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Argon Plasma Transport Properties at Reduced Pressures

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Argon plasma transport properties at low pressures (0.01 atm) are calculated using a modified Debye length suggested by T. Kihara et al. Electrons and heavy species are treated as two different gases, and the method of calculation is based on the simplified theory for transport properties developed by R. S. Devoto. A generalized Saha equation is used to calculate the species composition, and experimental data by Y. Itikawa for momentum transfer cross sections are adopted for the evaluation of electron-atom collision cross sections.

KEY WORDS: Argon plasma transport properties; two-temperature plasmas; reduced pressures; calculation.

1. INTRODUCTION

High-power-density plasma systems operated at reduced pressures are attracting increasing interest in connection with plasma deposition, plasma sintering, plasma synthesis, and other related applications. In contrast to plasmas in local thermodynamic equilibrium (LTE), calculations of transport properties under reduced pressure conditions are much more complex due to deviations from kinetic as well as chemical equilibrium.

For an argon plasma at low pressure, the theory of transport properties has been treated by a number of authors. Bose *et al.*[1-3] studied various two-temperature gas properties based on a simplified theory developed by Devoto.[4-6] Miller *et al.*[7] calculated the transport properties of a two-temperature, partially ionized argon plasma by using the Chapman–Enskog method and perturbed-Lorentzian solutions. But in their calculation, the plasma composition was calculated without considering the effect of deviation of the electron temperature from the heavy-particle temperature.

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There are little reliable data available for the relatively low temperature region, because of the uncertainty of using the Debye cutoff Coulomb potential. The necessity of modifying the cut-off distance for cases of relaxation between electron temperature and heavy-particle temperature has been noticed by Kihara and Aono[8,9] in their unified theory. The basic concept in this unified theory is the assumption that the rate of relaxation between ion and electron temperature is proportional to the time rate of change in the mean kinetic energy of the ions. Classical impact theory does not consider collective interactions, which causes the divergence of the collision integral. Thus, the screening of the Coulomb field of charged particles is not properly considered. In the case of wave theory, the lack of information about close collisions leads to the divergence of the collision integral. These problems are avoided by introducing the cut-off Debye length. Instead of using the Debye length as cut-off criterion for the impact theory, Kihara and Aono unified the two theories, i.e., impact and wave theory, into an exact theory, so that no cut-off procedure of the diverging integrals is needed.

The shielding is shared by many particles within a sphere of the shielding radius. This is based on the assumption that the plasma is close to an ideal gas, i.e., the absolute value of the potential energy between two particles at the mean distance is assumed to be much smaller than the kinetic energy of the particles. In the case of relaxation between electron and ion temperature, ions are completely screened by the surrounding electrons since ions are moving very slowly compared to electrons, and there is only partial shielding by the other ions.[10] Hence the screening distance of ion-electron interaction must fall between the Debye length for electrons only and the one considering both electrons and ions.

The first attempt to apply this unified theory to the calculation of transport properties was made by Daybelge.[11,12] In his unified transport theory, he adopted the impact theory for the definition of the Chapman-Enskog's collision integral, i.e.,

$$\Omega_e^{(l)}(r) = \sqrt{\pi}(\mu/4T_e)^{r+3/2} \int_0^\infty g^{2r+3} \exp(-\mu g^2/4T_e)$$
$$\times \int_{b>0} (1-\cos\chi) b\, db\, dg$$

where g is the relative velocity, μ is the reduced mass, b is the collision parameter, T_e is the electron temperature, and χ is the angle of deflection during collision. Instead of using the term

$$\int_{b>0} (1-\cos\chi) b\, db\, dg$$

in the collision integral, he replaced this by introducing the factor suggested by Kihara *et al.*,[8] i.e.,

$$\int_{b>0} (1-\cos\chi)\exp(-b^2/2b_0^2)\, b\, db\, dg$$

where b_0 is an arbitrary parameter which does not affect the final results.[8] Based on this modification of the collision integral, Daybelge[11] derived a unified transport theory for two-temperature properties which is different from the one suggested by Devoto.[4]

In this paper, instead of using the rather complex unified transport theory by Daybelge, the widely used approach by Devoto[4] is adopted, but the idea of the cut-off Debye length is modified to meet the spirit of the unified theory.

