非平衡プラズマの「電子温度」に関する統計力学的検討 ～酸素プラズマ、窒素プラズマ

平成27年度
「プラズマ科学における分光計測の高度化と原子分子過程研究の新展開」
「原子分子データ応用フォーラムセミナー」合同研究会
於 核融合科学研究所、平成28年1月28日

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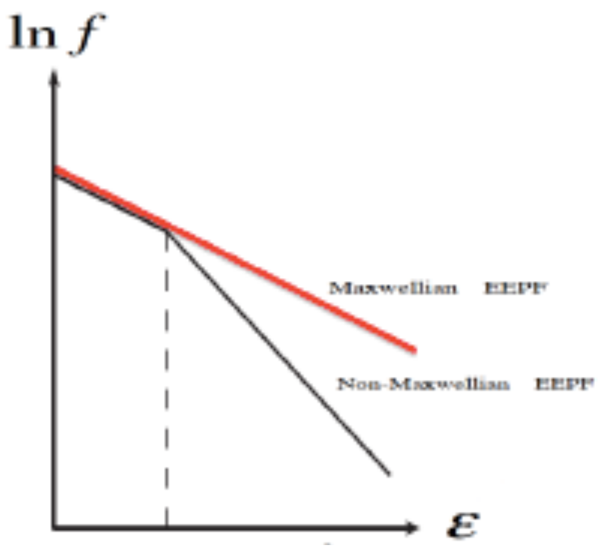
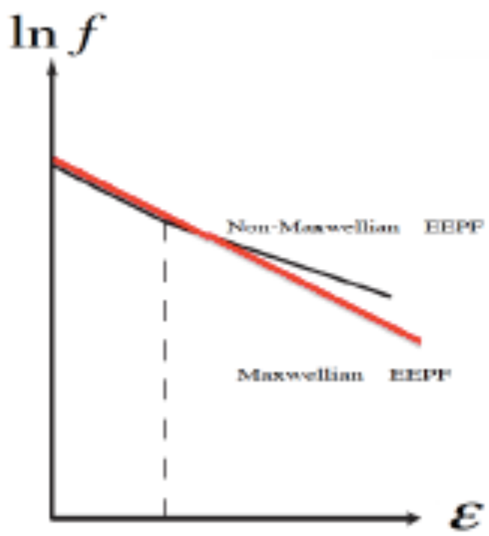
Background: Electron Energy Probabilistic Function (EEPF) of Weakly-Ionized Plasmas

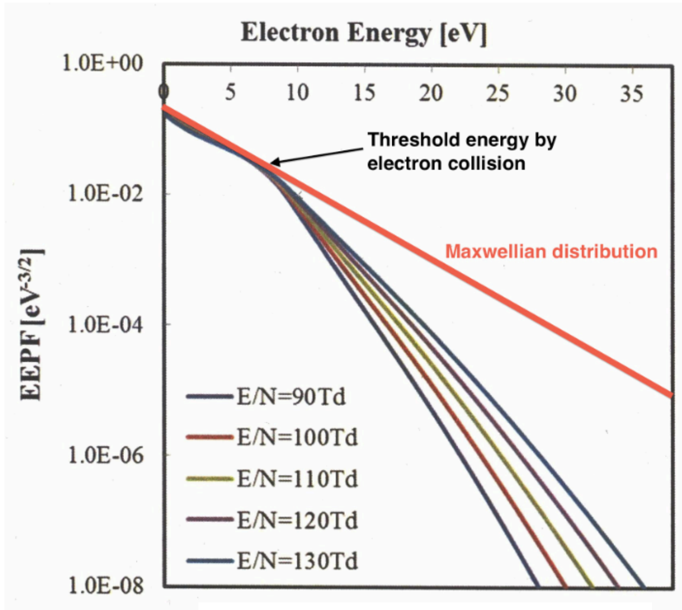
- Weakly-Ionized Plasmas
  - Electrons in them — Generally in a state of non-equilibrium
- Electron energy probabilistic function (EEPF)



Electron energy



Electron energy



Konno, Akatsuka et al, Meeting IEEJ, 2013

What should be called as “Electron Temperature”?

Why don't we return to the fundamentals?

- First law of thermodynamics $\mathrm{d}S = \frac{1}{T}\left(\mathrm{d}U + p\mathrm{d}V - \mu\mathrm{d}N\right)$
- Entropy $S = S(U, V, N)$,

$$\frac{\partial S}{\partial U} = \frac{1}{T}, \frac{\partial S}{\partial V} = \frac{p}{T}, \frac{\partial S}{\partial N} = -\frac{\mu}{T}$$

  - For simplicity, we suppose the following
  - Constant volume $\mathrm{d}V = 0$
    - Constant density
    - Then, the total number is constant $\mathrm{d}N = 0$
- Consequently,

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U$$

In short, $\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$

Entropy as statistical mechanics

- **Gibbs Entropy**
  - If a probabilistic distribution is given as p_i for the state i, the entropy is given as

$$S = -k \sum_i p_i \ln p_i,$$

  - which agrees with Shannon's entropy except for a factor as the Boltzmann constant.
  - For **continuous variables** like energy of free electrons,

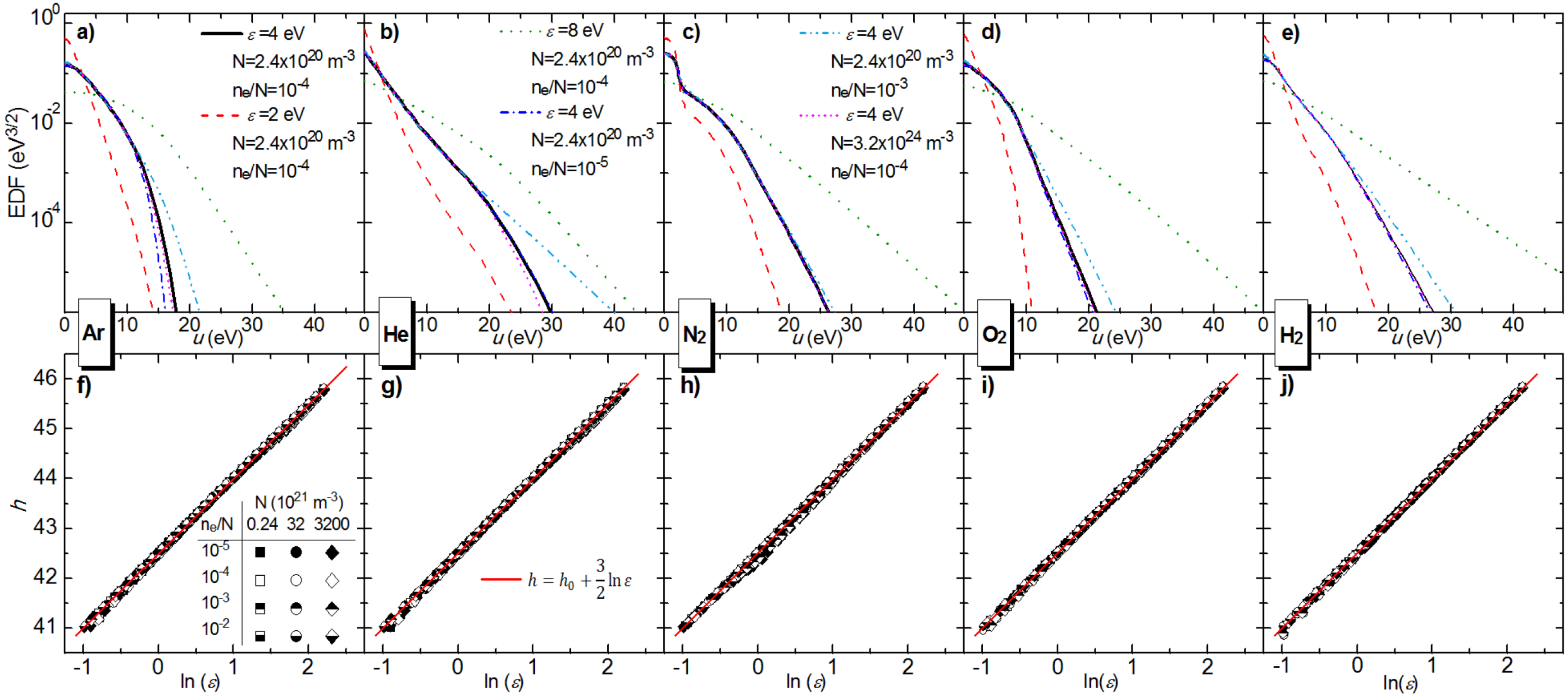
$$S = -k \int_0^\infty F(\varepsilon) \ln\left[F(\varepsilon)\right] \mathrm{d}\varepsilon$$

