NPP-2024, Moscow , 4. 12. 2024

Electrical Conductivity of WDM: DFT-MD Simulations Benchmarks, Virial Expansions, e-e Collisions

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Outline

- Electrical conductivity in WDM: Strongly Coupled Coulomb Systems, Quantum statistics
- Analytical calculations, Green's function method, exact results in some limiting cases (benchmarks).
- Numerical simulations: density-functional theory for electrons and molecular-dynamics for ions (DFT-MD) simulations. Path-Integral Monte-Carlo (PIMC)
- Combine different approaches: Example: the electrical conductivity $\sigma(T, n)$ of Hydrogen and Beryllium plasmas.

References:
H. Reinholz, G. R., S. Rosmej, R. Redmer, PRE **91**, 043105 (2015)
G. R., M. Schoerner, M. Bethkenhagen, R. Redmer, Phys. Rev. E **104,** 045204 (2021)
M. French, G. R., M. Schörner, M. Bethkenhagen, M.P. Desjarlais, R. Redmer, PRE **105**, 065204 (2022)
G. R., Contrib. Plasma Phys. 2023, e202300002; Phys. Plasmas **31**, 042301 (2024)

Pressure-Produced Ionization of Nonideal Degenerate Plasmas and Electrical Conductivity

Journal of Experimental and Theoretical Physics, Vol. 97, No. 2, 2003, pp. 259–278.
Translated from Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki, Vol. 124, No. 2, 2003, pp. 288–309.

PLASMA, GASES

Pressure-Produced Ionization of Nonideal Plasma in a Megabar Range of Dynamic Pressures

V. E. Fortov[a], V. Ya. Ternovoĭ[a], M. V. Zhernokletov[b], M. A. Mochalov[b], A. L. Mikhailov[b], A. S. Filimonov[a], A. A. Pyalling[a], V. B. Mintsev[a,*], V. K. Gryaznov[a,**], and I. L. Iosilevskiĭ[c]

Electron degeneracy: Θ=T/T_F

5. ELECTRICAL CONDUCTIVITY OF NONIDEAL PLASMAS

In order to describe the electrical conductivity over a broad range of parameters where electrons may obey either Boltzmann or Fermi statistics, expressions (3.1)–(3.4) were combined into an interpolation expression within the τ approximation [94]; that is,

$$\sigma = \frac{4e^2(k_BT)^{-3/2}}{3\sqrt{\pi}m_e}\frac{2}{\lambda_e^2}\int_0^\infty \varepsilon^{3/2}\tau(\varepsilon)\left(-\frac{\partial f_0}{\partial\varepsilon}\right)d\varepsilon, \qquad (5.1)$$

where f_0 is the electron distribution; τ is the relaxation time,

$$\tau^{-1}(\varepsilon) = \sqrt{\frac{2\varepsilon}{m_e}}\left[\sum_j \gamma_j n_j Q_{ej}(\varepsilon) + n_a Q_{ea}(\varepsilon)\right],$$

Q_{ea} and Q_{ei} are the transport cross sections for, respectively, electron–atom and electron–ion scattering; and γ_j is a correction for electron–electron scattering. For the case where the change in statistics occurs, this correction was interpolated as [22]

$$\gamma_j = \gamma_j^B - (\gamma_j^B - 1)\frac{T_F}{\sqrt{T_F^2 + T^2}}$$

with T_F being the Fermi temperature and γ_j^B is a correction for the Boltzmann plasma.

V. E. Fortov *et al.*, J. Exp. Theor. Phys. **97**, 259 (2003)

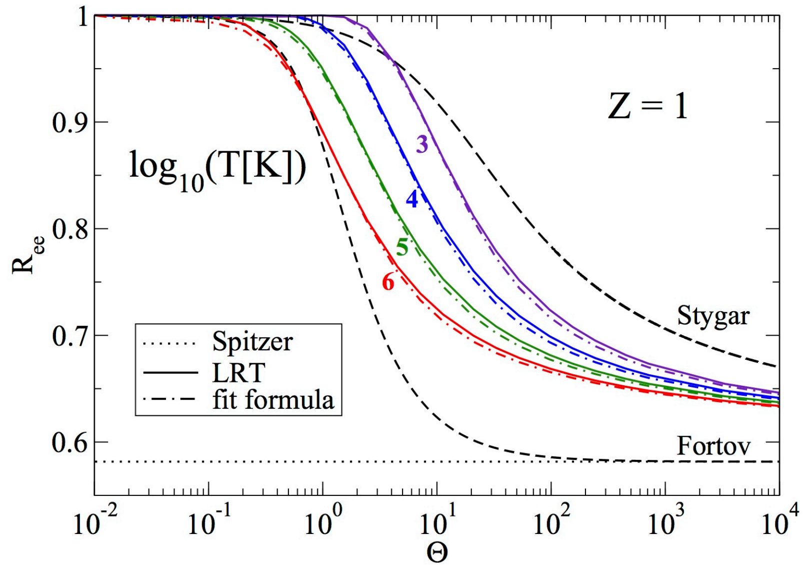


FIG. 1. (Color online) Correction factor R_{ee} of the conductivity due to *e*-*e* collisions as function of degeneracy parameter Θ at $Z = 1$ for different temperatures $T = (10^3, 10^4, 10^5, 10^6)$ K. Numerical calculations (LRT, full lines) are compared with the fit formula (34) (dot-dashed lines) and the approximations (40) of Stygar *et al.* [11] and (41) of Fortov *et al.* [12] (dashed lines).