2. CALCULATION OF SPECIES COMPOSITION

The number density of each species in the plasma can be calculated from the modified Saha equation for a two-temperature plasma which is written in the following form[13]:

$$n_e\left(\frac{n_{i+1}}{n_i}\right)^{1/\theta} = 2\frac{Z_{i+1}}{Z_i}\left(\frac{2\pi m_e k T_e}{h^2}\right)^{3/2}\exp\left(-\frac{E_i^\infty - \delta E_i^\infty}{kT_e}\right) \qquad (1)$$

where $\theta = T_e/T_h$ is the ratio between electron temperature and heavy particle temperature, Z_i is the partition function of species i, and δE_i^∞ is the lowering of ionization energy.

Equation (1) can be derived by writing the chemical potentials of the electrons, ions, and neutral particles separately and using the condition for ionization equilibrium. Because of the simplification made during the derivation, it can only be applied for a moderate range of temperature differences between heavy species and electrons.[14]

The lowering of the ionization energy is approximated as the Coulomb potential energy of charge $j+1$ at a Debye shielding distance λ_D,[14] i.e.,

$$\delta E_i^\infty = \frac{(i+1)e^2}{4\pi\varepsilon_0\lambda_D} \qquad (2)$$

The Debye shielding distance will be discussed later according to the unified theory.

This mass action law can be put into the form

$$n_e\left(\frac{n_{i+1}}{n_i}\right)^{1/\theta} = K_i \qquad (3)$$

where K_i represents the right-hand side of Eq. (1).

Using this expression in the general expression of the number density for species i, we obtain

$$n_i = n_0 \prod_{r=1}^{i} \left(\frac{K_r}{n_e}\right)^\theta \tag{4}$$

and

$$n_e = n_0 \sum_{i=1}^{i_{max}} i \prod_{r=1}^{i} \left(\frac{K_r}{n_e}\right)^\theta \tag{5}$$

$$n_t = n_0 \left(1 + \sum_{i=1}^{i_{max}} (i+1) \prod_{r=1}^{i} \left(\frac{K_r}{n_e}\right)^\theta\right) \tag{6}$$

where i_{max} is the maximum order of ionized species and n_t is the total number density of particles.

Combining Eqs. (5) and (6) results in a polynominal of degree $i_{max}+1$ in the form

$$n_e^{\theta(i_{max}+1)} + \sum_{i=1}^{i_{max}} (n_e^{\theta(i_{max}-i)+1}(i+1) - n_t n_e^{\theta(i_{max}-i)} i) \prod_{r=1}^{i} K_r^\theta = 0 \tag{7}$$

The equation of state of the two-temperature plasma is

$$p = kT_h\{n_t + (\theta - 1)n_e\} \tag{8}$$

In order to solve Eq. (7) for the electron number density, it is necessary to use an iterative approach since this number plays an important role in determining the lowering of the ionization potential. In the computer program this polynomial equation is solved by using a bi-section method.

For a partially ionized collision-dominated gas, it is common to assume that the electron and heavy species follow a Maxwell-Boltzmann distribution and the excitation temperature equals the free electron temperature, while the heavy species (atoms, ions) have the same temperature which is different from the electron temperature. In this two-temperature modeling of monatomic gas systems, the partition functions of the heavy species (ions and neutrals) can be uncoupled. For a detailed formulation on the calculation of thermodynamic properties (specific heat, enthalpy, etc.), see Ref. 13.

