Non equilibrium thermal and electrical transport coefficients for hot metals

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(Dated: October 4, 2018)

This work discusses about the transport coefficients for non equilibrium hot metals. First, we
review the role of the non equilibrium Kappa distribution in which the Kappa parameter varies with
the temperature. A brief discussion compares such distribution with the classical non equilibrium
function. Later, we analyze the generalized electrical conductivity obtained from the evolution
of the Kappa distribution. Also, we reexamine the connection between a material-dependent coefficient
which can be extracted from the thermionic emission and the melting point of the metal. We extend
previous studies by analyzing additional metals used as thermionic emitters. Finally, in the light
of the Wiedemann-Franz Law, we present a new generalized thermal conductivity, which is also
applied to several metals.

PACS numbers: 05.90.+m 72.15.Cz 64.70.dj

I. INTRODUCTION

As it is well known, metals in equilibrium are de-
scribed by means of the Fermi-Dirac distribution. How-
ever there are many situations in which the non equi-
librium is present, and it is difficult to assume that this
distribution depicts the electron population of such met-
als. This is the case of metals rapidly heated by means of
dense currents, [1]. Also, the non equilibrium is present
in metals exposed to a high power laser, [2]. The de-
viation from equilibrium has been also investigated con-
cerning the thermionic emission [3–5]. Moreover, there
are reported departures from equilibrium of metals near
their melting point [1, 6]. In addition, the departures
from equilibrium of particle distributions have been also
applied in wider contexts [6].

The Kappa distributions are used to a large extent
in statistical mechanics and other fields to study pop-
ulations near and far from equilibrium. The classical
Kappa is applied to nonequilibrium plasmas in space [7–
9]. These kinds of distributions can be cast from general
formalisms. The non-extensive q-statistics [10, 11], and
the so-called Beck-Cohen superstatistics provide physical
meaning to these distributions [12]. Besides, Kappa
distributions can be studied from the so called Kappa-
deformed algebras [13]. The non-extensive statistics have
been also applied to establish general purpose Kappa dis-
tributions for bosons and fermions [14, 15]. From another
point of view, the Kappa distribution can be regarded as
the solution of the Fokker-Planck equation regarding col-
collective effects and collisional processes, [10].

In this work we will apply the Fermi-Dirac Kappa func-
tion to study in a phenomenological way the behaviour of
the electron population in metals out of equilibrium. We
will focus on metals which are used as thermionic em-
ters. We will consider a small volume of a metal with

an external electric field applied to it. Additionally, such
metal is heated by means of an inner current. This heat-
ing can be increased until the melting point. Besides,
from the evolution of the Kappa energy distribution has
been derived a generalized Ohm law containing a gen-
eralized electrical conductivity, [6]. Such conductivity
evolves with the temperature, and it drops when such a
melting temperature is reached. According to [1, 6], the
starting mechanism of melting can be originated from the
enhancement of energy deposition on the metal lattice
caused by increasing high energy electron population.
Subsequently, it would increase the defect density on the
lattice leading to the melting.

Through this work, we will review this generalized elec-
trical conductivity and we will apply it to other metals.
Moreover, as we shall see, from such a generalized coef-
cient, the Wiedemann-Franz Law can be extended in a
phenomenological manner to the non-equilibrium, giving
rise to a generalized thermal conductivity. The result-
ing generalized law is applied later to study the thermal
conductivity of several metals.

