

NPP-2011

Работа посвящается памяти А.А. Ликальтера

**МЕТАЛЛИЗАЦИЯ АТОМАРНОГО ГАЗА
И ПЕРЕХОД ПАР-ЖИДКОСТЬ
В ПАРАХ ЩЕЛОЧНЫХ МЕТАЛЛОВ**

*Хомкин А.Л., Шумихин А.С.
Теоретический отдел им. Л.М. Бибермана
ОИВТ РАН*

NPP-2011

ПЛАН

1. ВВЕДЕНИЕ, ПОСТАНОВКА ЗАДАЧИ
2. ПОТЕНЦИАЛ КОРА
3. ЭНЕРГИЯ СВЯЗИ – “COHESIVE ENERGY”
4. ТЕРМОДИНАМИКА, УРАВНЕНИЕ СОСТОЯНИЯ
5. КРИТИЧЕСКАЯ ТОЧКА
6. СТЕПЕНЬ ДЕЛОАЛИЗАЦИИ («ИОНИЗАЦИИ») ПАРОВ ЩЕЛОЧНЫХ МЕТАЛЛОВ КРИТИЧЕСКОЙ ТОЧКЕ
7. ПРОВОДИМОСТЬ И ПЕРЕХОД МОТТА

NPP-2011

value of E_{coh} can be explained by the classic Wigner-Seitz formula¹

$$E_{\text{coh}} = \epsilon_s - (E_{\Gamma} + \frac{3}{5} \epsilon_F). \quad (1)$$

JULY, 1938 JOURNAL OF CHEMICAL PHYSICS VOLUME 6
An Improved Calculation of the Energies of Metallic Li and Na
J. BARDEEN*
Harvard University, Cambridge, Massachusetts
(Received April 13, 1938)

$$E_k = E_0 + \alpha \frac{k^2 \hbar^2}{2m}$$

NPP-2011

Cohesive Energy of Alkali Metals

HARVEY BROOKS

Division of Applied Science, Harvard University, Cambridge, Massachusetts

(Received June 9, 1953)

$$\Psi_l(r) = \sin(\pi\delta_l)W_{n, l+\frac{1}{2}}(2r/n) + (-1)^l [(n+l)!/(2l+1)!] \sin(\pi(n+\delta_l))M_{n, l+\frac{1}{2}}(2r/n), \quad (1)$$

where $n=1/\sqrt{\epsilon}$, ϵ in Rydbergs, and δ_l is the quantum defect which can be found as a smooth function of the energy parameter ϵ by straightforward extrapolation using the free atom term values for each l . The ground state energy ϵ_0 depends on the s -functions, while the Fermi energy depends on the p -functions. The latter

The calculated total energies at three lattice constants were fitted to an expression:

$$E_{\text{coh}} = Ar_s^{-1} + Br_s^{-2} + Cr_s^{-3}. \quad (3)$$

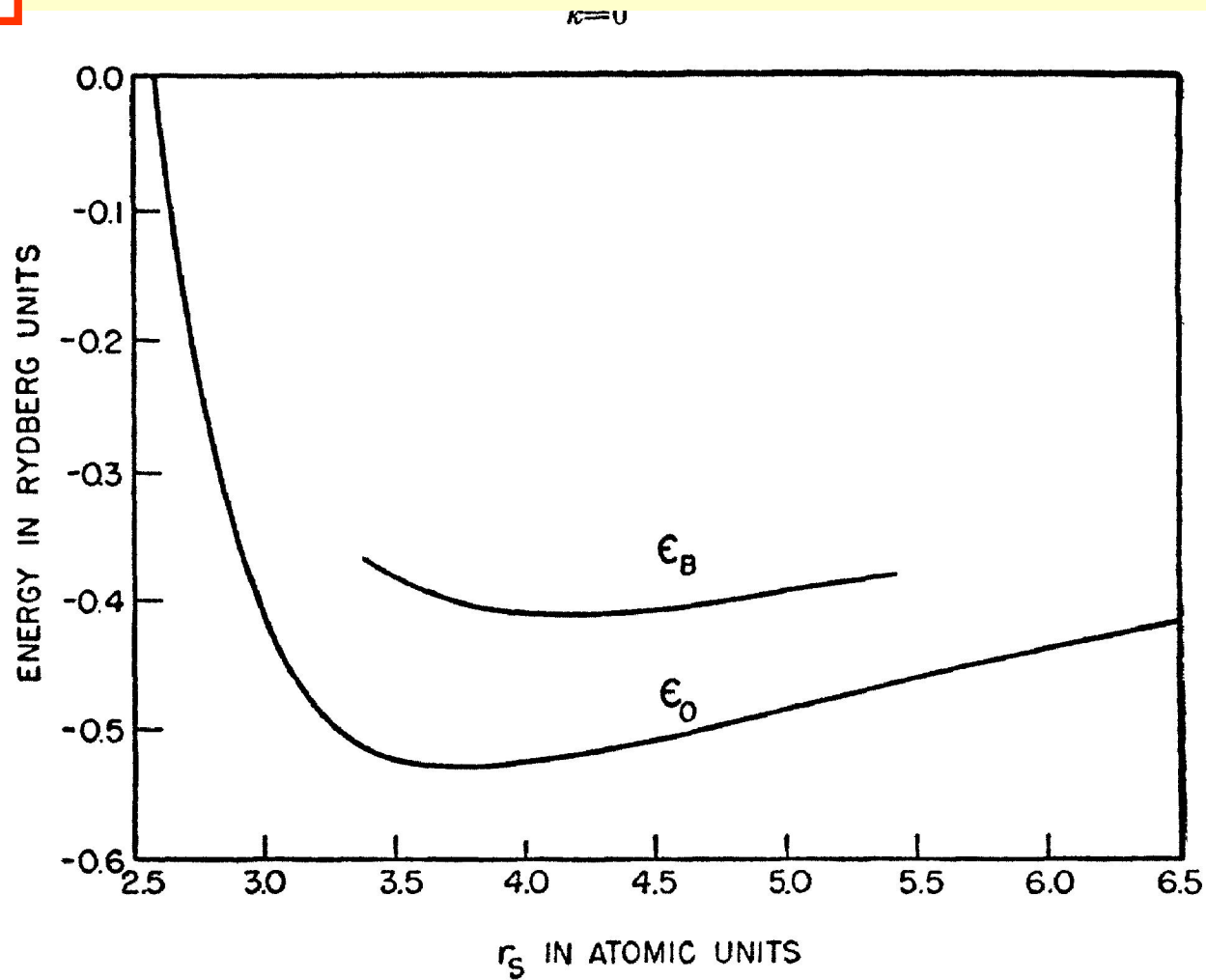


FIG. 3. Ground state and total energy *vs.* sphere radius for potassium (complete computation).