3. COLLISION CROSS SECTIONS

The most widely used method of Chapman and Enskog[15] for evaluation of the transport coefficients entails the calculation of certain weighted total collision cross sections. If the interaction potential between charged particles is chosen as the shielded Coulomb potential, it is necessary to choose an effective shielding distance, commonly the Debye shielding distance. For temperature and particle number density ranges where the Debye distance is much greater than the interparticle distance, as long as the plasma conditions remain ideal (Lieberman *et al.*[16]), the Debye length is used as the shielding distance for the Coulomb potential. But in cases of only a few particles within a Debye sphere, such as in nonideal plasmas, the previously described approach becomes questionable.

Thus, the effective shielding distance is chosen according to Kihara *et al.*[8] as

$$k_{\mathrm{eff}} = k_1 \exp\left(\frac{k_1^2 + k_2^2}{2k_2^2} \ln\left(\frac{k_1^2 + k_2^2}{k_1^2}\right) - 1/2\right) \tag{9}$$

where

$$k_1 = 1/\lambda_{\mathrm{D}_e} = \sqrt{e^2 n_e/\varepsilon_0 k T_e}$$

$$k_2 = 1/\lambda_{\mathrm{D}_i} = \sqrt{e^2 \sum_{i=1}^{i_{\max}} i n_i \bigg/ \varepsilon_0 k T_i}$$

Thus

$$\lambda_{\mathrm{D}_{\mathrm{eff}}} = 1/k_{\mathrm{eff}}$$

The quantity $\lambda_{\mathrm{D}_{\mathrm{eff}}}$ is chosen to evaluate the collision integrals of the Chapman and Enskog type.

4. ATOM–ATOM INTERACTION

The most popular potential model for neutrals is the Lennard-Jones model. But because of the complexity of evaluating the collision integrals, simplified interaction potentials have been suggested by Amdur and Mason.[17] In their repulsive potential model, the relative insensitivity of the attraction potential in the high-temperature region is taken into account.

Thus

$$\phi = \phi_0 \exp(-r/r_0)$$

is adopted with $\phi_0 = 7100$ eV and $r_0 = 0.258$ Å.

5. ION–ATOM INTERACTION

There are two different types of ion–atom interactions. One of them causes charge transfer from the ion to the atom, and the other is a purely elastic collision. For elastic collisions the repulsive potential model of atom–atom collisions is used with $\phi_0 = 4640$ eV and $r_0 = 0.306$ Å. For charge transfer collision cross sections, a good approximation has been suggested by Dalgarno[18] in the form

$$Q^{(l)} = (A - B \ln g)^2$$

where g is the relative speed of the particles and A and B are constants. The values $A = 25.61$ and $B = 1.196$ are suggested by Dalgarno[18] for Q in $(\text{Å})^2$ and g in cm/s, and Devoto[4] used these values in his work. Later on Devoto[6] used $A = 31.8$ and $B = 1.725$ to correct for a polarization effect in the low-temperature regime. Choosing the larger values for A and B may reflect the effect of polarization reasonably, but in the relatively high energy regime it may underestimate the collision cross section. Several other chosen values for A and B are listed in the paper by Bose.[3] Since the calculation domain that is of interest in this paper falls in the low-pressure ranges, $A = 36.74$ and $B = 2.11$ are chosen to account for the polarization effect in the low-temperature region.[3]

6. ELECTRON–ATOM INTERACTION

The collision cross section between electrons and neutral particles can be determined from experimental data of momentum-transfer cross sections. Although experimental values for momentum cross sections are available, the energy range covered by those data is restricted, and the classical method of determining the collision cross section from the interaction potential cannot be used because of the Ramsauer effect.