II. THE KAPPA DISTRIBUTION IN METALS

The general purpose form for the generalized Kappa
Fermi-Dirac distribution can be put as follows [8, 15],

\[ f_{\kappa}^{FD}(T, E) = \left[ 1 + \left( 1 + \frac{E - \epsilon_F}{\phi(\kappa)} \right)^{(\kappa+1)} \right]^{-1} \]  \hspace{1cm} (2.1)

where \( T \) is the temperature, \( E \), the electron energy, \( \epsilon_F \) being the Fermi energy. Here, \( \phi(\kappa) \) is a linear function proportional to \( k_B T \), with \( k_B \) being the Boltzmann constant. Such \( \phi \) function can be extracted from a charac-
teristic velocity which is related with the mean square velocity \( \langle v^2 \rangle \), [4, 8]. This distribution, as it can be seen
in Figure 1 is able to develop high energy tails as the
Kappa value becomes lower. The FD distribution is re-
covered for high Kappa values. Moreover, the Fermi en-

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compare the distribution to describe nonequilibrium metals. We can describe the out of equilibrium electron population of a metal merged into a vacuum chamber and heated with a DC current, $J$. By means of a sweep system, the emitted current from the wire surface is measured. From these experiments, a departure from the RD expression can be observed when the wire temperature becomes higher. The high values of the measured emitted current at high temperature can not be recovered from the classical expression. The deviation from equilibrium was calculated using Eq. (2.4) as a function of the $\kappa$ parameter. As an experimental result, the $\kappa$ parameter was found to be temperature dependent, $\kappa(T)$. The possibility of a $\kappa(T)$ dependence has been also pointed out in a more general study on suprathermal distribution.

\[
J_{\kappa}(T) = B_{\kappa}(T) \times \left(1 + \frac{W_f}{E_{\kappa} + \epsilon_F}\right)^{-\kappa+1}
\]

Here, $B_{\kappa}(T)$ is a factor, and $W_f$ is the usual work function. For small $\kappa$ values this expression predicts thermionic currents much higher than those calculated by the Richardson-Dushman (RD) law. In the limit for large $\kappa$, the above Equation (2.5) recovers the RD law.

To test Equation (2.5), in a previous work, $\kappa$, a set of experiments has been done. Briefly, it consists of a Tungsten wire merged into a vacuum chamber and heated with a DC current. $J$. By means of a sweep system, the emitted current from the wire surface is measured. From these experiments, a departure from the RD expression can be observed when the wire temperature becomes higher. The high values of the measured emitted current at high temperature can not be recovered from the classical expression. The deviation from equilibrium was calculated using Eq. (2.4) as a function of the $\kappa$ parameter. As an experimental result, the $\kappa$ parameter was found to be temperature dependent, $\kappa(T)$. The possibility of a $\kappa(T)$ dependence has been also pointed out in a more general study on suprathermal distribution. $\kappa(T)$ is a \textit{tk}

\[
\kappa(T) = a - bT
\]
Figure 2: (color on line) Comparison between the usual perturbed distribution of metals $f_p$ (dot-dashed line) and the linearized $f_κ$ (solid line): $T = 3000K; F = 1.9kV$

Figure 3: (color on line) Electrical conductivity. Comparison of $σ_κ$ with the experimental data: Case of Tantalum.

III. GENERALIZED THERMAL AND ELECTRICAL CONDUCTIVITY OF METALS

In this section, we will analyze the impact of the $κ(T)$ law when the Kappa distribution evolves according to the Boltzmann Transport Equation (BTE).

$$\left[ \frac{\partial f}{\partial t} \right]_{coll} = v_x \left[ \frac{\partial f_κ}{\partial T} \frac{dT}{dx} + e F \frac{\partial f_κ}{\partial E} \right]$$ (3.1)

In which we use the BTE with $f_κ(T)$, Eqs. (2.2) and (2.6). The calculations lead to a generalized Ohm Law $J = σ_κ F$ with an electrical conductivity, $σ_κ$, which can be written as,

$$σ_κ = σ \left[ 1 + C_κ(T,E) \right]$$ (3.2)

Here, $σ$ stands for the usual, equilibrium, electrical conductivity. The corrective term is labeled as $C_κ(T,E)$, and it becomes zero for large $κ$. Therefore the usual Ohm law is recovered for metals in equilibrium. The explicit form of $σ_κ$ can be read in Equation (2.20) of [6]. As the temperature approaches the melting point, $T_m$, this correction begins to be important. When $T_m$ is reached, the $σ_κ$ becomes singular and subsequently it drops. The responsible for this vanishing conductivity is the singular behaviour of the Digamma function, $ψ[κ(b,T)]$, contained within the corrective term. Such Digamma depends on the temperature and the material properties through Kappa. As the temperature rises the Kappa value decreases and it is controlled by the slope $b$.