Simplified local-density theory of the cohesive energy of metals

John A. Moriarty

Department of Physics, College of William and Mary, Williamsburg, Virginia 23185

(Received 6 July 1978)

A simplified but accurate theory of the cohesive energy of metals has been developed from the density-functional formalism of Kohn and Sham. In this theory, the total energy of both the free atom and the solid is expressed as a sum of a core and a valence binding energy, and the cohesive energy is reduced (apart from a zero-point vibrational term) to a difference in binding energies. The free-atom binding energy is directly calculated, and accurately (to within 3%) matches the experimental ionization energy in nonrelativistic elements. The binding energy of the metal, on the other hand, is obtained by the generalized pseudopotential method developed previously by the author. This latter step permits all band-structure and self-consistent screening effects to be incorporated analytically. The calculated cohesive energy agrees well with both experiment (to about 20%) and heavy numerical computation (to about 10%) in simple as well as *d*-band metals. More importantly, the method permits the physical origins of the cohesion to be identified in each case, and these are discussed for 22 nontransition metals. It is found that band-structure effects are important in all nonalkali metals and, in particular, that *sd* hybridization contributes 30%–60% of the cohesion in the alkaline-earth and noble metals. In addition, the large relativistic energy shifts inherent in the binding energies of the heavy metals are seen to approximately cancel in the cohesive energy.

Critical Point of Metals from the van der Waals Model*

David A. Young and Berni J. Alder

Lawrence Radiation Laboratory, University of California, Livermore, California 94550

(Received 17 August 1970)

The classical van der Waals model of fluids is modified by a more accurate equation of state for hard spheres. The hard-sphere diameter and the van der Waals constant a are obtained from experimental data. The model is used to predict the critical constants of metals, as well as the equation of state, cohesive energy, and coexistence curves near the critical point. The model is also applied to rare gases and ionic salts. The semiquantitative predictions of the model are at least as accurate as those of other theories. Of the three critical constants, the critical temperature is most accurately predicted, being within 11% of experiment. More information about the interatomic potential in metals is needed before the theory can be substantially improved.

$$p = p_0 - a/V^2$$

$$p_0 = \frac{RT}{V} \frac{1 + \gamma + \gamma^2 - \gamma^3}{(1 - \gamma)^3}$$

$$\gamma = \pi N \sigma^3 / 6V$$

The constant a is equal to $-E_0 V_0$, where E_0 is the molar cohesive energy and V_0 is the molar volume of the metal. The subscripts refer to some reference state. Theoretically, the reference state is

NPP-2011

ЛИКАЛЬТЕР А.А

1. Перекрывание атомных оболочек в окрестности крит.точки
2. Газообразный металл
3. Квазиатомы и их взаимодействие
4. Два сорта электронов
5. Скейлинг
6. Уравнение состояния

NPP-2011

Рассмотрим достаточно плотный газ атомов щелочных металлов,

$$N_a, \quad V, \quad T$$

При перекрытии классически доступных областей движения связанных электронов представление о парности взаимодействия теряет смысл.

*В окрестности критической точки взаимодействие становится коллективным и квантовым за счет обмена электронами. **Возникает металлизированный газ.***

Спектр состояний такого газа и энергия связи получены в работе Лауреата Нобелевской премии Дж. Бардина и мы используем эту теорию для термодинамических расчетов.

NPP-2011

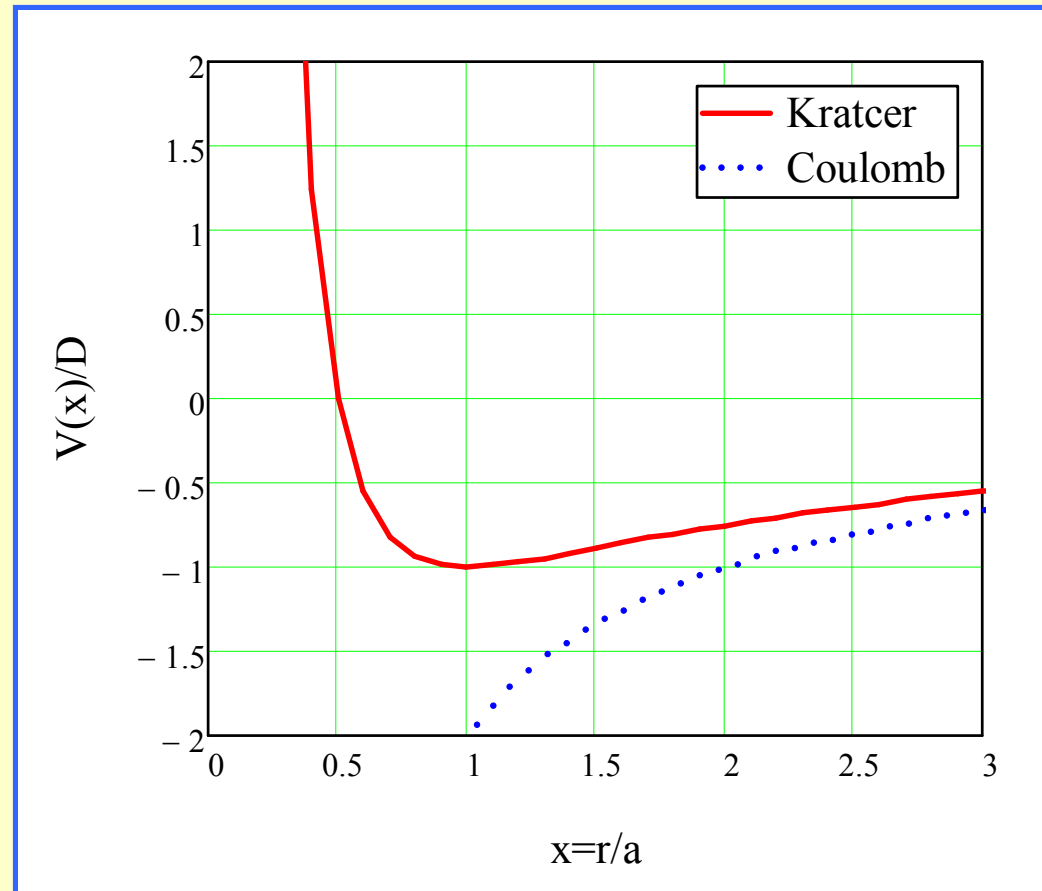
Потенциал Кратцера

$$V(r) = -2D \left(\frac{a}{r} - \frac{1}{2} \frac{a^2}{r^2} \right)$$

$$x = r / a$$

$$\beta^2 = -\frac{2ma^2}{\hbar^2} E$$

$$\gamma^2 = \frac{2ma^2}{\hbar^2} D$$



$$R_l(x) = x^{\lambda-1} \exp(-\beta x) F\left(\lambda - \frac{\gamma^2}{\beta}, 2\lambda; 2\beta x\right)$$

