\tau_p \) are dimensionless variables/parameters. With this, equation (5.28) reduces to,

\[
\frac{\partial f_e(\epsilon, \tau)}{\partial \tau} - \frac{\partial f_e(\epsilon, \tau)}{\partial \ln \epsilon} = -\frac{\partial f_e(\epsilon, \tau)}{\alpha_{r-p}} \tag{6.29}
\]

Equation (5.29) can be solved analytically to give:

\[
f_e(\epsilon, \tau) = f_0 e^{-\tau/\alpha_{r-p}} \Theta(-\tau - \ln[\epsilon/(\epsilon_c + \epsilon_L)]) \tag{6.30}
\]

Here \( \Theta() \) is a step function, and we have assumed an initial delta-function laser pulse of photon energy \( \epsilon_L \) that excites electrons in the energy interval \( \epsilon_c \leq \epsilon \leq \epsilon_c + \epsilon_L \) in the conduction band and a similar hole population in the valence band. \( \epsilon_c \) is the conduction band minimum energy, and \( \epsilon_L > \epsilon_g \) (the band-gap energy). Inasmuch as Eq. (5.29) has only the forward propagating solutions (in energy space) we can readily incorporate the slow process effective at the bottom of the conduction band by simply introducing a longer relaxation time \( \tau_{pe} \geq \tau_p \) there. This gives rise to the peaking effect referred to above. Equation (5.30) is our basic result. In terms of it, we can calculate the total number \( N_{pe}(\tau) \) of the hot electrons piled up in the bottom of conduction band, and also the total number of hot electrons \( N_{hot}(\tau) \) above \( \epsilon_c \). The number of hot electrons in the pile-up, \( N_>(\tau) \equiv N_{hot}(\tau) - N_{pe}(\tau) \), with energy \( \epsilon > \epsilon_c \) (for uniform excitation of scale height, \( f_0 \)) is:

\[
\frac{\partial N_{pe}(\tau)}{\partial \tau} + \frac{\partial N_>(\tau)}{\partial \tau} = -\frac{\partial N_{pe}(\tau)}{\beta_{pe}}, \quad \beta_{pe} = \frac{\tau_{pe}}{\tau_p} \tag{6.31}
\]
Now \( N_>(\tau) = \int_{\varepsilon_c}^{\varepsilon_L} f_\varepsilon(\varepsilon, \tau) d\varepsilon = f_0 e^{-\tau/\alpha_{\tau-p}} \int_{\varepsilon_c}^{\varepsilon_L} \Theta(-\tau - \ln(\varepsilon/|\varepsilon_c + \varepsilon_L|)) d\varepsilon. \) We consider energy loss through phononic friction only, with this we get

\[
N_>(\tau) = f_0 (\varepsilon_c + \varepsilon_L) e^{-\tau}
\]

(6.32)

From equations (5.31) and (5.32) we have

\[
\frac{\partial N_{pe}(\tau)}{\partial \tau} - f_0 (\varepsilon_c + \varepsilon_L) e^{-\tau} = -\eta N_{pe}(\tau), \quad \eta = \frac{1}{\beta_{pe}}
\]

(6.33)

Solving by Laplace transforms we have

\[
N_{pe}(\tau) = \frac{f_0 (\varepsilon_c + \varepsilon_L) e^{-\eta \tau}}{1 - \eta} [1 - e^{-(1-\eta)\tau}],
\]

(6.34)

and the total number of hot electrons

\[
N_{hot}(\tau) = N_{pe}(\tau) + N_>(\tau) = f_0 (\varepsilon_c + \varepsilon_L) e^{-\tau} \left[1 + \frac{e^{(1-\eta)\tau}}{1 - \eta} (1 - e^{-(1-\eta)\tau})\right].
\]

(6.35)

Time evolution of these two populations are plotted in Figs. (5.4) and (5.5).

6.4.1.2 **The phonon friction is nonlinear (algebraic) in the electron velocity: nonlinear model**

\[
\frac{\partial f_\varepsilon(\varepsilon, t; n)}{\partial t} + \dot{\varepsilon} \frac{\partial f_\varepsilon(\varepsilon, t; n)}{\partial \varepsilon} = -\frac{f_\varepsilon(\varepsilon, t; n)}{\tau_r}
\]

(6.36)

With \( \dot{\varepsilon} = -\frac{\varepsilon}{\tau_p} \left[\frac{\varepsilon}{\varepsilon_0}\right]^n \) and \( \varepsilon_0 \) is an associated energy scale. In line with the linear model, this kinetic equation has the solution,

\[
f_\varepsilon(\varepsilon, \tau; n) = e^{-\tau/\alpha_{\tau-p}} \Theta \left(-\tau - \frac{1}{n} \left(\frac{\varepsilon_0}{\varepsilon_L + \varepsilon_c}\right)^n \left[1 - \left(\frac{\varepsilon_L + \varepsilon_c}{\varepsilon_c}\right)^n\right]\right).
\]

(6.37)
Figure 6.5: Decay of hot electrons, $N_{\text{hot}}(\tau)$, for $\eta = 0.5$.