Since such a coefficient is material dependent, this suggests that it contains specific information about how the particular metal departs from equilibrium, [6].

If there is available experimental data about the slope of $κ(T)$ of a metal from its thermionic emission, it can be used within equation (3.2) in order to predict its melting point. Conversely, using the value of the melting points of metals, $T_m$, as an input, by finding roots from equation (3.2) the $b$ coefficient can be obtained, [6].

In this work we provide the study about the $σ_κ$ and $b$ for Tantalum, since it is also used as a thermionic emitter, [21]. Figure 3 shows the comparison of the experimental behaviour of the electrical conductivity of Tantalum with the temperature and the obtained values from equation (3.2). The experimental data relevant to this study was collected from [21–23]. The calculated coefficient is $b = 0.02 K^{-1}$ from its melting point $T_m(Ta)= 3293K$. The typical Kappa values far from the melting point are $κ(T = 1500K) = 39$; a high value which would correspond to a distribution almost in equilibrium. Near the melting $κ(T = 3180K) = 5$, it shows the transition toward non-equilibrium. These results are similar to those found in other thermionic metals in reference [6].

The $b$ slope was found to be material dependent. For thermionic metals, this value is $b \approx 10^{-2}(K^{-1})$ [6]. By inserting this $κ(T)$ law into the emitted current $J_e(T)$, the experimental results are recovered with a very good agreement over the entire temperature range. Therefore, the experiments and this later law, indicate that the departure from the equilibrium of metals is governed by the temperature modulated by the $b$ coefficient. The scope and the suitability of such a linear $κ(T)$ law will be discussed later.
to the enhancement of energy deposition on the particular metal lattice. Subsequently this absorption increases the defect density in the lattice [1], leading to melting.

On the other hand, we can use the Equation (3.2) to generalize the Wiedemann-Franz law (WFL). First, we define the generalized thermal conductivity, $\chi_\kappa$,

$$\chi_\kappa = \chi \left[ 1 + C_\kappa(T, E) \right]$$  \hspace{1cm} (3.3)

where $\chi$ stands for the usual thermal conductivity of metal in equilibrium. The $C_\kappa$ within brackets corresponds to the same corrective term of Equation (3.2).

The classical WFL reads as,

$$\frac{\chi}{\sigma T} = L_N$$  \hspace{1cm} (3.4)

where, again, $\sigma$ is the equilibrium electrical conductivity, and $L_N$ is the Lorentz number. We can rewrite the WFL in terms of the generalized electrical conductivity. Hence, by inserting Equations (3.2) and (3.3) into the above expression we attain,

$$\frac{\chi_\kappa}{\sigma_\kappa T} = L_N$$  \hspace{1cm} (3.5)

Therefore, the same WFL holds by replacing the usual transport coefficients with their respective generalized expressions. Also, from Equation (3.5) it is possible to calculate $\chi_\kappa$ through a knowledge of the generalized electrical conductivity of a particular metal.

In Figures 4 and 5 we can observe the results of $\chi_\kappa$ obtained for Tungsten and Platinum using Eqs.(3.2) and (3.3) for different energies, in $E_F$ units. In the first case the $\sigma_\kappa$ were obtained from the experimental $b$ coefficient for Tungsten. In the Pt case the corresponding $\sigma_\kappa$ were calculated from the experimental melting point. Both cases agree with the available experimental extrapolations. These extrapolations are based on different experiments on thermal conductivity near the melting point, [24]. As a new feature, the predicted thermal conductivity of the solid phase of the metal drops when the melting point is reached.