Thus, in order to evaluate the collision integrals in the form

$$\bar{Q}^{(l,s)}(T) = \frac{1}{(s+1)!} \int_0^{\infty} Q^{(1)} x^{s+1} \exp(-x)\, dx$$

where

$$x = \frac{\mu g^2}{2kT}$$

a cut-off procedure for the upper limit is required in connection with using experimental data for $Q^{(1)}$. This is done within the availability of data for the momentum-transfer cross section. Itikawa's[19] momentum-transfer cross section is used, and the integration is performed by using the Gauss–Laguerre 32-point formula.[20]

7. INTERACTION BETWEEN CHARGED PARTICLES

Cross-section data for charged particles using as potential model either the shielded Coulomb potential (Mason *et al.*[21]) or the Morse potential (Samuilov *et al.*[22]) are available.

In Ref. 22 the Morse potential has been used as

$$\phi(r) = \phi_0(\exp(-2(C/\sigma)(r - r_c)) - 2\exp(-(C/\sigma(r - r_c)))$$

where

$$C = \sigma \ln 2/(r_c - \sigma)$$

Because of a finite value at $r = 0$ in the Morse potential which is physically unrealistic, the authors of Ref. 22 used an infinite potential for $r < 0.3\sigma$ in order to prevent particle trajectories through the center of the interacting particles.

In Ref. 21 a shielded Coulomb potential was used to tabulate the dimensionless form of the collision integrals

$$\Omega^{(l,s)*} = \bar{Q}^{(l,s)}(i,j)/\pi\sigma_{i,j}^2$$

where

$$\bar{Q}^{(l,s)}(i,j) = \frac{4(l+1)}{(s+1)!(2l+1-(-1)^l)} \int_0^\infty \exp(-x)x^{s+1}Q^{(l)}(g)\,dx$$

and

$$x = \frac{\mu g^2}{2kT}$$

$\sigma_{i,j}$ is the effective shielding distance. The data from Mason *et al.*[21] are used for charged particle collision integrals with the effective shielding distance mentioned above.

8. RESULTS AND DISCUSSIONS

Figure 1 shows the difference between variously defined shielding distances. The effective shielding distance has been used in this calculation. As can be seen from this plot, choosing the shielding distance according to different definitions can lead to different charged particle collision cross sections that deviate from each other by a factor of 2 or 3.

The plasma composition is plotted in Fig. 2 for $\theta = 1$, and Fig. 3 shows the varying electron number densities for increasing θ. The starting temperature for ionization increases as the relaxation rate between electrons and ions increases, and the maximum ionization also increases, as shown in Fig. 4. But in real situations, it is expected that strong electron diffusion takes place as the nonequilibrium rate increases. Thus, the higher peak with increasing θ may not be seen in actual experiments.

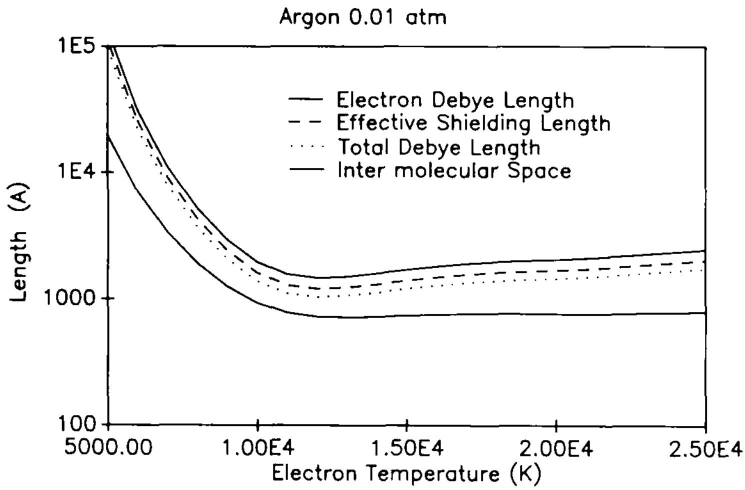

Fig. 1. Comparison of characteristic lengths of plasmas at 0.01 atm.