$$\lambda = \frac{1}{2} + \sqrt{\gamma^2 + \left(l + \frac{1}{2}\right)^2}$$

$$E_v = -\frac{\hbar^2}{2ma^2} \frac{\gamma^4}{(v + \lambda)^2}; \quad v = 0, 1, 2, \dots$$

$$2Da = e^2 \quad E_0 = -I$$

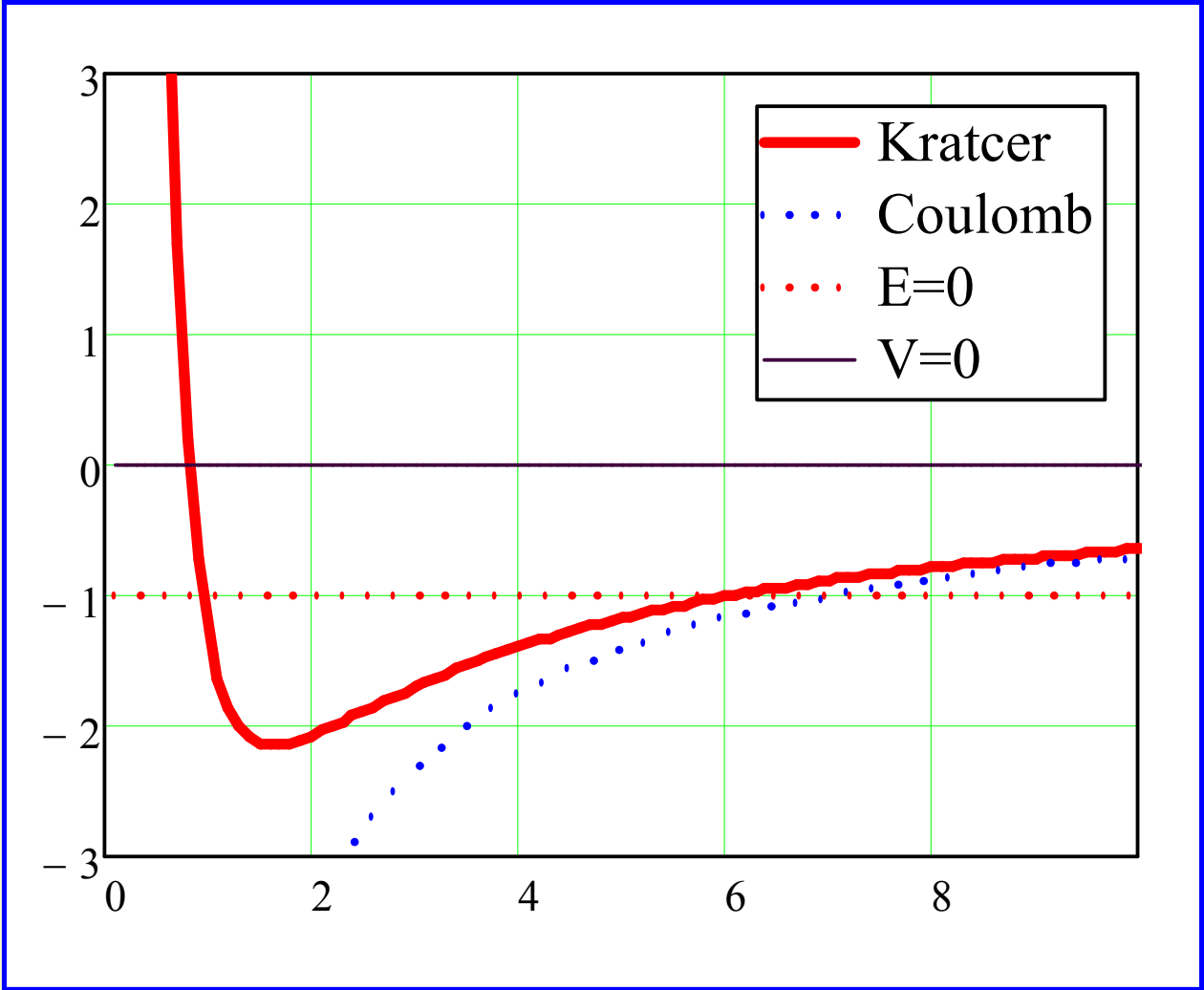
$$\frac{D}{Ry} = \frac{1}{\left(\sqrt{\frac{Ry}{I}} - \frac{1}{2}\right)^2 - \frac{1}{4}} \quad \frac{a}{a_0} = \left(\sqrt{\frac{Ry}{I}} - \frac{1}{2}\right)^2 - \frac{1}{4}$$

$$V(r) = -2D \left(\frac{a}{r} - \frac{1}{2} \frac{a^2}{r^2} \right)$$

NPP-2011

Cs

$$\frac{V(y)}{I}$$



r/a

NPP-2011

МЕТАЛИЗОВАННЫЙ ГАЗ
ГАЗООБРАЗНЫЙ МЕТАЛЛ

JULY, 1938 JOURNAL OF CHEMICAL PHYSICS VOLUME 6
An Improved Calculation of the Energies of Metallic Li and Na

J. BARDEEN*

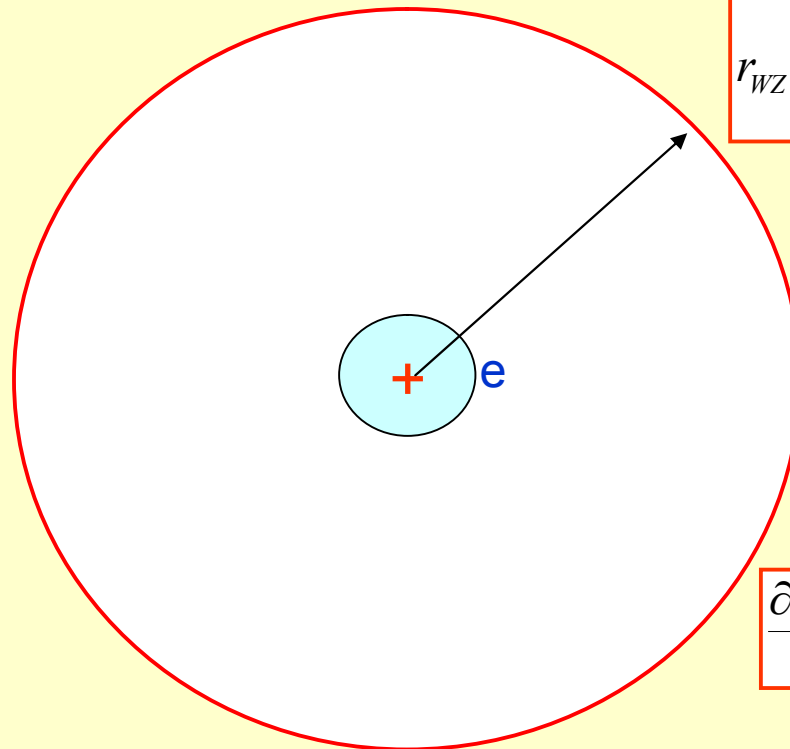
Harvard University, Cambridge, Massachusetts