IV. CONCLUSIONS

In this work we have studied the previously modeled ad-hoc Kappa distribution for metals, which comes from the general Kappa Fermi-Dirac. This $f_\kappa$ function is normalized to the electron density of the metal. By analyzing the thermionic emission of several metals, it was found that the Kappa parameter depends on temperature. From the experiments, this $\kappa(T)$ law was found to be linear. At this point it must be noticed that this linear law was extracted in a phenomenological way within a limited temperature range, not from theory. Therefore, the possibility to find this law as an effective expression constrained to a small temperature range can not be discarded.

The $b$ slope actually measures the rate of change of $\kappa$ with respect to the temperature and it could entangle the physics of such a mechanism. In addition, to analyze the suitability of $f_\kappa$ for metals, we compared it with the classical perturbed distribution function for metals, finding a similar behaviour. This latter function depends on the electric field applied to the metal. As it is well known such a field is a source of disequilibrium [17, 18]. Therefore it supports the idea the $\kappa(T)$ law is an effective expression. It is expected the Kappa parameter depends not only on the temperature, but it should be also a function of the applied electric field. Looking at the linear $\kappa(T)$ law, it suggests the $b$ coefficient entangles information not only about the features of the metal, but
also the conditions leading to nonequilibrium. Hence, it is mandatory to obtain an explicit expression of this $\kappa(T, F, \ldots)$ law. This work is in progress.

Concerning the mechanism of the development of high energy tails, again it is entangled within the $b$ coefficient of the $\kappa(T)$ index. The phase transition is mainly described by the Digamma terms within $C_\kappa(T, E)$. As mentioned, the Kappa distributions develop through the adjustable Kappa parameter. Such an index is modeled on the terms of the wave-electron interactions and strengths, $\kappa(T, E)$. Near the phase transition it is expected that the lattice oscillations will become larger. Their interactions with the electron-lattice waves could be the origin of the development of such (low-Kappa) high energy tails. Similar effects analyzing the interaction between the phonons and electrons in heterolayers have been reported. In this latter case the cause of the increasing energy of the electron distribution comes from the reabsorption of non-equilibrium phonons. In our case, as the temperature rises, the increasing defect density in the metal lattice will become larger. Their interactions with the electron-lattice waves could be the origin of the development of high energy tails, again it is entangled within the $b$ coefficient of the $\kappa(T)$ index. The phase transition is mainly described by the Digamma terms within $C_\kappa(T, E)$. As mentioned, the Kappa distributions develop through the adjustable Kappa parameter. Such an index is modeled on the terms of the wave-electron interactions and strengths, $\kappa(T, E)$. Near the phase transition it is expected that the lattice oscillations will become larger. Their interactions with the electron-lattice waves could be the origin of the development of such (low-Kappa) high energy tails. Similar effects analyzing the interaction between the phonons and electrons in heterolayers have been reported. In this latter case the cause of the increasing energy of the electron distribution comes from the reabsorption of non-equilibrium phonons. In our case, as the temperature rises, the increasing defect density in the metal lattice could play the role of the heterointerfaces. Again, more effort is needed to clarify such a topic.

On the other hand, in this work we extended previous studies by applying the generalized expression of the electrical conductivity to the case of Tantalum. This latter metal is also used as a thermionic emitter. We found all the values extracted are consistent with previous results from other metal emitters. Finally, in light of the Wiedemann-Franz Law, we presented a new generalized thermal conductivity. This Kappa transport coefficient led us to generalize the WFL to non-equilibrium. As well, this generalized WFL allowed us to calculate the thermal conductivity values near the melting point of several metals. These values are consistent with the experimental extrapolations of the thermal conductivity near their melting points. In addition, as a new feature, such an expression makes the thermal conductivity vanish when the melting point of the solid phase is reached.

Acknowledgments

This work was funded by the MINECO, Spanish Ministry, under Grant ESP2013-41078-R.