and Fortov *et al.* [12],

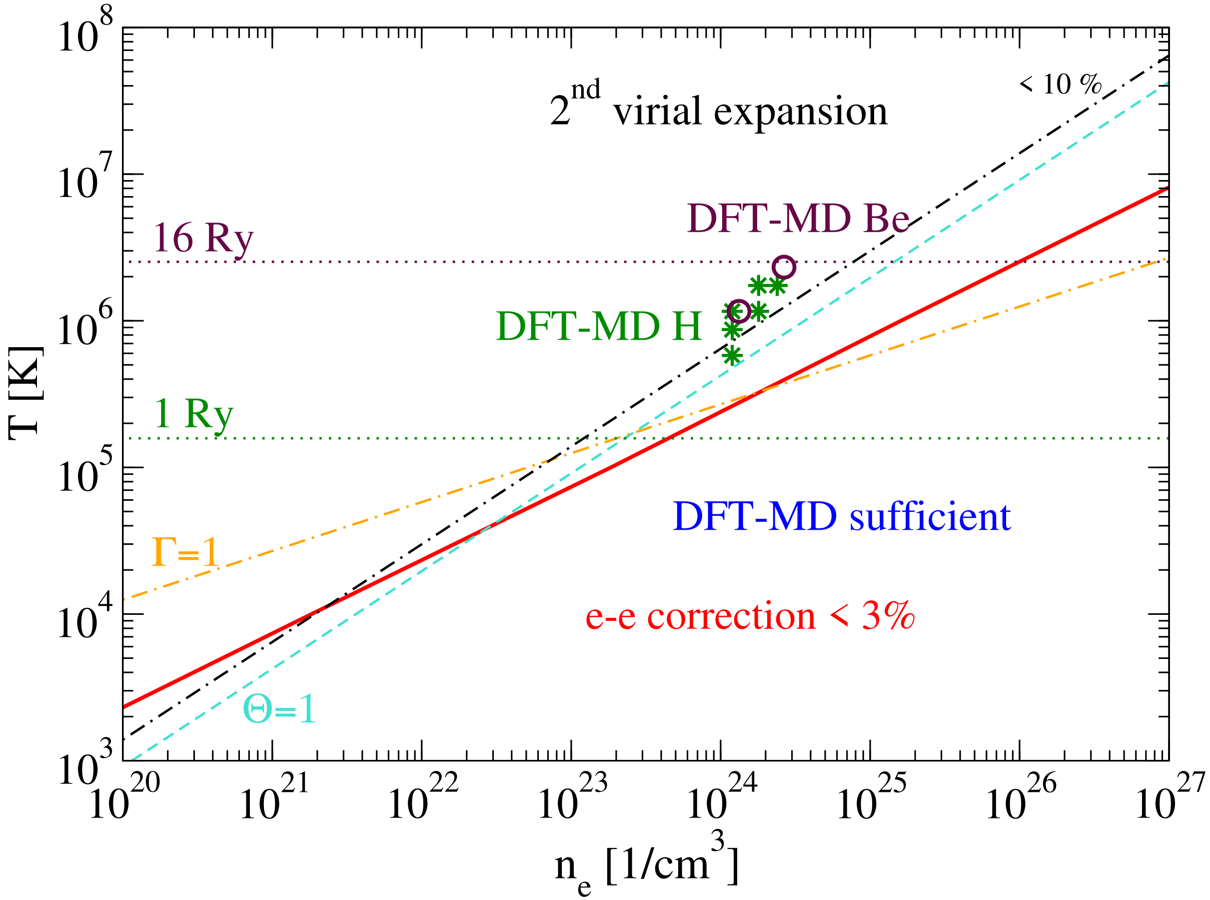
$$R_{ee}^{\rm Fortov}(\Theta, Z) = R_{ee}^{\rm KT}(Z) + \frac{1 - R_{ee}^{\rm KT}(Z)}{\sqrt{1+\Theta^2}}, \qquad (41)$$

with the Spitzer values $R_{ee}^{\rm KT}(Z=1) = 0.582$, see Eq. (29),

H. Reinholz *et al.*, Phys. Rev. E **91**, 043105 (2015).

Plasma parameter T, n_e

Phase diagram: e – e collisions and DFT-MD simulations



“ab initio” calculations vs. analytic expressions

quantum statistical, many-particle approaches

physical properties – correlation functions

thermodynamics: equation of state (EoS)

transport coefficients: electrical, thermal,…

electrical conductivity: Kubo formula

$$\sigma(T,\mu) = \frac{e^2\beta}{3m^2\mathrm{Vol}} \int_{-\infty}^{0} dt e^{\epsilon t} \int_0^1 d\lambda \langle \mathbf{P} \cdot \mathbf{P}(t+i\hbar\beta\lambda)\rangle$$

electron total momentum $\mathbf{P} = \sum_k \hbar\,\mathbf{k}\, a_k^\dagger a_k$ known equilibrium statistical operator

Green's functions:
perturbation theory,
partial summations
quasiparticle, screening

limiting cases

DFT-MD simulations
Exchange-correlation
functional

electron-ion interaction

PIMC simulations
sign problem
limited particle number

uniform electron gas

Virial Expansion of the Electrical Conductivity of Hydrogen Plasmas

dc conductivity $$\sigma(n,T) = \frac{(k_B T)^{3/2}(4\pi\epsilon_0)^2}{m_e^{1/2} e^2}\,\sigma^*(n,T)$$

dimensionless resistivity: virial expansion

$$\rho^*(n,T) = 1/\sigma^*(n,T) = \rho_1(T)\ln\frac{1}{n} + \rho_2(T) + \rho_3(T)\,n^{1/2}\,\ln\frac{1}{n} + \dots$$

dimensionless parameters $\Gamma = \frac{e^2}{4\pi\epsilon_0 k_B T}\left(\frac{4\pi}{3}\hat{n}_e\right)^{1/3}$ $\Theta = \frac{2 m_e k_B T}{\hbar^2}(3\pi^2\hat{n}_e)^{-2/3}$

$$\rho^*(n,T) = \tilde{\rho}_1(T)\ln\left(\frac{\Theta}{\Gamma}\right) + \tilde{\rho}_2(T) + \dots .$$

$$\tilde{\rho}(x,T) = \frac{\rho^*}{\ln(\Theta/\Gamma)} = \tilde{\rho}_1(T) + \tilde{\rho}_2(T)x + \dots \qquad x = 1/\ln(\Theta/\Gamma)$$ virial plot

exact results $\rho_1^{\mathrm{Spitzer}} = 0.846$ $\lim_{T\to\infty}\tilde{\rho}_2(T) = \tilde{\rho}_2^{\mathrm{QLB}} = 0.4917$