The specific heat is composed of three parts, i.e., electron, heavy species, and the contribution of reactions between electrons and heavy particles. The total specific heat is the sum of each contribution of those parts and depends heavily on the reaction part. In Fig. 5 each contribution is plotted, and in Fig. 6 the total specific heat for various θ is shown. The relatively

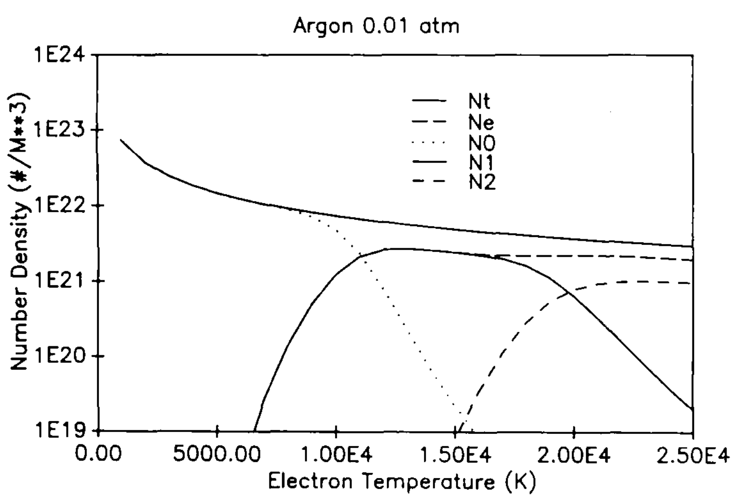

Fig. 2. Composition of an argon plasma at 0.01 atm.

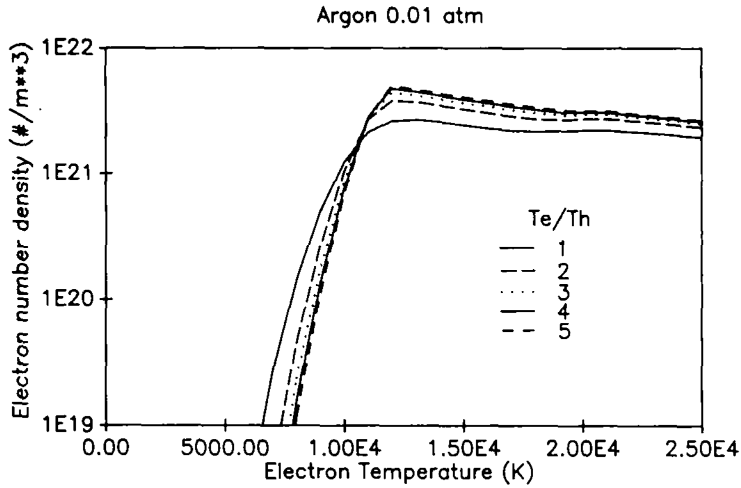

Fig. 3. Electron number density of an argon plasma at 0.01 atm for different θ.

sharp peaks are associated with the rapid change of the ionization rate around 11,000 and 20,000 K which are temperatures where the maximum number densities of first and second ions occur (see Fig. 2). Figure 7 shows the corresponding enthalpies. The rather abrupt changes of the specific heat and enthalpies at large θ are due to the strong dependence of those properties

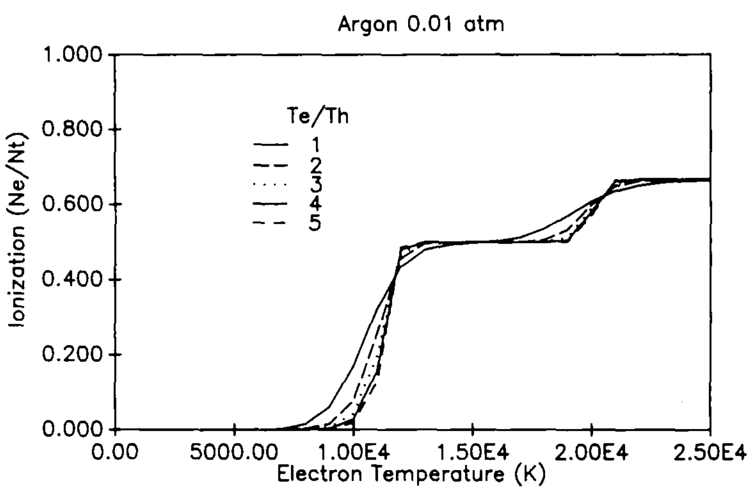

Fig. 4. Degree of ionization of an argon plasma at 0.01 atm for different θ.