Objectives of the present study

- First, to find EEPF $f(\varepsilon)$ of weakly-ionized plasma as function of ***E/N*** by the Boltzmann equation,
- Then, by applying $f(\varepsilon)$ to find
  - **Electron mean energy** as internal energy of electron gas $U = \langle \varepsilon \rangle = \int_0^\infty \varepsilon F(\varepsilon) \mathrm{d}\varepsilon$
  - and **Entropy** $S = -k \int_0^\infty F(\varepsilon) \ln[F(\varepsilon)] \mathrm{d}\varepsilon,$
- And finally, to calculate
  - And discuss the "temperature". $T = \left(\dfrac{\partial S}{\partial U} \right)^{-1}$

Similar foregoing research

- "On the kinetic and thermodynamic electron temperatures in non-thermal plasmas", R. Alvarez, J. Cotrino and A. Palmero, EPL, **105,** 15001 (2014).



They concluded ***S* = *S*$_0$ + (3/2)ln *U*** for any gas discharge plasmas. Is it really the case???

Numerical Method

- We also coded a Boltzmann solver to find the EEPF *f*.
- By a global model, we solved rate equations for main excited species of oxygen and nitrogen.

Boltzmann equation in two-term approximation for oxygen plasma

$$-\frac{\mathrm{d}}{\mathrm{d}u}\left[\frac{1}{3}\left(\frac{E}{N}\right)^2 \frac{u}{\Sigma\delta_S\sigma_c(u)}\frac{\mathrm{d}f}{\mathrm{d}u} + \left(\sum_s \delta_S \frac{2m}{M}\sigma_c(u)\right)u^2\left(f + \frac{kT_g}{e}\frac{\mathrm{d}f}{\mathrm{d}u}\right)\right]$$

$$+\sum_i u\sigma_{si}(u)f(u) = 0$$

Inelastic collisions

$$e + O_2(X^3\Sigma_g^-) \rightarrow e + O_2(Y)$$

$$Y = O_2(a^1\Delta_g, b^1\Sigma_g^+, 4.5\,\mathrm{eV}, 6.0\,\mathrm{eV}, 8.4\,\mathrm{eV}, 9.97\,\mathrm{eV}, 14.7\,\mathrm{eV})$$

$$e + O(2p^{4\,3}P) \rightarrow e + O(Y)$$

$$Y = O(2p^{4\,1}D, 2p^{4\,1}S, 3s\,^5S^o, 3s\,^3S^o, 3p\,^5P, 3p\,^3P,)$$

$$e + O_2(X^3\Sigma_g^-) \rightarrow e + e + O_2^+$$

$$e + O(2p^{4\,3}P) \rightarrow e + e + O^+$$

$$e + O_2(X^3\Sigma_g^-) \rightarrow e + O + O^-$$

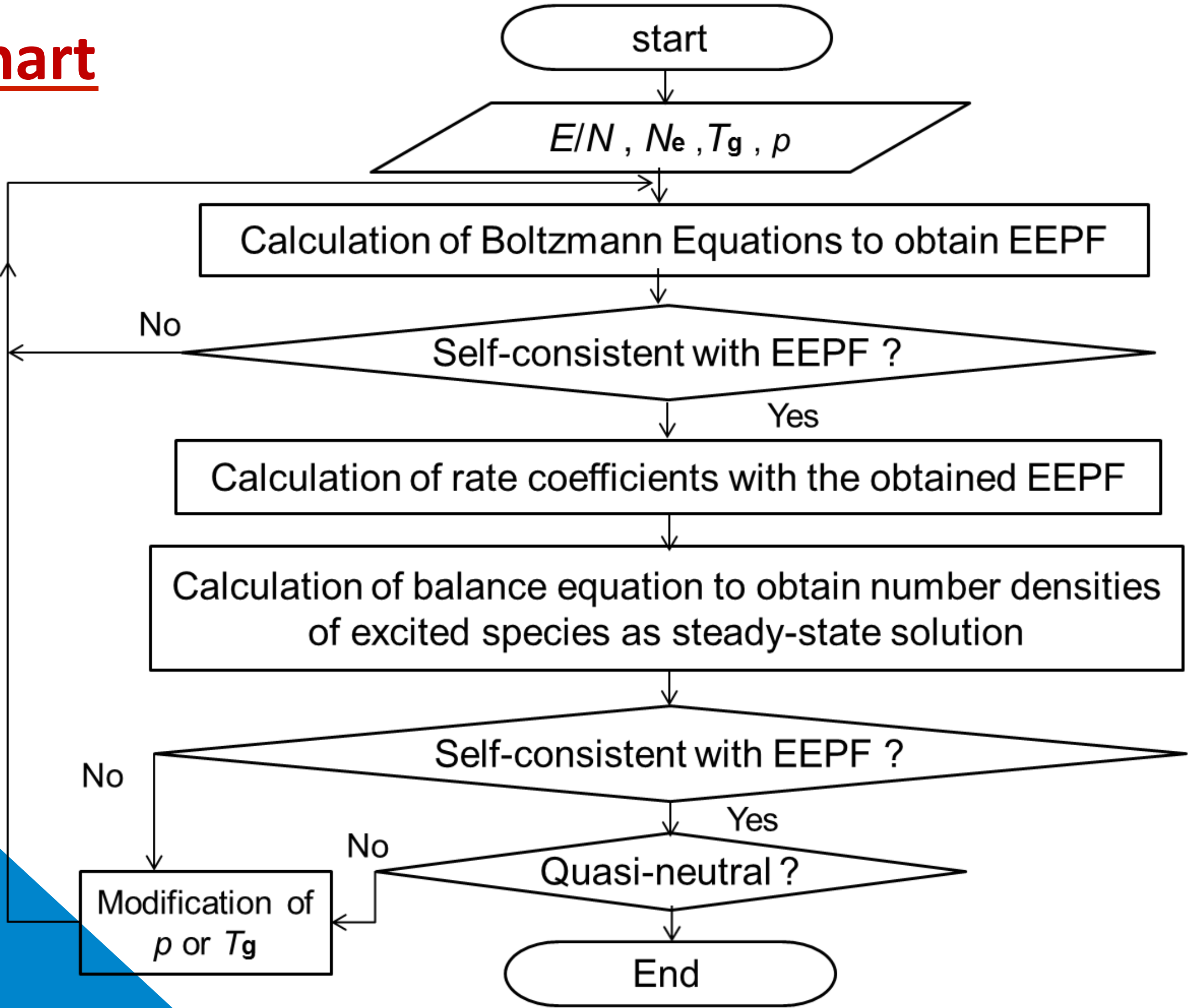
$$e + O_2(X^3\Sigma_g^-, 0) \rightarrow e + O_2(X^3\Sigma_g^-, w) \quad (1 \le w \le 2)$$