[1] S.V. Lebedev and A.I. Savvatimskii, *Metals during rapid heating by dense currents* Sov. Phys. Usp. 27, (1984) 749.
[2] B.Y. Mueller and B. Rethfeld, *relaxation dynamics in laser-excited metals under nonequilibrium conditions*, Phys.Rev.B 87, (2013) 035139.
[3] V.E. Zakharov, V.I. Karas *Nonequilibrium Kolmogorov-type particle distributions and their applications*, Physics-Uspekhi 56(1) (2013) 49.
[4] J.L. Domenech-Garret, S.P. Tierno and L. Conde, *Enhanced thermionic currents by non equilibrium electron populations of metals*, Eur. Phys. J. B 86,(2013)382.
[5] J.L. Domenech-Garret, S.P. Tierno and L. Conde, *Non-equilibrium thermionic electron emission for metals at high temperatures [arXiv:1505.05378][cond-mat.mes-hall]*, J. of Appl. Phys. 118, (2015)074904.
[6] J.L. Domenech-Garret, *Generalized electrical conductivity and the melting point of thermionic metals*, J. Stat. Mech. (Vol.2015), (2015).P08001
[7] J.J. Podesta, NASA Reports, CR-2004-212770, (2004).
[8] B.D. Shizgal, *Superthermal particle distributions in space physics: Kappa distributions and entropy*, Astrophys. Space Sci. 312, (2007) 227.
[9] G. Livadiotis, D.J. McComas, Astrophys.J. 741:88 (2011). doi:10.1088/0004-637X/741/2/88.
[10] C. Tsallis, *Possible generalization of Boltzmann-Gibbs statistics*, J. Stat. Phys. 52 (1988) 479.
[11] C. Tsallis, *Nonextensive physics*, Phys. Lett. A 195, (1994)329.
[12] C. Beck, E.G.D. Cohen, *Superstatistics*, Physica A 322 (2003) 267.
[13] G. Kaniadakis, *Non-linear kinetics underlying generalized statistics* Physica A 296, 405 (2001).
[14] A. Algin and M. Senay, *High-temperature behavior of a deformed Fermi gas obeying interpolating statistics* Phys. Rev. E 85,(2012)041123.
[15] R.A. Treumann, Europhys. Lett. 48 (1),(1999) 8.
[16] A. Hasegawa, K. Mima and MinhDuong-van, *Plasma Distribution Function in a Superthermal Radiation Field* Phys. Rev. Lett. 54, (24), (1985) 2608.
[17] B.G. Lindsay, *Introduction to Physical Statistics* (J.Wiley and Sons,New York 1962) Chapter 10.
[18] J.M Ziman, *Electron and phonons: The theory of transport phenomena in solids.* (Oxford University Press, 1960).
[19] J.M Ziman, *Electrons in metals: A short guide to the Fermi Surface* (Taylor and Francis, London 1963),Chapters I and IV.
[20] P.L. Bhatnagar, E.P. Gross, and M. Krook, *A model for collision processes in gases I.* Phys.Rev.94(3),(1954) 511.
[21] F. Cardarelli, *Materials Handbook* (Springer, N.Y., 2008), Chapter 9.
[22] P.D. Desay, T.K. Chu, H.M. James, C.Y. Ho *Electrical Resistivity of Selected Elements* J. Chem. Phys. Ref. Data 13 (4),(1984) 1069.
[23] D.R. Lide, ed., *CRC Handbook of Chemistry and Physics* (CRC Press LLC 1995-2005), Section 12.
[24] R.W. Powell, C.Y. Ho, and P.E. Liley, *Thermal Conductivity of Selected Materials* (NSRDS-NBS-8 National Bureau of Standards, U.S. Government Printing office,1966), Category 5.
[25] K. Kim and C. Hess, *Monte Carlo study of electron heating and enhanced thermionic emission by hot phonons in heterolayers* Appl. Phys. Lett. 52(14), (1988) 1167.