(benchmarks)

V. S. Karakhtanov, Contrib. Plasma Phys. **56**, 343 (2016)

The Zubarev Nonequilibrium Statistical Operator

Generalized
linear response theory

Thermodynamic
Green's functions,
Feynman diagrams

ТЕОРЕТИЧЕСКАЯ
И МАТЕМАТИЧЕСКАЯ
ФИЗИКА
Том 194, № 1
январь, 2018

 Г. Рёпке*

ЭЛЕКТРОПРОВОДНОСТЬ СИСТЕМ ЗАРЯЖЕННЫХ ЧАСТИЦ И МЕТОД НЕРАВНОВЕСНОГО СТАТИСТИЧЕСКОГО ОПЕРАТОРА ЗУБАРЕВА

Одной из фундаментальных проблем физики, до сих пор не получившей строгого решения, является статистическая механика неравновесных процессов. Важный вклад в теорию необратимых процессов, берущую начало в обратимой гамильтоновой механике, внес Д. Н. Зубарев, создавший метод неравновесного статистического оператора. Обсуждается подход неравновесного статистического оператора, в частности расширенное уравнение фон Неймана. В качестве примера рассматривается электропроводность системы заряженных частиц. Обсуждается проблема отбора множества релевантных наблюдаемых. Продемонстрирована связь между кинетической теорией и теорией линейного отклика. С помощью термодинамических функций Грина систематически рассмотрены корреляционные функции, однако сходимость разложений требует дальнейшего изучения. Проведено сравнение различных выражений для проводимости, а также перечислены открытые проблемы.

Exact benchmarks from analytical approaches

G. R. and R. Redmer, Phys. Rev. A 39, 907 (1989)
R. Redmer, G. R., F. Morales, and K. Kilimann, Phys. Fluids B 2, 390 (1990).
V.S. Karakhtanov, R. Redmer, H. Reinholz, and G. R., Contrib. Plasma Phys. 51, 355 (2011)
V.S. Karakhtanov, R. Redmer, H. Reinholz, and G. R., Contrib. Plasma Phys. 53, 639 (2013)
V.S. Karakhtanov, Contrib. Plasma Phys. 56, 343 (2016).
V.S. Karakhtanov, Contrib. Plasma Phys. 62, e202100145 (2021).

Two-moment approximation

$$\rho^{(2)} = \rho_{\rm Ziman} \frac{1}{D_{00}^{ei}} \frac{D_{00}^{ei}(D_{11}^{ei} + D_{11}^{ee}) - (D_{01}^{ei})^2}{(25/4)D_{00}^{ei} + D_{11}^{ei} + D_{11}^{ee} - 5D_{01}^{ei}}$$

$$\kappa^2 = s\frac{ne^2}{\epsilon_0 k_B T} = 4\pi s \frac{n_{\rm Bohr}}{T_{\rm Ha}}$$

$$s_{ei} = 4/e = 1.4715$$

$$s_{ee} = 0.5367$$

$$\tilde\rho_{ei}^{(1)} = \rho_{ei}^{*,(1)} x = \rho^*_{\rm Ziman}(s_{ei})\, x = 1.67109 - 0.6217\, x$$

$$\rho^{*,(2)}_{\rm Lorentz} x = \rho_{ei}^{*,(2)} x = 0.51419 + 0.63934x$$

$$\rho^{*,(2)}_{ei+ee} x = 0.8649 + 0.4844x$$

$$\rho^{*,(6)}_{ei+ee} x = 0.8467 + 0.4921x.$$

$$\rho^{*,\rm DFT-MD} x = 0.492 + 0.989x$$

Ziman formula

$$\rho^* = 2^{1/2}\pi\Theta^{3/2}\int_0^\infty dq\, q^3 f_e(q/2)\left|\frac{V_{ei}(q)}{\epsilon_e(q,0)}\right|^2 \frac{\epsilon_0^2}{e^4} S_{ii}(q)$$

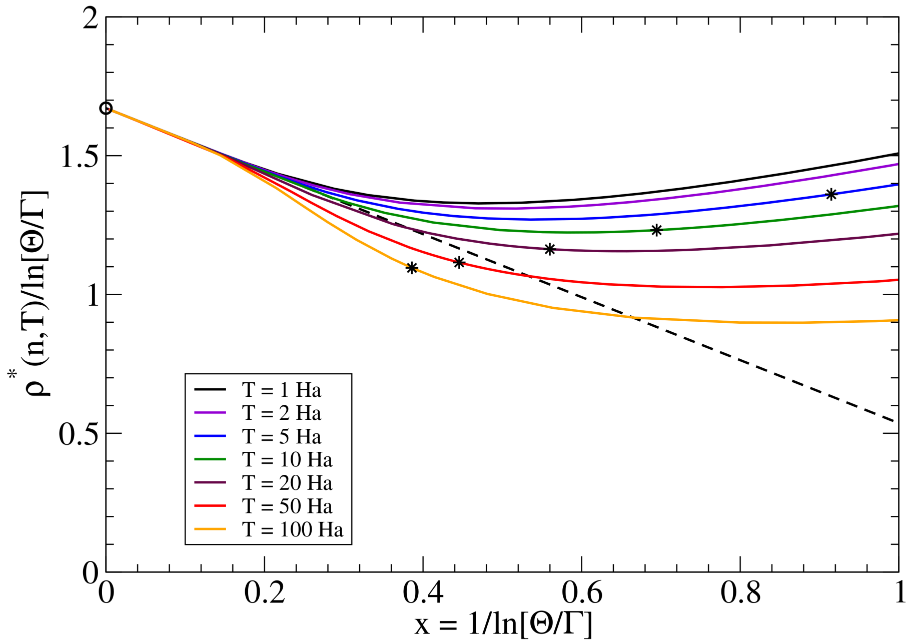
ion-ion structure factor

dielectric function

$$\rho^*_{\mathrm{Ziman}}(n,T,Z,s) = 2^{1/2}\pi\Theta^{3/2} Z\int_0^\infty dq\, \frac{q^3}{(q^2+\kappa^2)^2}\frac{1}{e^{\frac{\hbar^2 q^2}{8 m_e k_B T} - \frac{\mu_e}{k_B T}}+1}$$

screening parameter

$$\kappa^2 = s\frac{ne^2}{\epsilon_0 k_B T} \approx (1+Z)\frac{ne^2}{\epsilon_0 k_B T}$$