σ_{sc} momentum transfer cross section ($\delta_s = \delta_{atom}$, $\delta_{molecule}$、$\delta_{atom} + \delta_{molecule} = 1$)
σ_{si} i-th inelastic cross section
T_g gas temperature
m electron mass
M neutral mass (for molecule, 2 x atom)
e elementary charge

Ichikawa, Sakamoto, Akatsuka et al, 2010.

Model of excitation kinetics

Flow Chart



Rate Equations (Global Model)

We treat steady-state microwave discharge in a cylindrical discharge tube with its diameter 2*R*.

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\nu_{\mathrm{W}}[\mathrm{A}] + G = 0$$

$$\mathrm{A} = \mathrm{O_2}(\mathrm{X}\,^3\Sigma_g^-), \mathrm{O_2}(\mathrm{a}\,^1\Delta_g), \mathrm{O_2}(\mathrm{b}\,^1\Sigma_g),$$

$$\mathrm{O}(^3\mathrm{P}), \mathrm{O}(^1\mathrm{D}), \mathrm{O_2^+}, \mathrm{O^-}, \mathrm{O_3}$$

Boundary conditions on a tube surface

$$\nu_W = \frac{\gamma \bar{c}}{2R} \qquad (\gamma << 1)$$

$$= \frac{(2.405)^2 D}{R^2} \quad (\gamma \approx 1)$$

γ Loss coefficient at wall collision

$\bar{c}$ thermal velocity

D diffusion coefficient

G source term by collisions

E.g., for $O_2(a\,^1\Delta_g)$ formation by

$$\mathrm{O_2}(\mathrm{X}\,^3\Sigma_g^-) + e^- \rightarrow \mathrm{O_2}(\mathrm{a}\,^1\Delta_g) + e^-,$$

we set

$$G = k \cdot [\mathrm{O_2}(\mathrm{X}\,^3\Sigma_g^-)] \cdot N_e$$

where

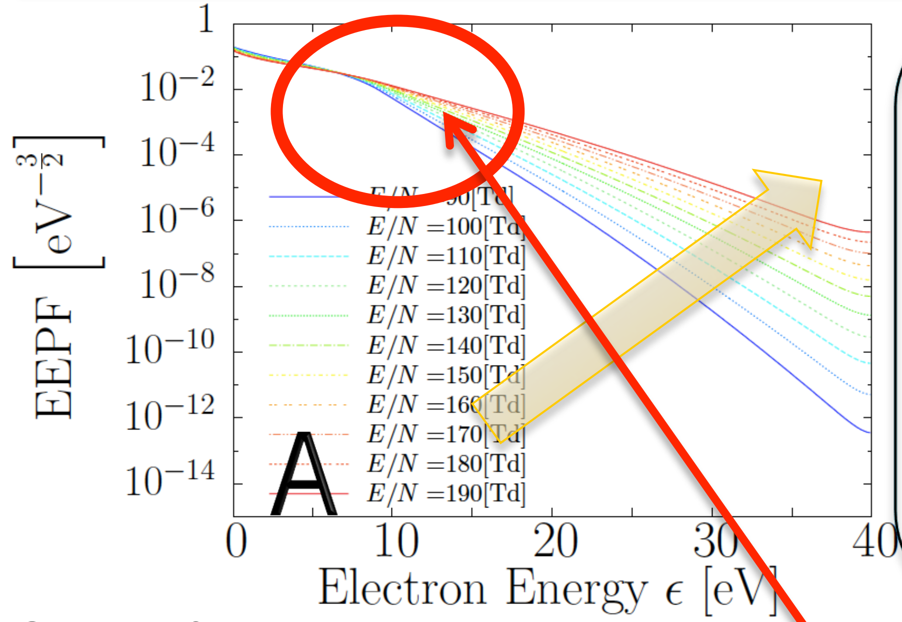
$$k = \sqrt{\frac{2}{m_e}} \int_0^\infty \sigma(\varepsilon)\varepsilon f(\varepsilon)\mathrm{d}\varepsilon$$

$f(\varepsilon)$: EEPF

Konno, Akatsuka et al, Meeting IEEJ, 2013

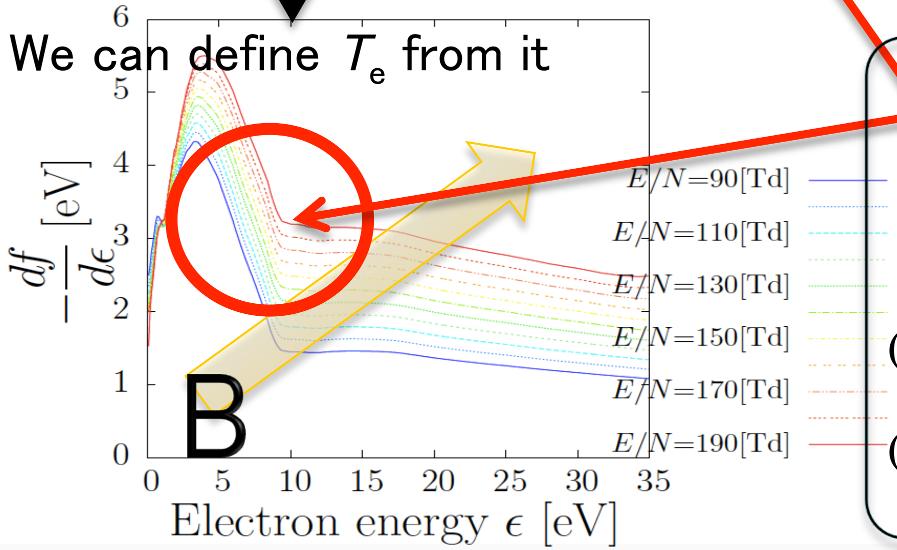
RESULTS and DISCUSSION
(1) O_2 Discharge Plasma

(1) T_e as a slope of non-Maxwellian EEPF



Slope of EEPF

We can define T_e from it



◆ When the reduced electric field increases,

A EEPF comes close to Maxwellian,

B It does not mean being equilibrated.