(Received April 13, 1938)

$$E_k = E_0 + \alpha \frac{\hbar^2 k^2}{2m}$$

Энергия основного состояния атома в газообразном металле

Wigner-Seitz cell



$$r_{WZ} = \left(\frac{3}{4\pi n_a} \right)^{1/3}$$

$$\left. \frac{\partial \Psi(r)}{\partial r} \right|_{r=r_{WZ}} = 0$$

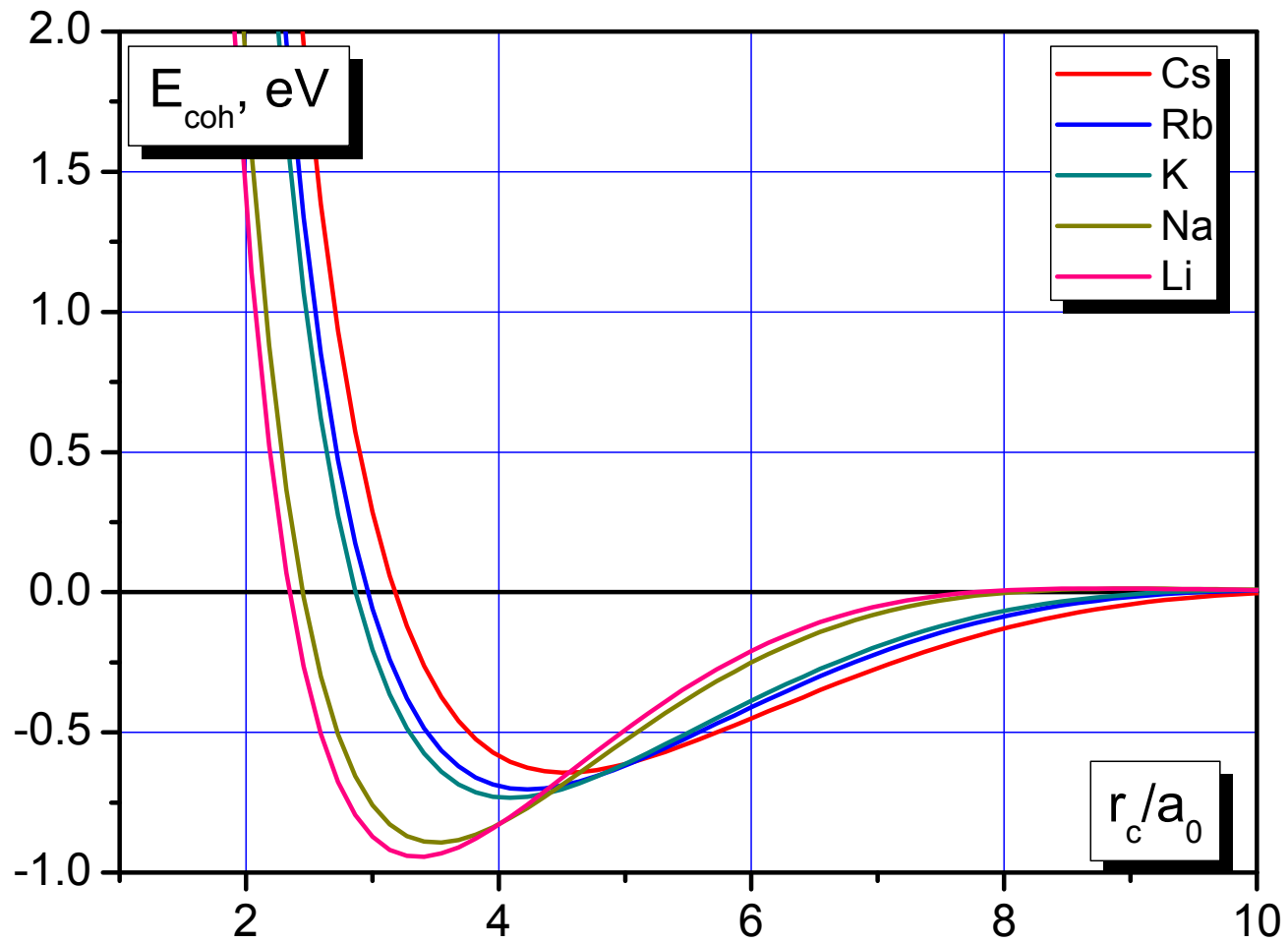
$E_0 :$

$$E_{coh} = E_a + I$$

$$E_a = E_0 + \alpha \frac{3}{5} E_F$$

$$\alpha = \left[\frac{4\pi}{3} R_0^2(r_c) \right] \left[\frac{r}{R_1(r)} \frac{dR_1(r)}{dr} \right]_{r=r_c}$$

$$R_l(x) = x^{\lambda-1} \exp(-\beta x) F\left(\lambda - \frac{\gamma^2}{\beta}, 2\lambda; 2\beta x\right)$$



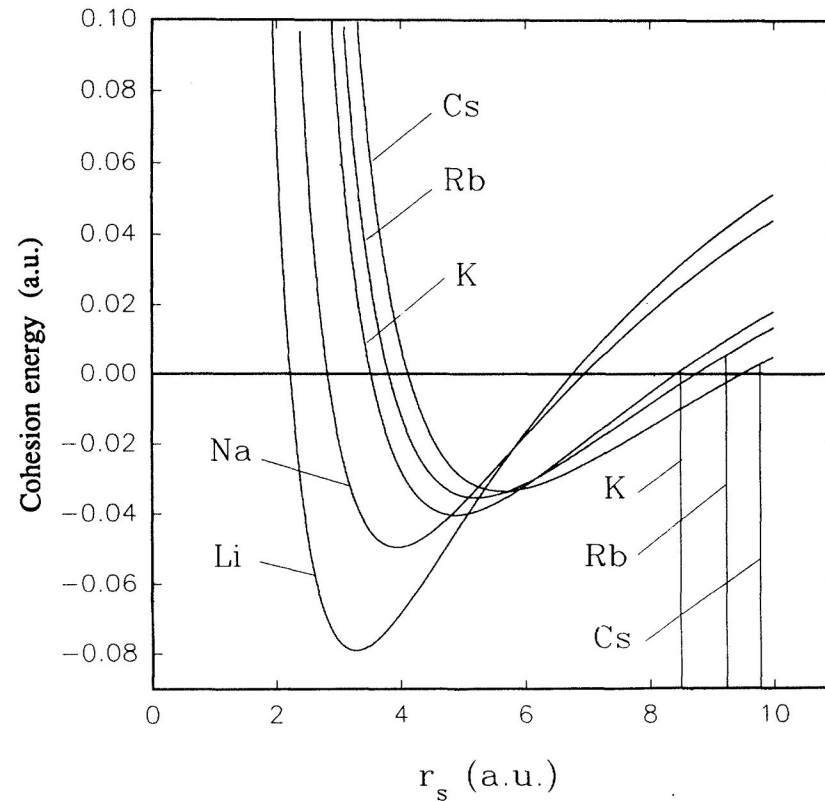
Critical phenomena in metallic one-component liquids