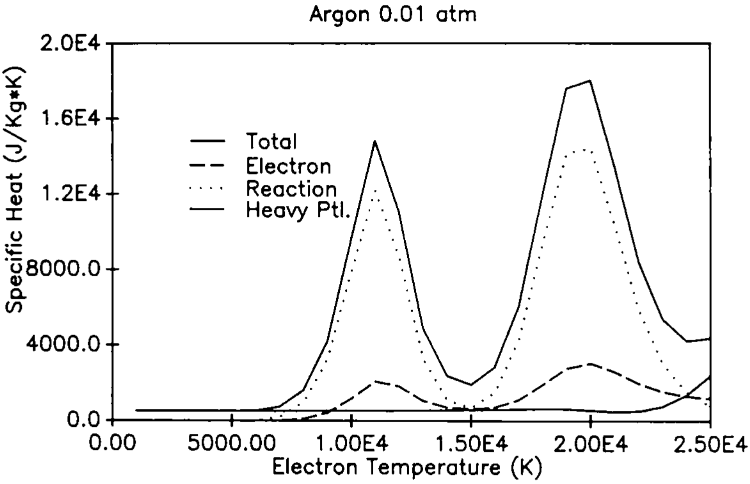

Fig. 5. Species contribution to the specific heat of an argon plasma at 0.01 atm for different θ.

on the reaction between electrons and heavy species, which sharply increases with increasing deviation from equilibrium.

Viscosities are shown in Fig. 8 for different values of θ. Compared with the results of Bose *et al.*,[1] good agreement of the equilibrium viscosity (i.e., $\theta = 1$) is found, but for the nonequilibrium viscosities, discrepancies

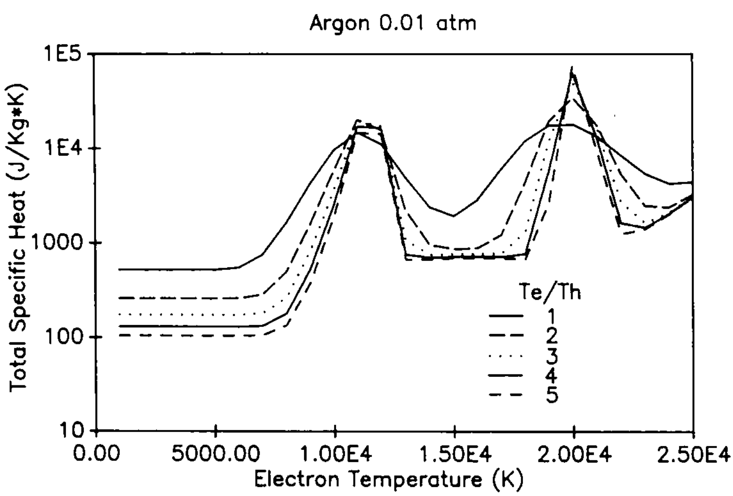

Fig. 6. Total specific heat of an argon plasma at 0.01 atm for different θ.