◆ Depletion in high-energy electron

At ~ 8 eV

Essential processes — Threshold energy

(1) $O_2 + e^- \rightarrow O(^3P) + O(^3P) + e^-$ 5.9 eV

(2) $O_2 + e^- \rightarrow O(^3P) + O(^1D) + e^-$ 8.4 eV

(2) “T_e” as a slope in each energy region

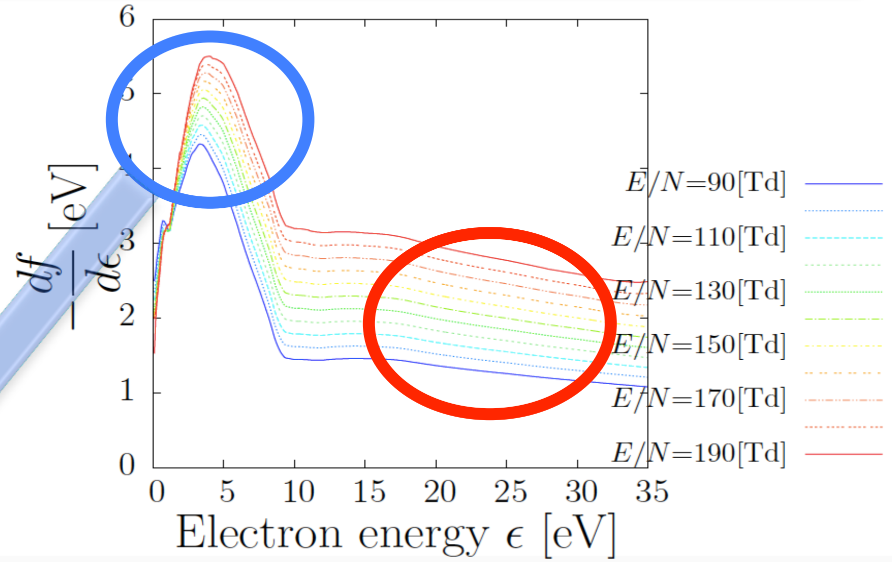
◆ Definition of energy region

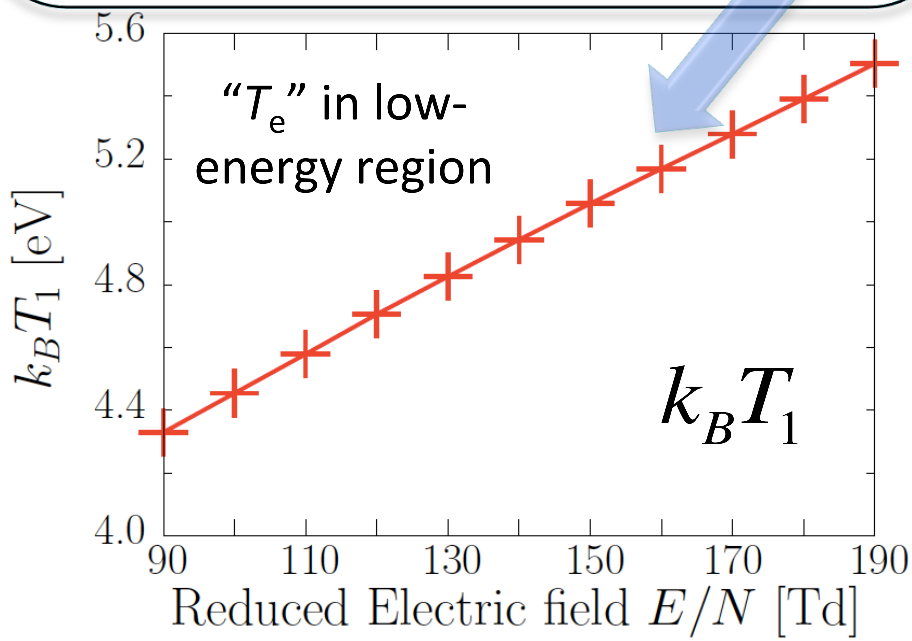
Low-energy region $k_B T_1$

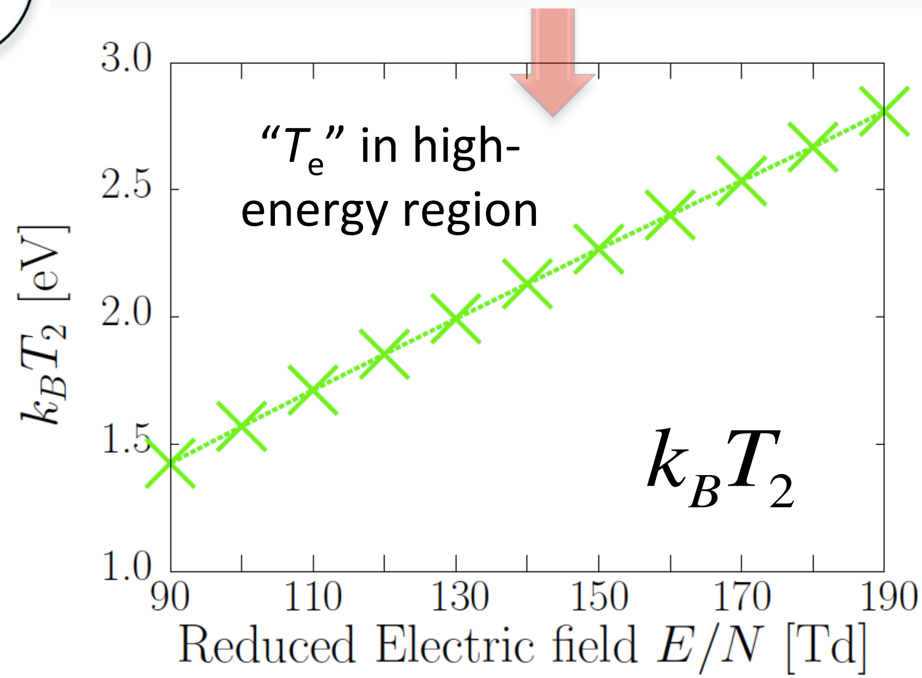
Maximum value is adopted.

High-energy region $k_B T_2$

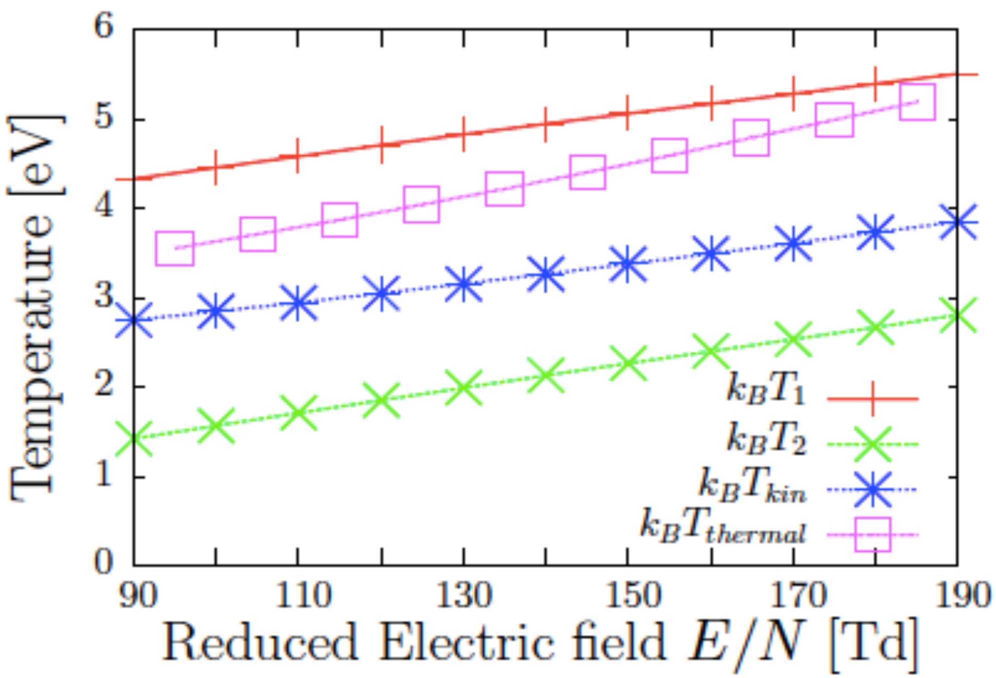
Average value of electrons with its energy $\varepsilon \geq 9$ eV is adopted.