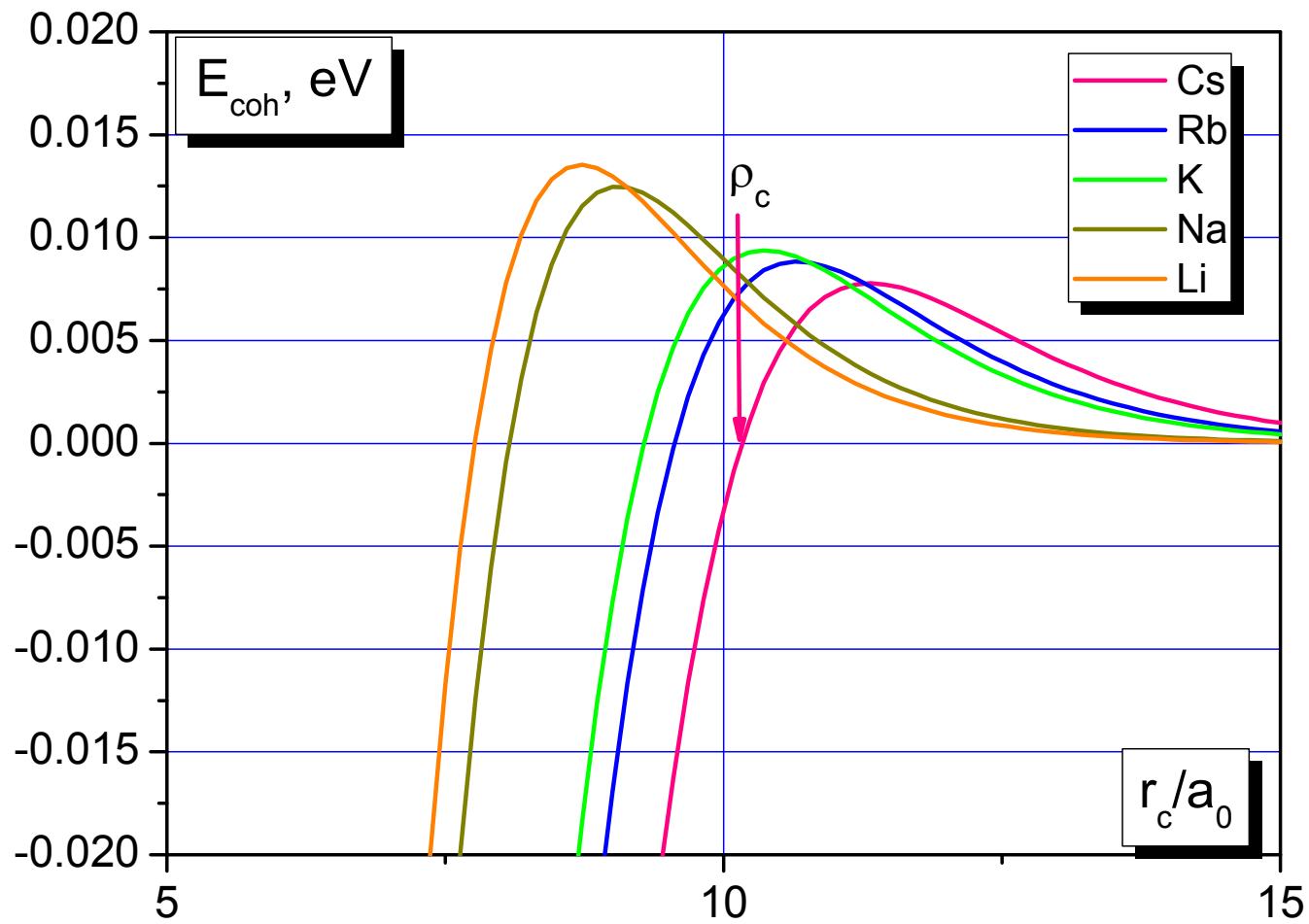
S. M. Stishov*

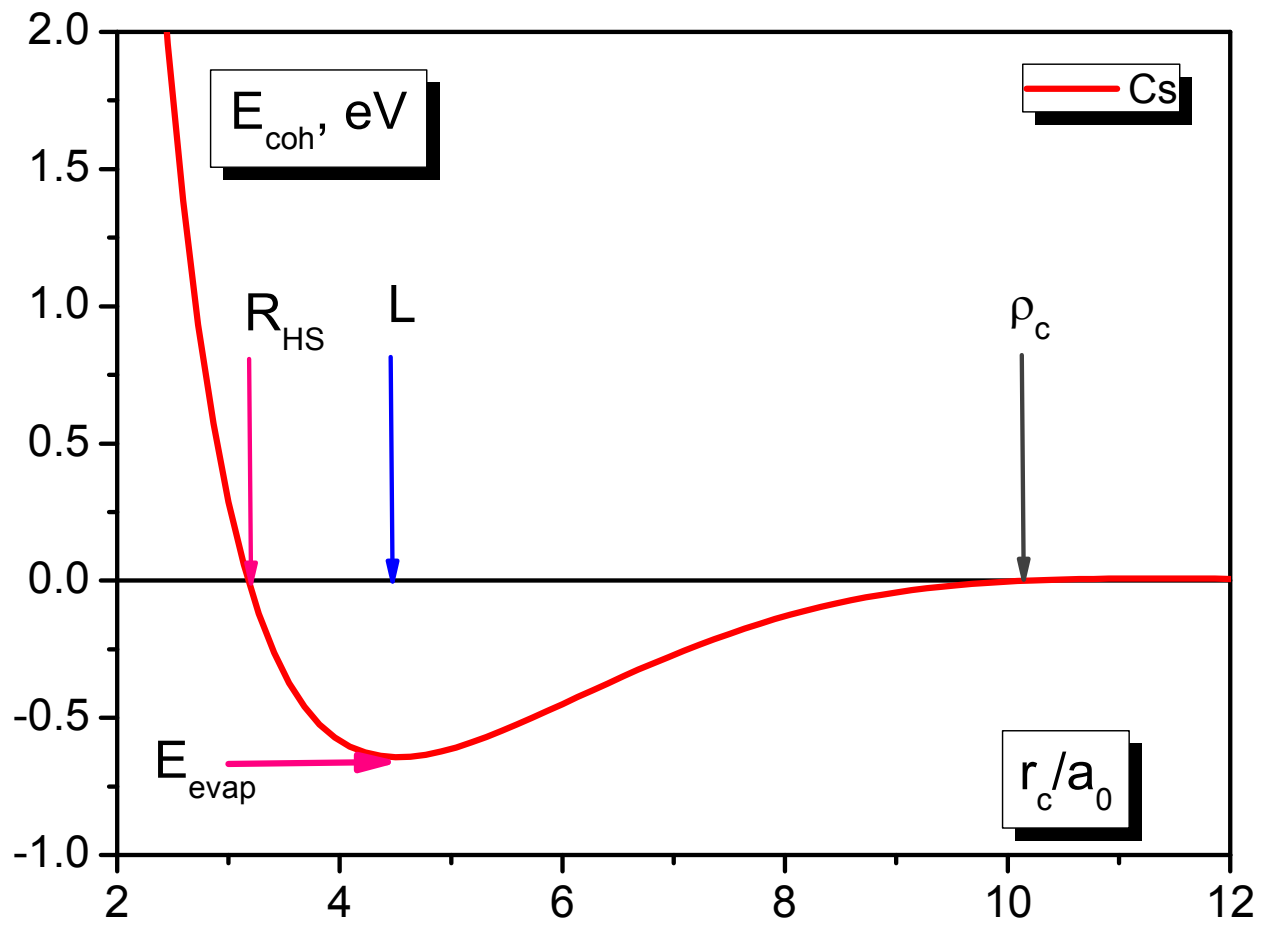
*Miller Institute for Basic Research in Science and Department of Geology and Geophysics, University of California,
Berkeley, California 94720*