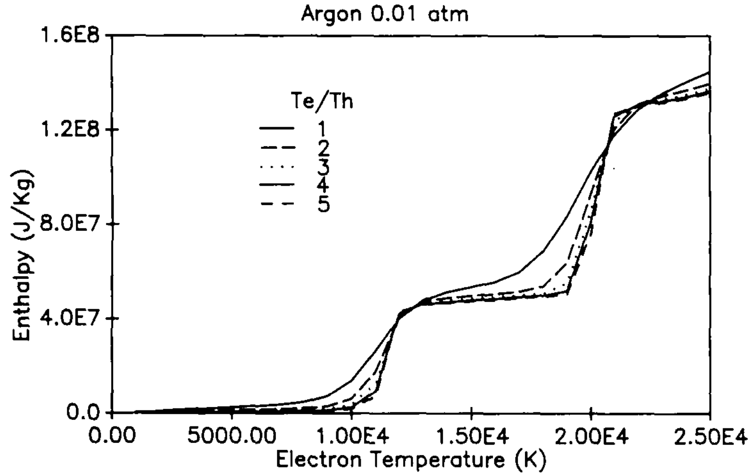

Fig. 7. Enthalpy of an argon plasma at 0.01 atm for different θ.

exist, and this is believed to be due to the different collision cross sections used.

Electrical conductivities are plotted in Fig. 9 and compared with experimental data in Fig. 10 provided by Lin *et al.*[23] Thermal conductivities are calculated by adopting the formulation of Ref. 2 for the nonequilibrium

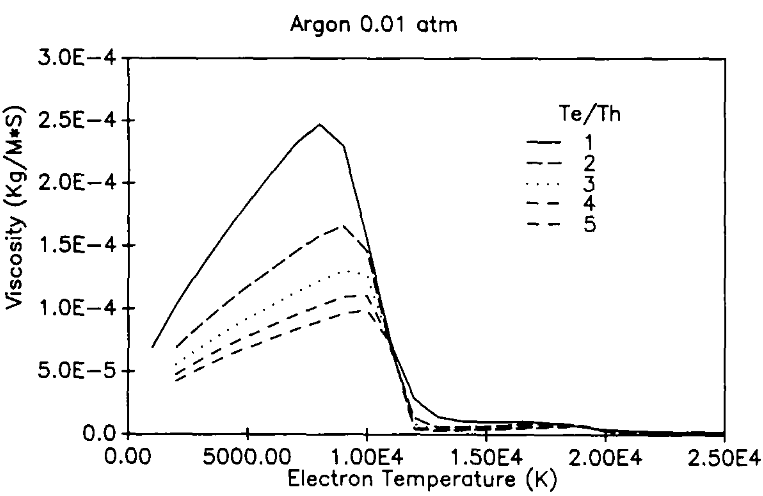

Fig. 8. Viscosity of an argon plasma at 0.01 atm for different θ.

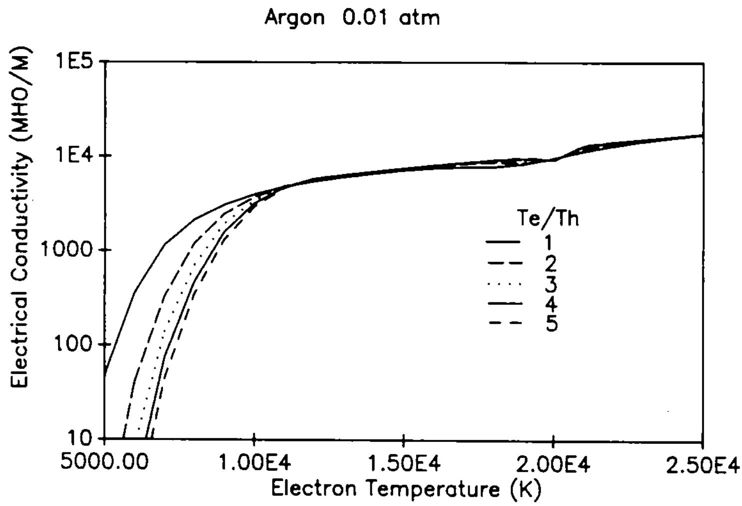

Fig. 9. Electrical conductivity of an argon plasma at 0.01 atm for different θ.