(3) Comparison of these electron temperatures



Bulk region has larger weight.

◆ "$T_{e,\ thermal}$" derived from thermodynamic relationship

$$k_BT_{thermal} \sim 3.5 - 5.2 \text{ eV}$$

- R. Alvarez, *et al.* $k_BT_{thermal} = k_BT_{kin}$

- Our present study $k_BT_{thermal} \Rightarrow k_BT_1$ $k_BT_{thermal} \neq k_BT_{kin}$

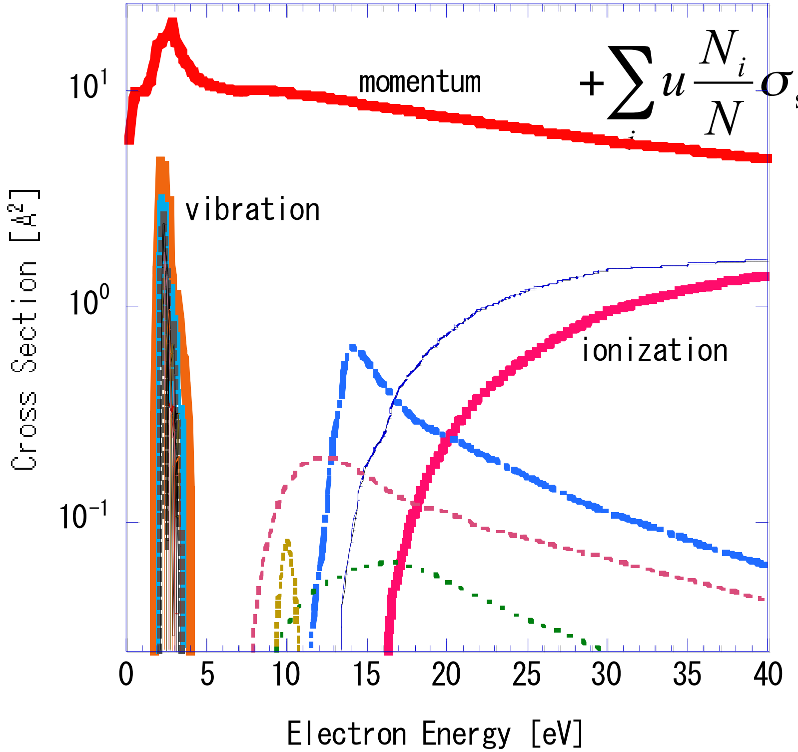
RESULTS and DISCUSSION
(2) N_2 Discharge Plasma

EEDF — Eq. for EEPF

- Two-term approximation for $f_0(u)$
  - The Boltzmann equation for nitrogen plasma

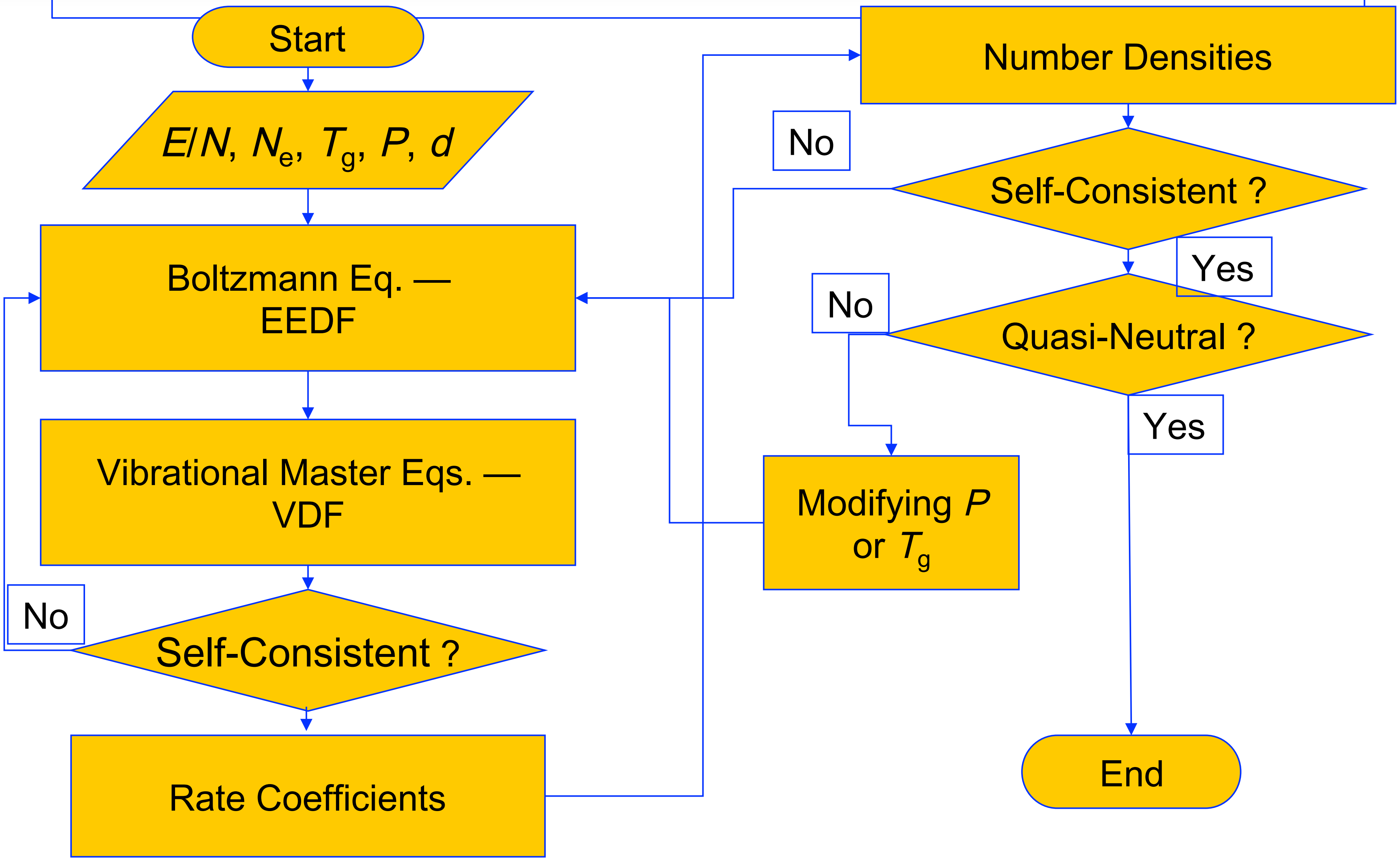
$$-\frac{\mathrm{d}}{\mathrm{d}u}\left[\frac{1}{3}\left(\frac{E}{N}\right)^2 \frac{u}{\sigma_\mathrm{c}(u)+\sum_i \sigma_{\mathrm{s}i}(u)}\frac{\mathrm{d}f}{\mathrm{d}u}+\frac{2m}{M}\sigma_\mathrm{c}(u)u^2\left(f+\frac{kT_\mathrm{g}}{e}\frac{\mathrm{d}f}{\mathrm{d}u}\right)\right]$$