Electrical conductivity of plasmas

Kinetic theory (Boltzmann equation): Spitzer (low-density limit)

Linear response theory: Kubo formula (warm dense matter)

$$\sigma(T,\mu) = \frac{e^2\beta}{3m^2 \mathrm{Vol}} \int_{-\infty}^{0} dt e^{\epsilon t} \int_0^1 d\lambda \langle \mathbf{P} \cdot \mathbf{P}(t + i\hbar\beta\lambda)\rangle$$

electron total momentum $\mathbf{P} = \sum_k \hbar \mathbf{k}\, a_k^\dagger a_k$

Kubo-Greenwood formula, DFT-MD simulations: electron-electron collisions included?

M. P. Desjarlais et al. 2017, N.R. Shaffer and C.E. Starrett, Phys. Rev. E **101**, 053204 (2020)

$$\mathrm{Re}\,[\sigma(\omega)] = \frac{2\pi e^2}{3m_e^2\omega\Omega} \sum_k w_k \sum_{j=1}^{N} \sum_{i=1}^{N} \sum_{\alpha=1}^{3} \left[f(\epsilon_{j,k}) - f(\epsilon_{i,k})\right] |\langle \Psi_{j,k}|\hat{p}_\alpha|\Psi_{i,k}\rangle|^2 \delta(\epsilon_{i,k} - \epsilon_{j,k} - \hbar\omega)$$

Conductivity of warm dense matter including electron-electron collisions:
H. Reinholz, G. R., S. Rosmej, R. Redmer, Phys. Rev. E **91**, 043105 (2015).
DFT-MD contains e-e interaction only in mean-field approximation,
wrong low-density limit of electrical conductivity (Lorentz-model)

Thermoelectric transport coefficients: $\sigma(T, n)$, $\alpha(T, n)$, $\lambda(T, n)$

M. French, G. R., M. Schörner, M. Bethkenhagen, M. P. Desjarlais, R. Redmer, Phys. Rev. E **105**, 065204 (2022)

Solution of the kinetic equations

Higher moments of the distribution function $\mathbf{P}_m = \sum_{\mathbf{k}\sigma} \hbar\mathbf{k} \left(\frac{\hbar^2}{2mk_BT}k^2\right)^m n_{\mathbf{k}\sigma}$

$$\tilde{\rho}_{ei}^{(1)} = \rho_{ei}^{*,(1)}x = \rho^{\mathrm{Ziman}}x = 1.67109 - 0.62166x \qquad \rho^{(2)} = \frac{\rho^{\mathrm{Ziman}}}{d_{00}^{ei}} \frac{d_{00}^{ei}(d_{11}^{ei}+d_{11}^{ee}) - (d_{01}^{ei})^2}{(25/4)d_{00}^{ei} + d_{11}^{ei} + d_{11}^{ee} - 5d_{01}^{ei}}$$

Quantum Lenard Balescu

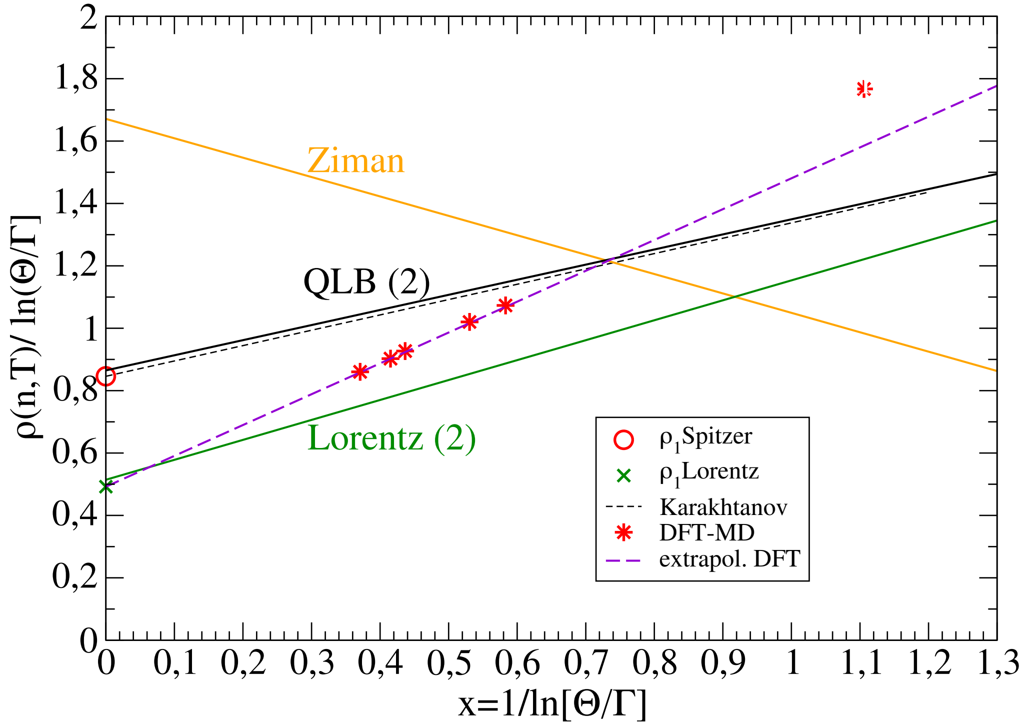
$$\rho_{ei+ee}^{*,(2)}x = 0.8649 + 0.4844x$$