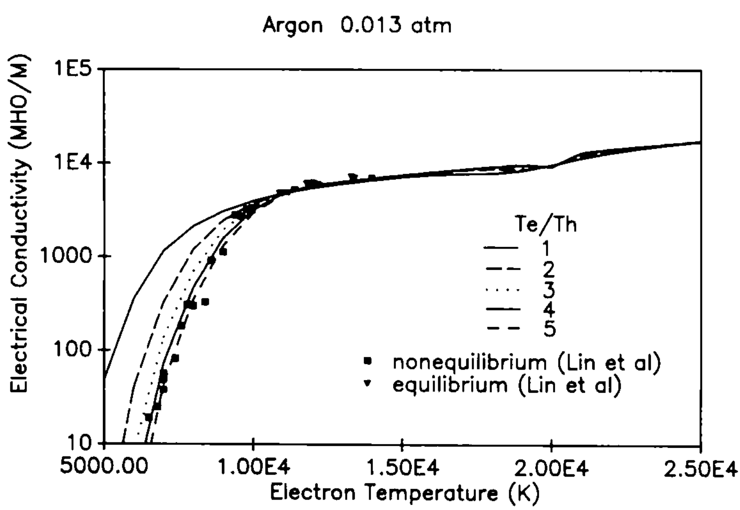

Fig. 10. Comparison of the electrical conductivity of an argon plasma at 0.013 atm with experimental data by Lin *et al.*[23]

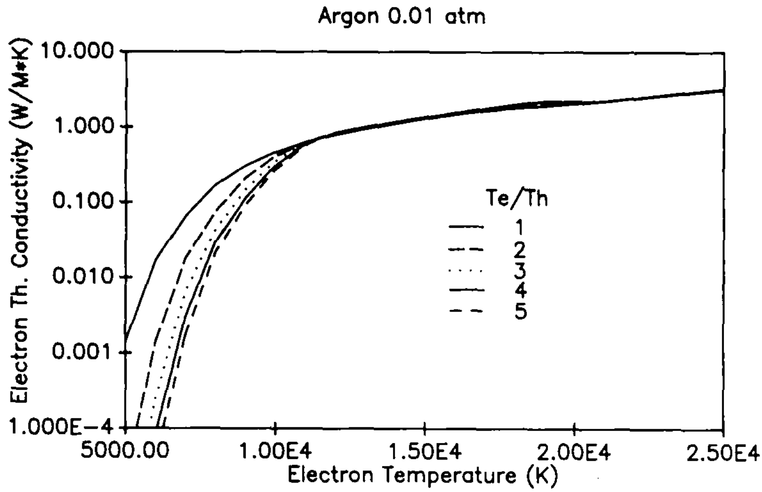

Fig. 11. Electron thermal conductivity of an argon plasma at 0.01 atm for different θ.

plasma case. The reactive thermal conductivity accounts for the heat transferred by the diffusion of ions and electrons to form neutral atoms and to release the ionization energy. Electron thermal conductivities are plotted in Fig. 11. In Lin *et al.*'s shock tube measurements, it was indicated that the electron conductivity was determined by the cross sections for electron-atom collisions which were measured by mobility and scattering techniques. Figure 4 shows that the equilibrium degree of ionization approaches 1% at 9000 K at 0.01 atm, and decreases to 0.1% as the temperature relaxation rate increases to 5. Thus, it is believed that in nonequilibrium cases, because of the increasing temperature difference between electrons and heavy particles, the degree of ionization decreases and, as a result, the deviation from equilibrium becomes larger. As a consequence, the experimental conditions for θ in Ref. 23 are expected to be between 4 and 5.

CONCLUSIONS

It has been found that using a modified Debye length as the shielding distance results in a more reasonable match with experimental data for the electrical conductivity. For the temperature region where nonequilibrium effects prevail, the transport properties predicted by the conventional Debye length[1] are higher than those calculated by the modified Debye length.

Thus, it is believed that in nonequilibrium cases where the temperature difference between electrons and heavy particles is high, using the modified

Debye length as the cut-off distance provides more reasonable values for the transport properties.

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