$$+\sum_i u\frac{N_i}{N}\sigma_{\mathrm{s}i}(u)f(u)-\sum_i\left(u+u_{\mathrm{s}i}\right)\frac{N_i}{N}\sigma_{\mathrm{s}i}\left(u+u_{\mathrm{s}i}\right)f\left(u+u_{\mathrm{s}i}\right)=0$$



$$\int_0^\infty f(u)u^{1/2}\mathrm{d}u=1$$

Numerical Model



Ref: Yosuke Ichikawa, Takeshi Sakamoto, Atsushi Nezu, Haruaki Matusura, and Hiroshi Akatsuka: Jpn. J. Appl. Phys. **49** (2010) 106101

EEDF — Collision term

- Low ionization degree — negligence of Coulomb collisions
- Electron collision — Phelps(1985)
  - Vibrational excitation of X —with super-elastic collision
    - Between vibrational levels
  - Electronic excitation and ionization —from the ground state only (Guerra et al., 2004)
  - Reactions considered

$$e^- + N_2\left(X^1\Sigma_g^+\right) \rightarrow e^- + N_2\left(Y\right)$$

$$Y = N_2\left(A^3\Sigma_u^+, B^3\Pi_g, C^3\Pi_u, a'^1\Sigma_u^-, a^1\Pi_g, w^1\Delta_u, B'^3\Sigma_u^-, W^3\Delta_u\right)$$

$$e^- + N_2\left(X^1\Sigma_g^+\right) \rightarrow e^- + e^- + N_2^+$$

$$e^- + N_2\left(X^1\Sigma_g^+, v\right) \underline{\leftrightarrow} e^- + N_2\left(X^1\Sigma_g^+, w\right) \quad \left(v, w = 0 - 8\right)$$

VDF — Processes to be considered

$$e^- + N_2\left(X^1\Sigma_g^+, v\right) \leftrightarrow e^- + N_2\left(X^1\Sigma_g^+, w\right) \quad \left(v, w = 0 - 45\right)$$

$$N_2\left(X, v\right) + N_2\left(X, w\right) \leftrightarrow N_2\left(X, v-1\right) + N_2\left(X, w+1\right)$$

$$N_2\left(X, v\right) + N_2 \leftrightarrow N_2\left(X, v-1\right) + N_2$$

$$N_2\left(X, v\right) + N_2\left(X, w = 45\right) \rightarrow N_2\left(X, v-1\right) + N + N$$

$$N_2 + N_2\left(X, w = 45\right) \rightarrow N_2 + N + N$$

$$N_2\left(X, v\right) + N \leftrightarrow N_2\left(X, w\right) + N \quad \left(v - 5 \le w \le v - 1\right)$$

$$N_2\left(X, v\right) + \text{wall} \rightarrow N_2\left(X, v-1\right) + \text{wall}$$