$$\rho_{ei+ee}^{*,(6)}x = 0.8467 + 0.4921x.$$

Lorentz

$$\rho_{ei}^{*,(2)}x = 0.51419 + 0.63934x$$

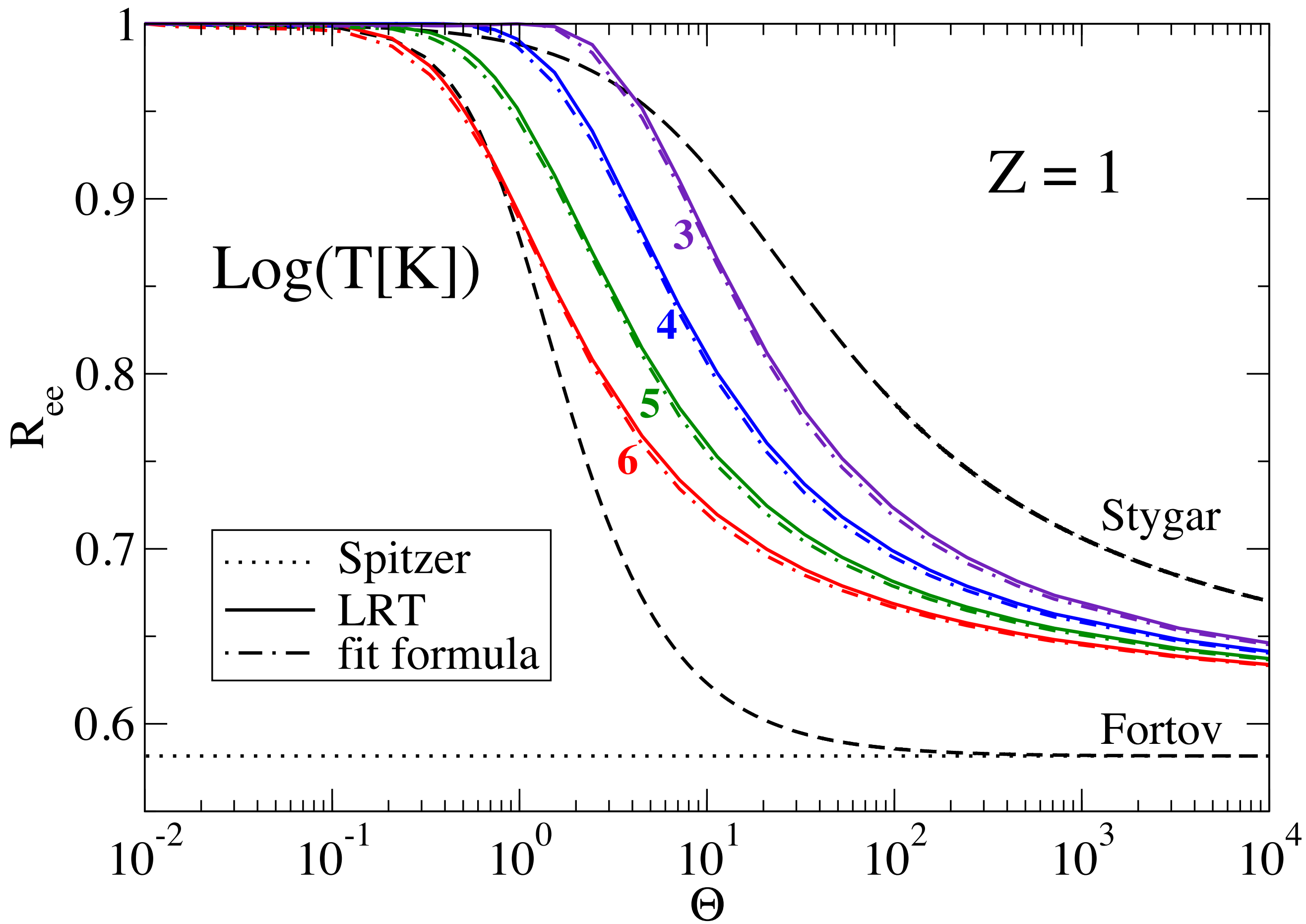
$$\rho^{*,\mathrm{DFT-MD}}x = 0.492 + 0.9886x$$



G. R., M. Schoerner, M. Bethkenhagen, R. Redmer, Phys. Rev. E **104**, 045204 (2021)
G. R., Contrib. Plasma Phys. 2023, e202300002

Correction factor

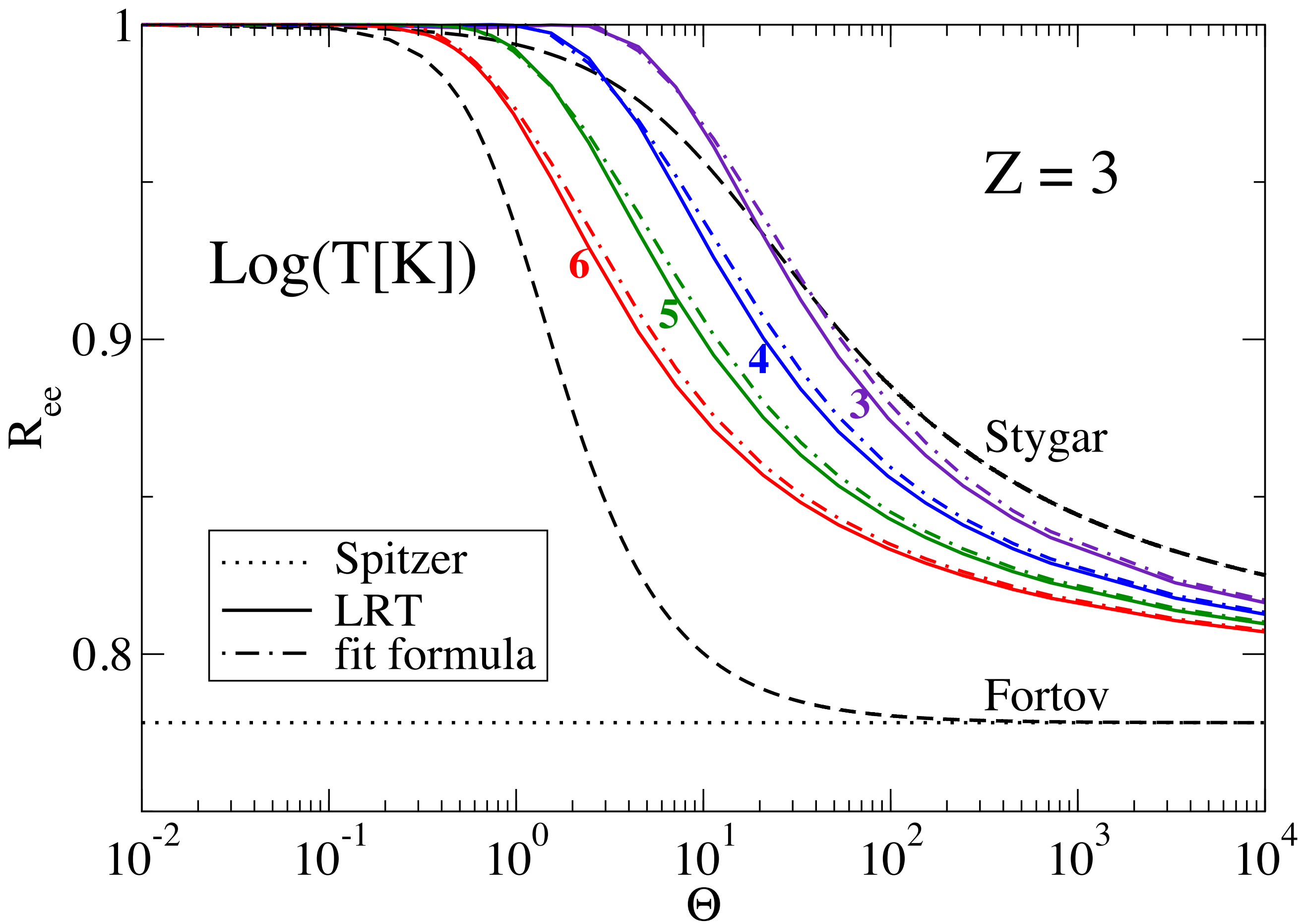
$$R_{ee} = \frac{\sigma_{ei+ee}}{\sigma_{ei}}$$