(Received 1 October 1992)

Proofs are given that the cohesive energy of liquid alkali metals tends to zero at the critical point. This leads to the conclusion that, in a case of alkali metals, the Coulomb energy of interaction at the critical density is very close in magnitude to the ionization potential of the isolated atoms.



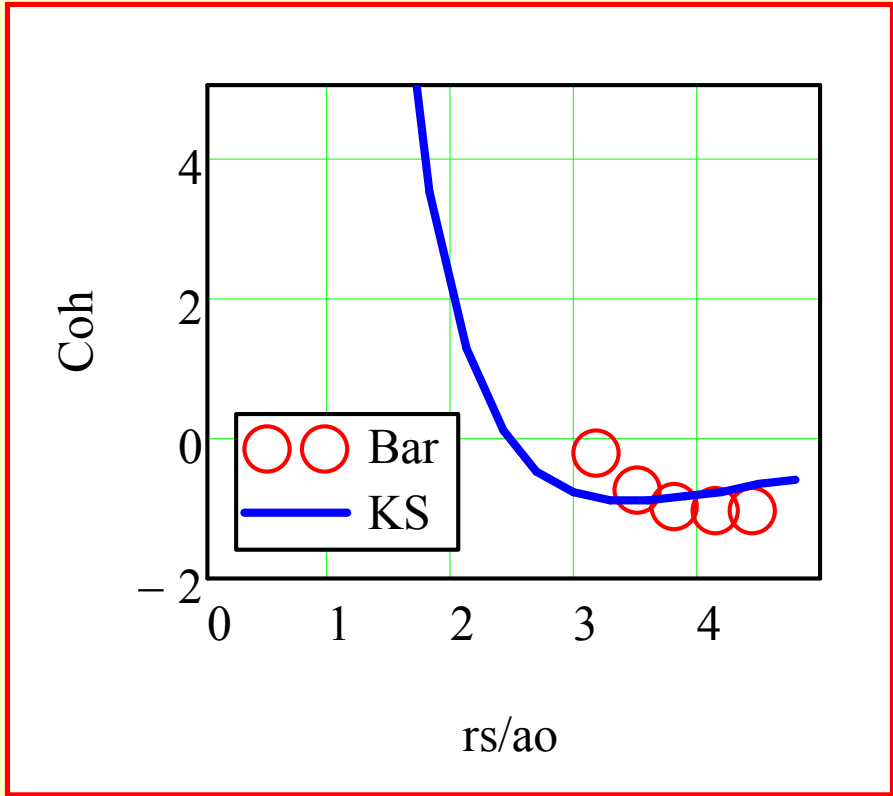
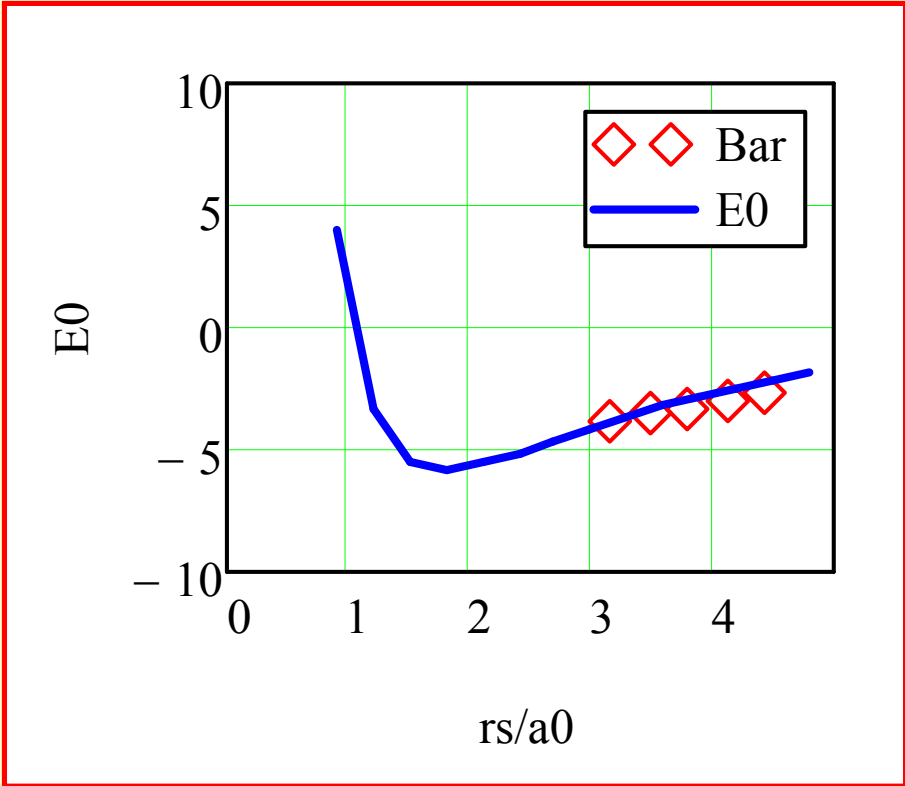