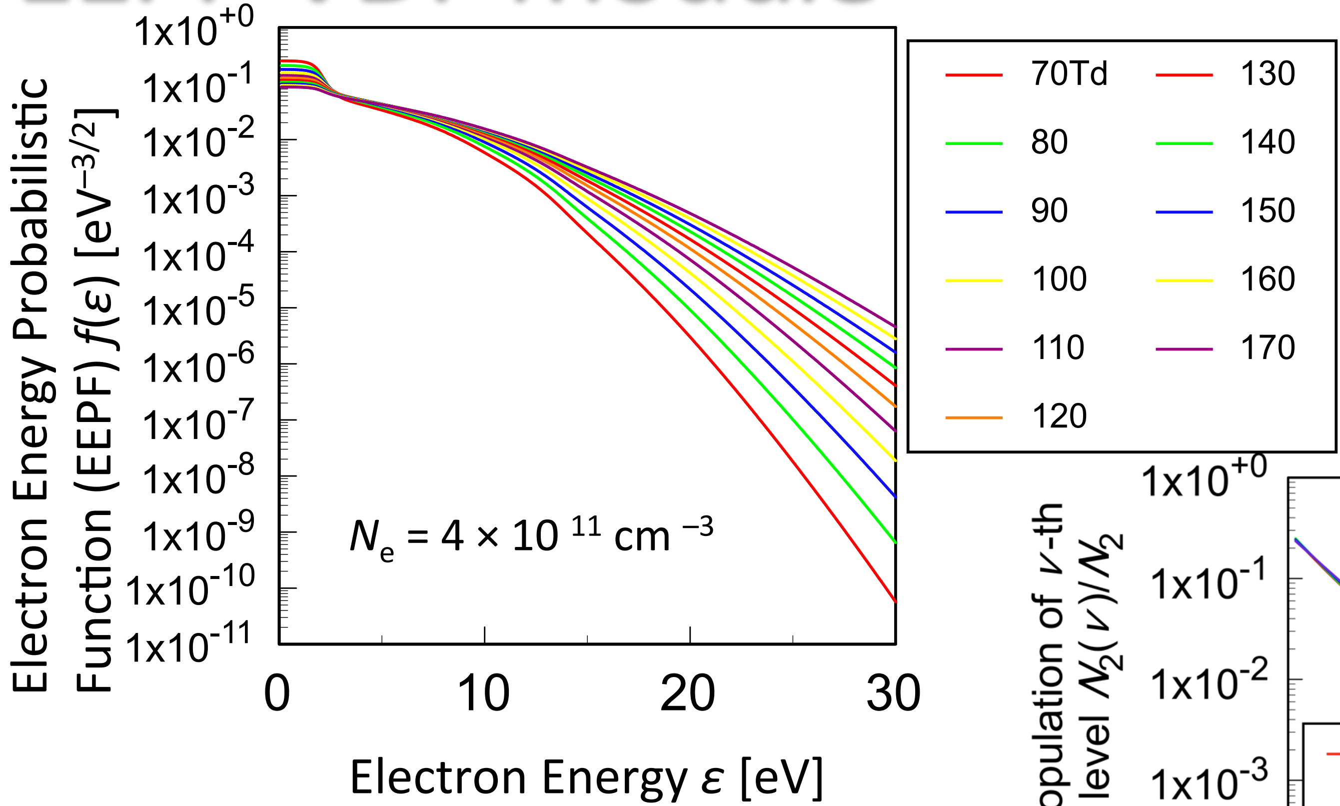
VDF — Master equation

- Temporal variation in the number density of v-th vibrational level N_v

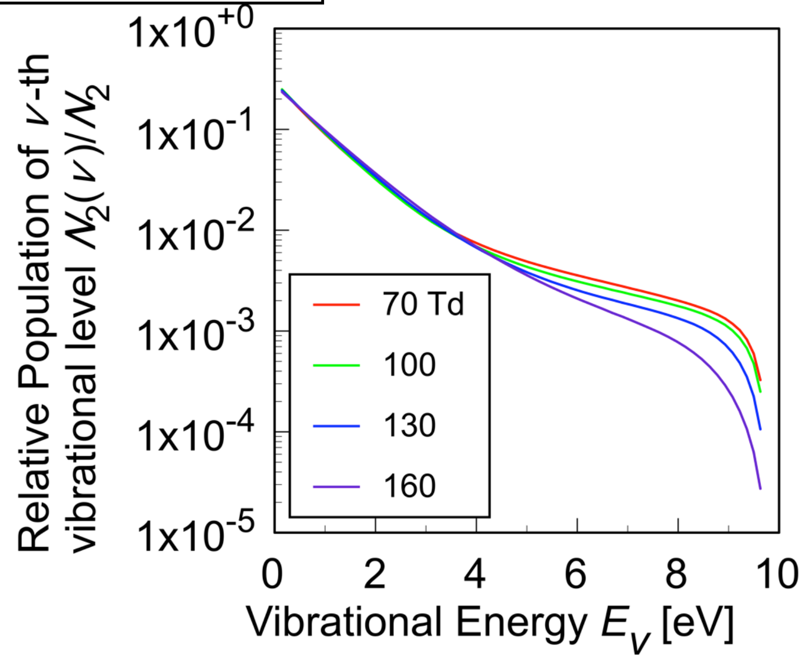
$$\frac{\mathrm{d}N_v}{\mathrm{d}t} = N_\mathrm{e} \sum_{w=0,\neq v}^{M} N_w C_w^v - N_\mathrm{e} N_v \sum_{w=0,\neq v}^{M} C_v^w$$
$$+N_{v-1} \sum_{w=0,\neq v}^{M-1} N_{w+1} Q_{v-1,v}^{w+1,w} + N_{v+1} \sum_{w=0,\neq v}^{M-1} N_w Q_{v+1,v}^{w,w+1} - N_v \left(\sum_{w=0,\neq v}^{M-1} N_{w+1} Q_{v,v+1}^{w+1,w} + \sum_{w=0,\neq v}^{M-1} N_w Q_{v,v-1}^{w,w+1} \right)$$
$$+\left[\mathrm{N}_2\right]\left(N_{v-1} P_{v-1,v} + N_{v+1} P_{v+1,v}\right) - N_v \left[\mathrm{N}_2\right]\left(P_{v,v-1} + P_{v,v+1}\right) + R_v = 0$$

- Dissociation degree treated is low enough.
  - At this stage, dissociated atoms are assumed to be associate at once with the same probability into any vibrational levels (rate R_v)

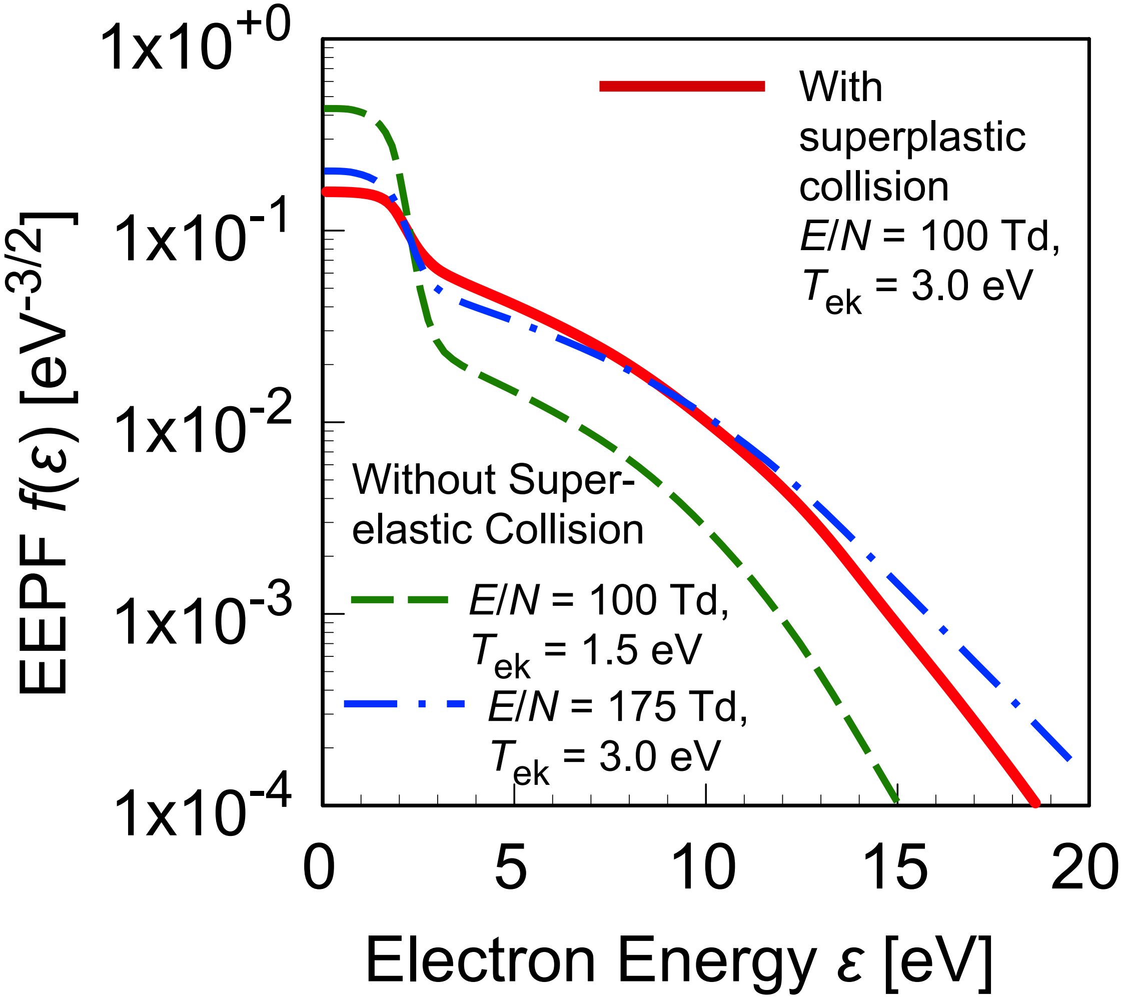
Example of numerical results of EEPF-VDF module