H. Reinholz et al., PRE **91**, 043105 (2015)

Correction factor

$$R_{ee} = \frac{\sigma_{ei+ee}}{\sigma_{ei}}$$



H. Reinholz et al., PRE **91**, 043105 (2015)

Correction factor from RPA screening

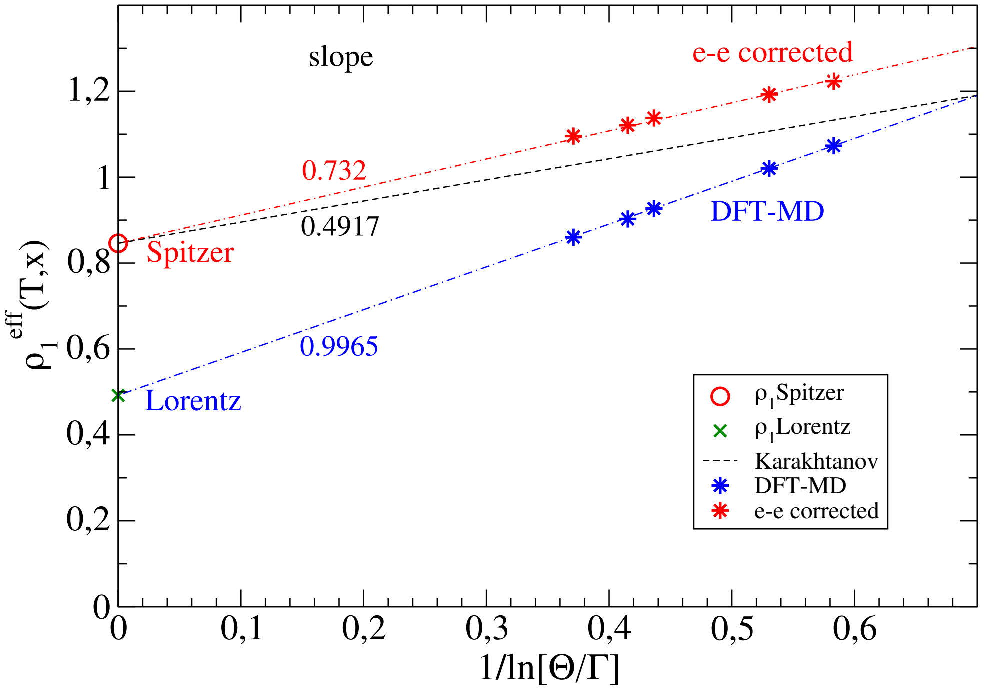
$$R_{ee}^{\mathrm{reference}}(T,n,Z) = \frac{\sigma(T,n,Z)}{\sigma^{\mathrm{reference}}(T,n,Z)}$$

RPA-Debye screening

$$R_{ee}^{\mathrm{RPA}}(T,n) = 0.5945 + \frac{0.5756}{\ln(\Theta/\Gamma)+0.323}$$

$$\tilde{\rho}^{\mathrm{DFT-MD}}/R_{ee}^{\mathrm{RPA}}(T,n) = 0.8467 + 0.732x$$

$$\lim_{T\to\infty} R_{ee}^{\mathrm{DFT-MD}}(T,x) = 0.58107 + 0.8298\,x$$



G. R., Phys. Plasmas **31**, 042301 (2024)

Generalized virial expansion

$$\rho_{\rm dc} = \frac{1}{\sigma_{\rm dc}} = \frac{e^2 m^{1/2}}{(k_B T)^{3/2}(4\pi\epsilon_0)^2}\left[\rho_1(T)\Lambda + \rho_{\Lambda,2}(T) + \mathcal{O}[n^{1/2}\ln(1/n)]\right]$$