Некоторые характеристики паров щелочных металлов
в различных состояниях

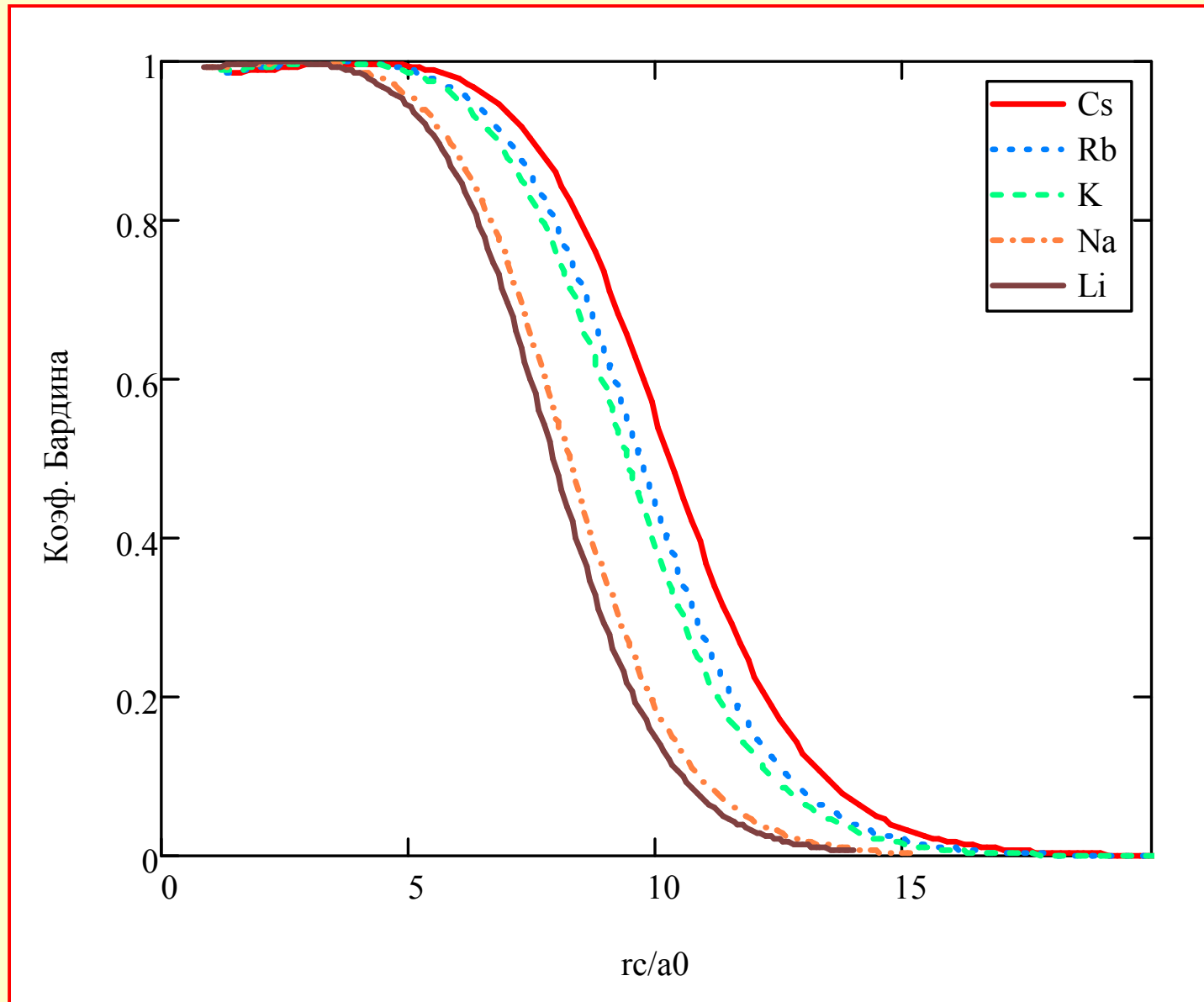
	I, eV	y_c	ρ_c , theor ρ_c , exp	y_{min} Lat/2	E_{min} E_{evap}	E_{min}/I E_{evap}/I	R_a , theor R_a , exp
Cs	3.89	10.155	0.341 0.38	4.518 5.71	0.644 0.74	0.166 0.19	3.174 (3.19-5.02)
Rb	4.19	9.549	0.263 0.29	4.221 5.29	0.704 0.78	0.168 0.189	2.94
K	4.34	9.279	0.131 0.17	4.088 4.95	0.734 0.87	0.169 0.2	2.86
Na	5.14	8.066	0.118 0.3	3.508 4.01	0.894 1.13	0.174 0.22	2.45
Li	5.39	7.756	0.04 0.04-0.1	3.362 3.266	0.944 1.69	0.175 0.314	2.34 (1.8-3.5)