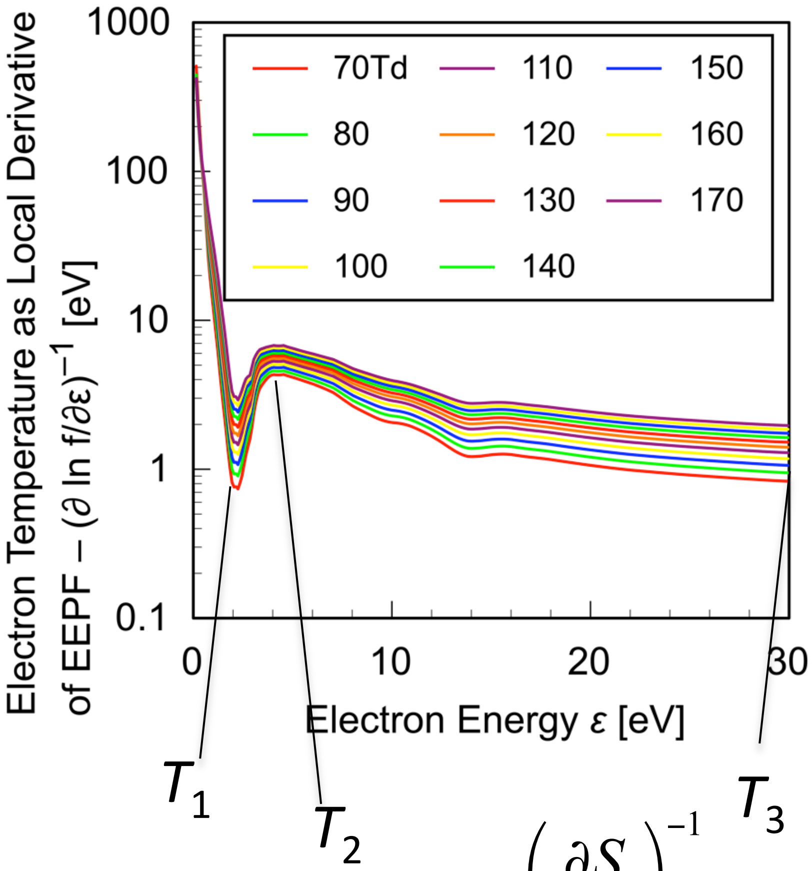
$N_e = 4 \times 10^{11}$ cm $^{-3}$
Discharge pressure 1 Torr
Gas temperature is modified to make N_e constant as above.
$T_g = 1000 – 2200$ K.

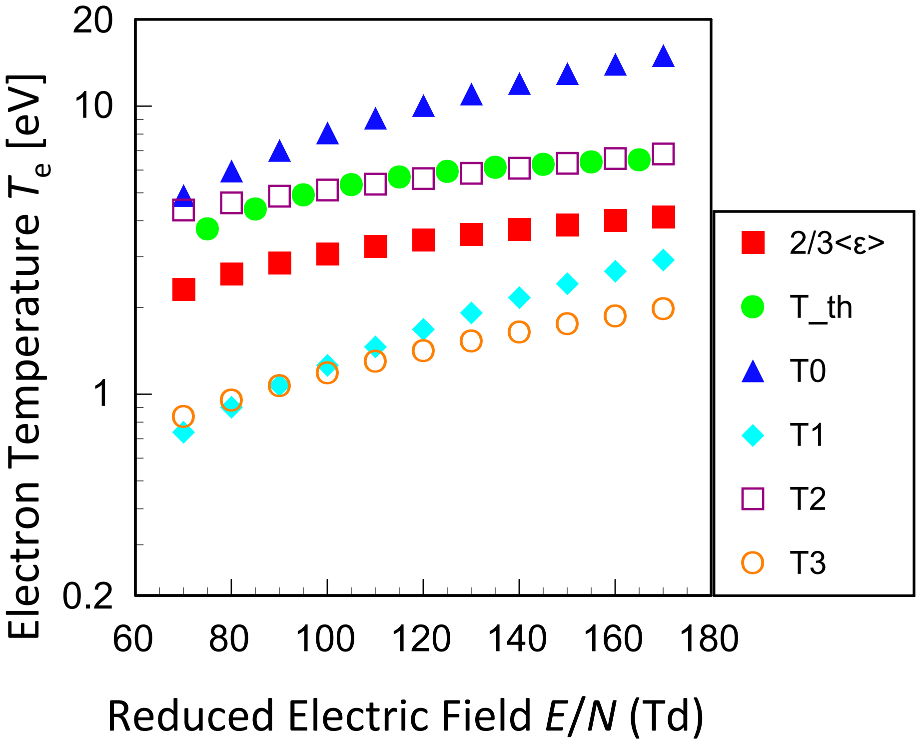


If we don't include superelastic collisions with vibrational levels, …



(2) Comparison of various temperatures





$$T_{\mathrm{th}} = \left(\frac{\partial S}{\partial U} \right)^{-1}$$

$$T_{\mathrm{kin}} = \frac{2}{3k} \langle \varepsilon \rangle = \frac{2}{3k} U$$

- Like oxygen plasma, $T_{\mathrm{th}} \neq T_{\mathrm{kin}}$ ($T_{\mathrm{th}} > T_{\mathrm{kin}}$)
- T_{th} is found to be close to T_2, which was situated at ε ~ 4 – 5 eV, also like O_2 plasma.

Further discussion for Tsallis Entropy

Possibility of Tsallis distribution of the EEDF

- Two-term approximated Boltzmann eq.

$$-\frac{\mathrm{d}}{\mathrm{d}u}\left[\frac{1}{3}\left(\frac{E}{N}\right)^2 \frac{u}{\sigma_c(u)+\sum_i \sigma_{si}(u)}\frac{\mathrm{d}f}{\mathrm{d}u} + \frac{2m}{M}\sigma_c(u)u^2\left(f+\frac{kT_g}{e}\frac{\mathrm{d}f}{\mathrm{d}u}\right)\right]$$

  - Since $\sum_i u \frac{N_i}{N}\sigma_{si}(u) f(u) - \sum_i (u+u_{si})\frac{N_i}{N}\sigma_{si}(u+u_{si}) f(u+u_{si}) = 0$ there is no possibility for Tsallis's power-law distribution.

- However, if parameters like N_i depend on f or df/du, this equation is reduced to

$$\rightarrow \quad \frac{\mathrm{d}f(u)}{\mathrm{d}u} = -C'\left[f(u)\right]^q, \quad (q \neq 1)$$

- E.g., when **O_2 dissociation** becomes essential, or **N_2 vibrational levels** become populated, …

If we introduce Tsallis Entropy,

Distribution Function $F(\varepsilon) \propto \exp_q(x) \equiv [1+(1-q)x]^{\frac{1}{1-q}}$

$(x = -C\varepsilon)$

Tsallis Entropy

$$S_q = \frac{k}{1-q}\left[\int_0^\infty F(\varepsilon)^q \,\mathrm{d}\varepsilon - 1\right]$$

Mean energy

$$U_q = \int_0^\infty \varepsilon F(\varepsilon)^q \mathrm{d}\varepsilon \Big/ \int_0^\infty F(\varepsilon)^q \mathrm{d}\varepsilon$$

Then, the generalized temperature is given as

$$\frac{1}{T_q} = \frac{1}{1+(1-q)S_q} \cdot \frac{\partial S_q}{\partial U_q}$$

Conclusion

●We recalculated the electron temperature of oxygen and nitrogen plasmas as $T_{thermal} = (\partial S/\partial U)^{-1}$.

●$T_{thermal}$ is different from the electron kinetic temperature T_{kin}, defined as 2/3 times of electron mean energy. Variation in the state of neutral background particles as collision partners is considered to be essential. (O_2 — dissociation, N_2 — vibrational levels)

●As the reduced electric field increases, $T_{thermal}$ becomes close to the electron temperature of the low-energy bulk region.

Future issues

●We need further case study other than O_2/N_2 discharge.

●We need discussion for the possibility of Tsallis's distribution to describe the EEPF of plasmas with low-ionization degree.