$$\Lambda(T,n) = \ln(1+b) - \frac{b}{1+b}$$

$$b = \frac{3T_{Ha}^2}{\pi x n_{Bohr}}$$

Λ_c : x = 1.5144:
zero second virial coefficient

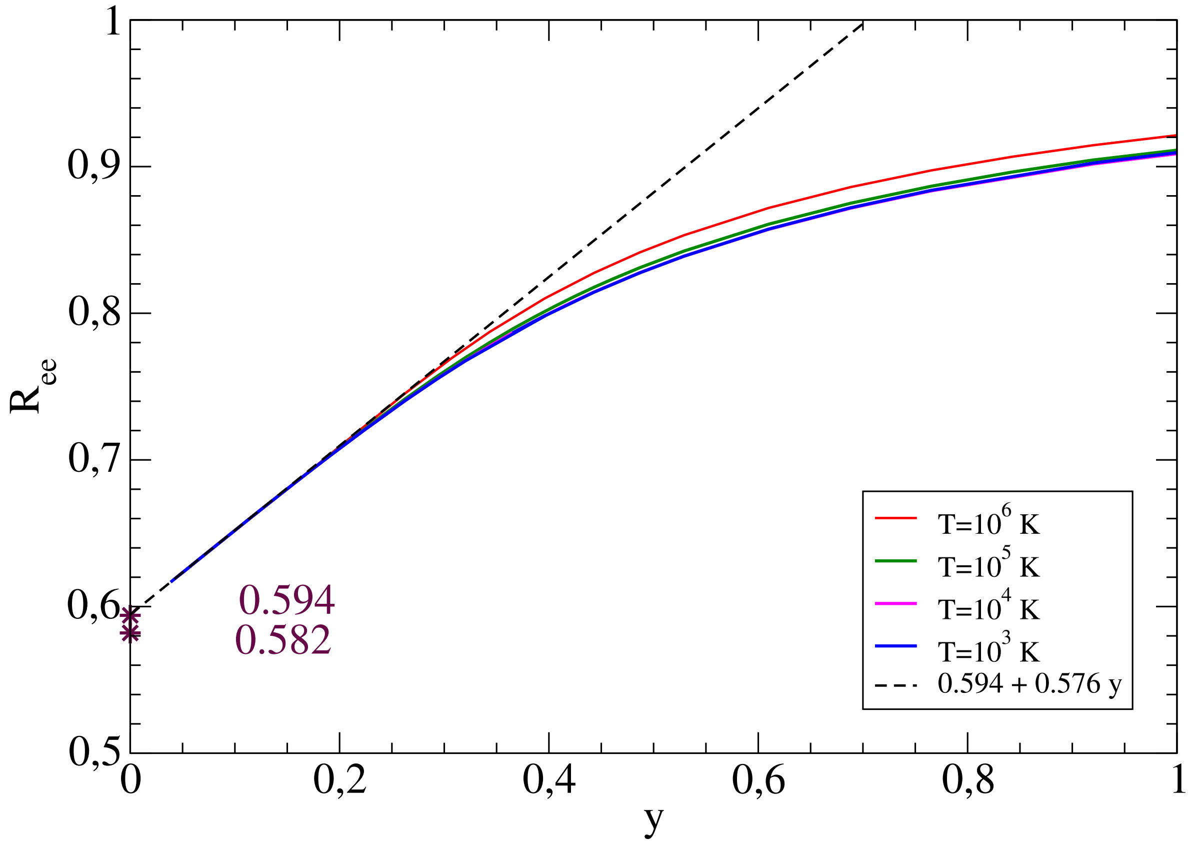
n (cm^{-3})	ρ (g cm^{-3})	T (eV)	Γ	Θ	σ (Ω^{-1} m^{-1})	$1/\Lambda_c$
1×10^{24}	1.67	20000	0.00116	549.1	7.9499×10^{9}	0.073381
1×10^{24}	1.67	10000	0.00232	274.5	3.129×10^{9}	0.081691
1×10^{24}	1.67	1000	0.0232	27.45	1.5862×10^{8}	0.13095
1×10^{24}	1.67	100	0.232	2.745	1.2493×10^{7}	0.32617
5.98×10^{24}	10	1000	0.04213	8.3252	2.0711×10^{8}	0.17987
5.98×10^{24}	10	100	0.4213	0.8325	2.6631×10^{7}	0.69527
5.98×10^{25}	100	1000	0.09076	1.7936	3.3978×10^{8}	0.28052