The number of hot electrons $N_{>n}(\tau)$ with energy greater than $\epsilon_e$ is

$$N_{>n}(\tau) = \int_{\epsilon_e}^{\epsilon_e+\epsilon_L} f_0(\epsilon, \tau; n) d\epsilon = f_0 n(\epsilon_e + \epsilon_L) \left[ 1 + \frac{\tau}{\beta} \right]^{-1/n}. \tag{6.38}$$

With $\beta = \frac{1}{n}(\chi/n, \chi = \frac{\epsilon_0}{\epsilon_e+\epsilon_L})$. As in the linear model, the number of hot electrons in the pile-up near the bottom of the conduction band comes out to be:

$$N_{\text{pe};n}(\tau) = f_0(\epsilon_e + \epsilon_L) \left[ \frac{n}{n+1} \right]^{n+1} \eta^{1/n} e^{-\eta(\tau+\chi/n)} \left[ \int_{\eta \beta}^{\eta(\tau+\beta)} y^{n+1} e^{\eta} dy \right]. \tag{6.39}$$

The total number of hot electrons $N_{\text{hot};n}(\tau)$ is $N_{\text{hot};n}(\tau) = N_{>n}(\tau) + N_{\text{pe};n}(\tau)$. In the limit $\tau << \beta$, or $t << \frac{\tau a}{n(\epsilon_e+\epsilon_L)}$. The expression for hot electrons in the pile up, and total number of hot electrons will reduce to:

$$N_{\text{pe};n}(\tau) = f_0(\epsilon_e + \epsilon_L) \frac{\chi^{-n} e^{-\eta \tau}}{\chi^{-n} - \eta} \left[ 1 - e^{-(\chi^{-n} - \eta)\tau} \right], \tag{6.40}$$

$$N_{\text{hot};n}(\tau) = f_0(\epsilon_e + \epsilon_L) \left[ (1 + n\chi^{-n}\tau)^{-1/n} + \frac{\chi^{-n} e^{-\eta \tau}}{\chi^{-n} - \eta} \left( 1 - e^{-(\chi^{-n} - \eta)\tau} \right) \right]. \tag{6.41}$$

In the limit $n$ going to zero, we recover the results of the linear model.

### 6.4.1.3 Incorporating pump-pulse duration

Here, we consider the system being pumped by a rectangular femtosecond pulse of duration $t_p$. The effect of the pulse can be taken as the convolution integral of the rectangular pulse with the respective hot-electron time-evolution curves (for the case $n=0$):

$$N_{f}(\tau) = \frac{1}{t_p} \int_{0}^{\min(t_p, \tau)} N_{\text{pe}}(\tau - x) dx, \tag{6.42}$$
Figure 6.6: Decay of hot electrons $N_{\text{hot},p}(\tau)$ in the pile up as a function of $\tau$ in the presence of a rectangular laser pulse with width $\tau_p = 3$. Top most curve is for $\eta = 0$, lowest for $\eta = 0.9$ with a step of 0.1.

Figure 6.7: Decay of hot electrons $N_{\text{hot},p}(\tau)$ as a function of $\tau$, with same set of parameters as in Fig.5.6.

$$N_f^p(\tau) = \frac{1}{\tau_p} \int_0^{\min(\tau_p, \tau)} N_{\text{hot}}(\tau - x) dx.$$ (6.43)

6.5 Conclusion

The distinctive feature of our calculated time evolution of the photoexcited electron distribution in the conduction band is its peaking effect, and is readily seen in Figs.5.4 and 5.5. It reflects the effect of a slow indirect transition. This can be, and should be probed in a pump-probe experiment. This calculation refers to a situation not describable by the usual two-temperature model[71]. Here, non-degenerate system of electrons relaxes
towards the bottom of the conduction band by energy loss to the phonons (intraband relaxation). This model is applicable under the condition \( \tau_{p-p} \ll \tau_{e-e}, \tau_{e-p} \gg \tau_{p-p} \) and \( \delta \sim K_b T_0 (mev) \ll \epsilon (ev) \), here \( \delta \) is the intraband energy level spacing. The lower limit to the size of a nanoparticle for the application of this model is, approximately given as \( (h/\sqrt{2mK_b T_0} \sim 2nm) \) for \( T_0 \sim 200K \). But such a situation is expected in a polar, indirect band-gap semiconductor, with a low electron concentration, strong electron-phonon coupling, and having high anharmonicity. The photoexcited electrons should accumulate at the bottom of the conduction band as one needs a phonon-assisted radiative interband transition for the final relaxation across the indirect gap.
Bibliography


[33] for a review, see S. Chandrasekhar, Rev. Mod. Phys. 15, 1(1943).

[34] P. Langevin, Comptes. Rendues 146, 530(1908).


[43] U. Weiss,(see for example, Quantum Dissipative Systems, WS, Singapur, 1999)


[67] H.P.Baltes, invited paper at the international meeting on the small particles and inorganic clusters, September 13-17, 1976, Universite’ Claude Bernard, Lyon, France.