error:
2 %,

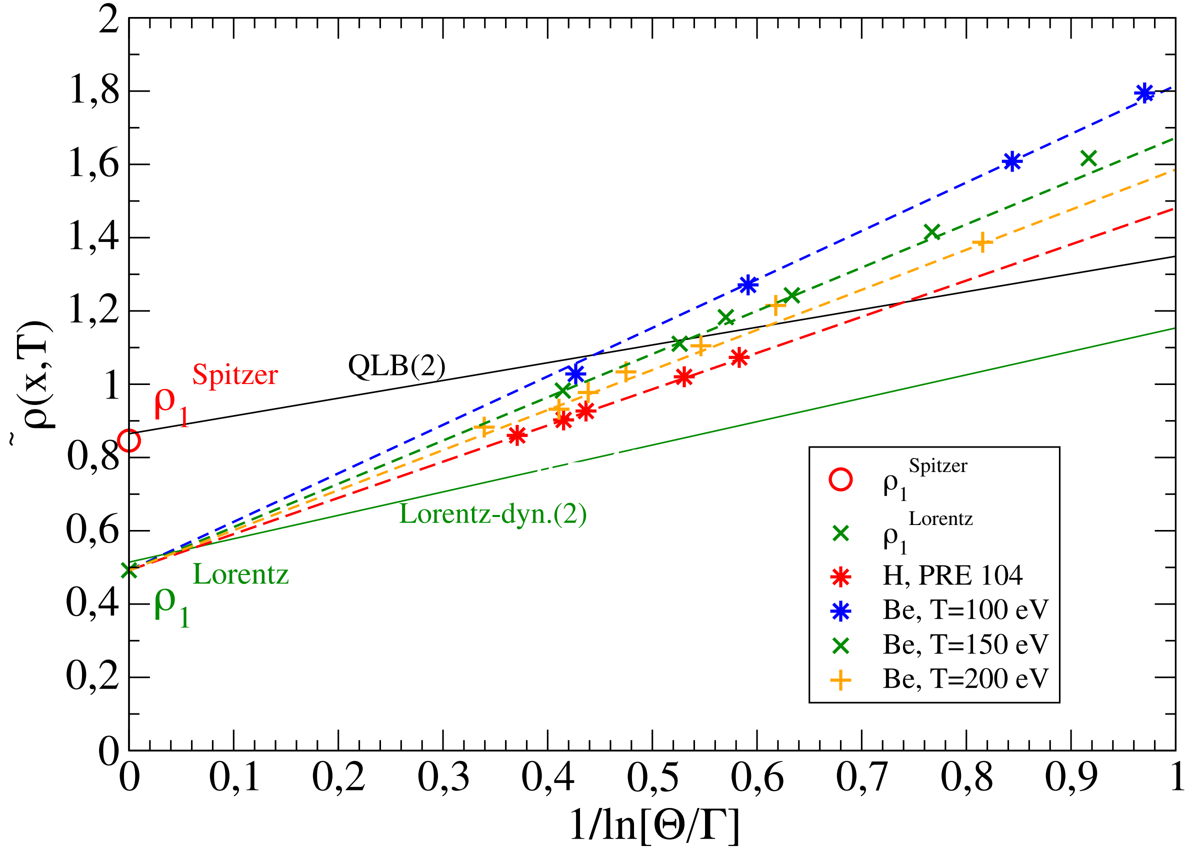
for 10/100:
10 %

G.R., CPP 63, e202300002 (2023)

Correction factor: benchmark

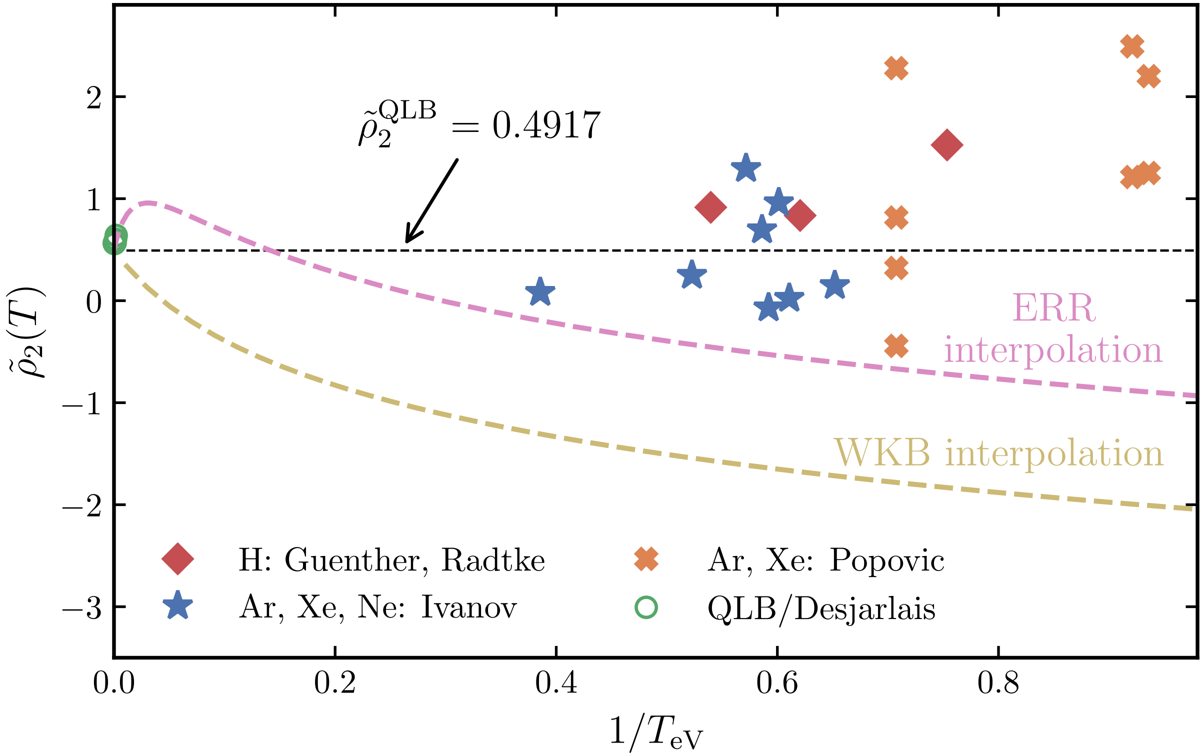


Virial plot: H and Be plasmas



Experiments

second virial coefficient: $\tilde{\rho}_2^{\mathrm{eff}}(n,T) = \dfrac{32405.4}{\sigma(n,T)[\Omega\mathrm{m}]}\left(\dfrac{T}{\mathrm{eV}}\right)^{3/2} - 0.846024\ \ln\left(\dfrac{\Theta}{\Gamma}\right)$



densities high,
temperatures low:

partially ionized plasmas;
ionization degree,
electron-atom collisions

Interpolation formulas, ERR: A Esser, R. Redmer, G. R., Contrib. Plasma Phys. **43**, 33 (2003).

WKB: $$\tilde{\rho}_2(T_{\mathrm{eV}}) \approx 0.4917 + 0.846 \ln\left[\frac{1 + 8.492/T_{\mathrm{eV}}}{1 + 25.83/T_{\mathrm{eV}} + 167.2/T_{\mathrm{eV}}^2}\right]$$

G. R., M. Schoerner, M. Bethkenhagen, R. Redmer, Phys. Rev. E **104**, 045204 (2021) Supplemental material

Conclusion

- Analytical calculations and Green's functions approaches provide us with exact results (benchmarks) in some limiting cases. We show where a virial expansion of the resistivity can be applied.
- Simulations become expansive and time consuming in some limiting cases (for instance, in the low-density limit). Comparison with analytical results can used to show the accuracy of calculations, to eliminate wrong results, and to construct interpolation formulas.
- We have shown that electron-electron collisions are not included in ab-initio DFT-MD calculations, we expect that PIMC calculations can provide us with correct results in the low-density region. A renormalization factor can be introduced to take the contribution of electron-electron interaction into account. One has to take care to avoid double counting, for instance with screening.