Na

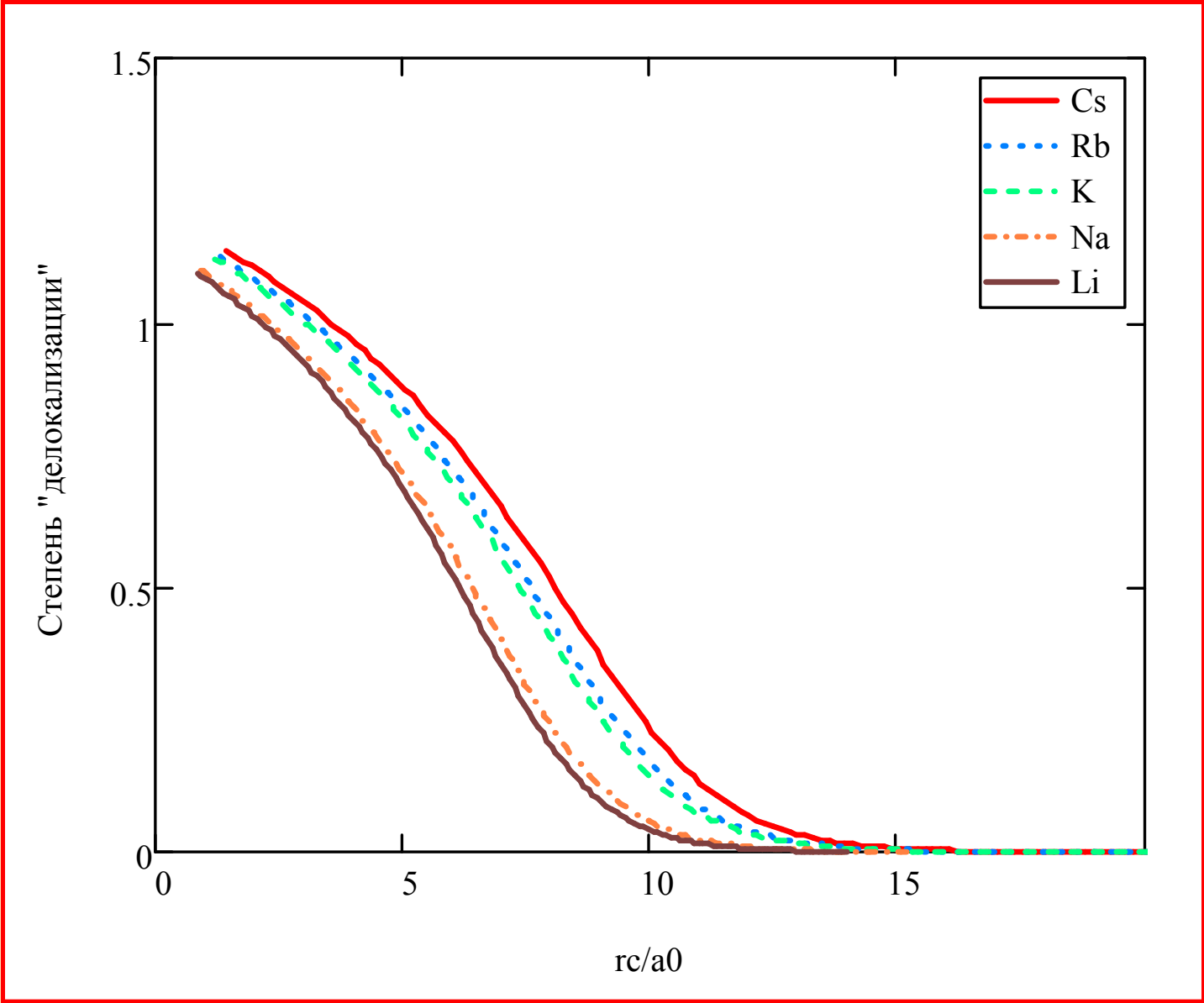


NPP-2011

NPP-2010



NPP-2011



$$F = F_0 + F_{HS} + F_{INT}$$

$$F_0 = -N_a kT \ln\left(\frac{eV}{N_a \lambda_a^3}\right)$$

$$F_{HS} = N_a kT \frac{4\eta - 3\eta^2}{(1 - \eta)^2}$$

$$F_{INT} = \frac{1}{2} N_a E_{coh}(y)$$

$$y = r_{WS} / a_0$$

$$\eta = \frac{4}{3} \pi \left[\frac{N_a}{V} r_a^3 \right]$$

Уравнение состояния

NPP-2011

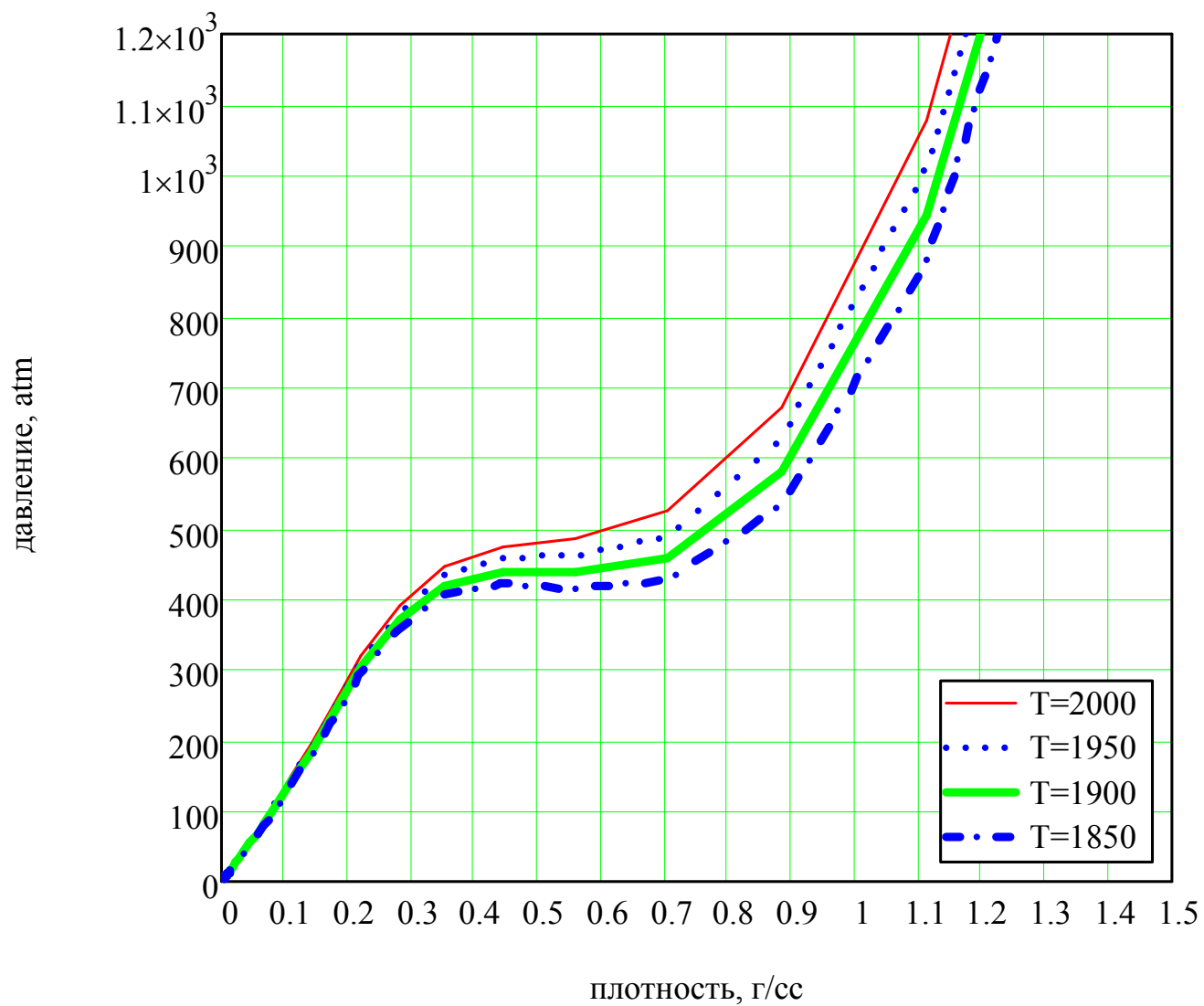
$$P = P_{IG} + P_{HS} + P_{INT}$$

$$P_{IG} + P_{HS} = kT \left(\frac{N_a}{V} \right) \left(\frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \right)$$

$$P_{INT} = - \frac{1}{2} \frac{N_a}{V} \frac{\partial E_{coh}(y)}{\partial y} \frac{y}{3}$$

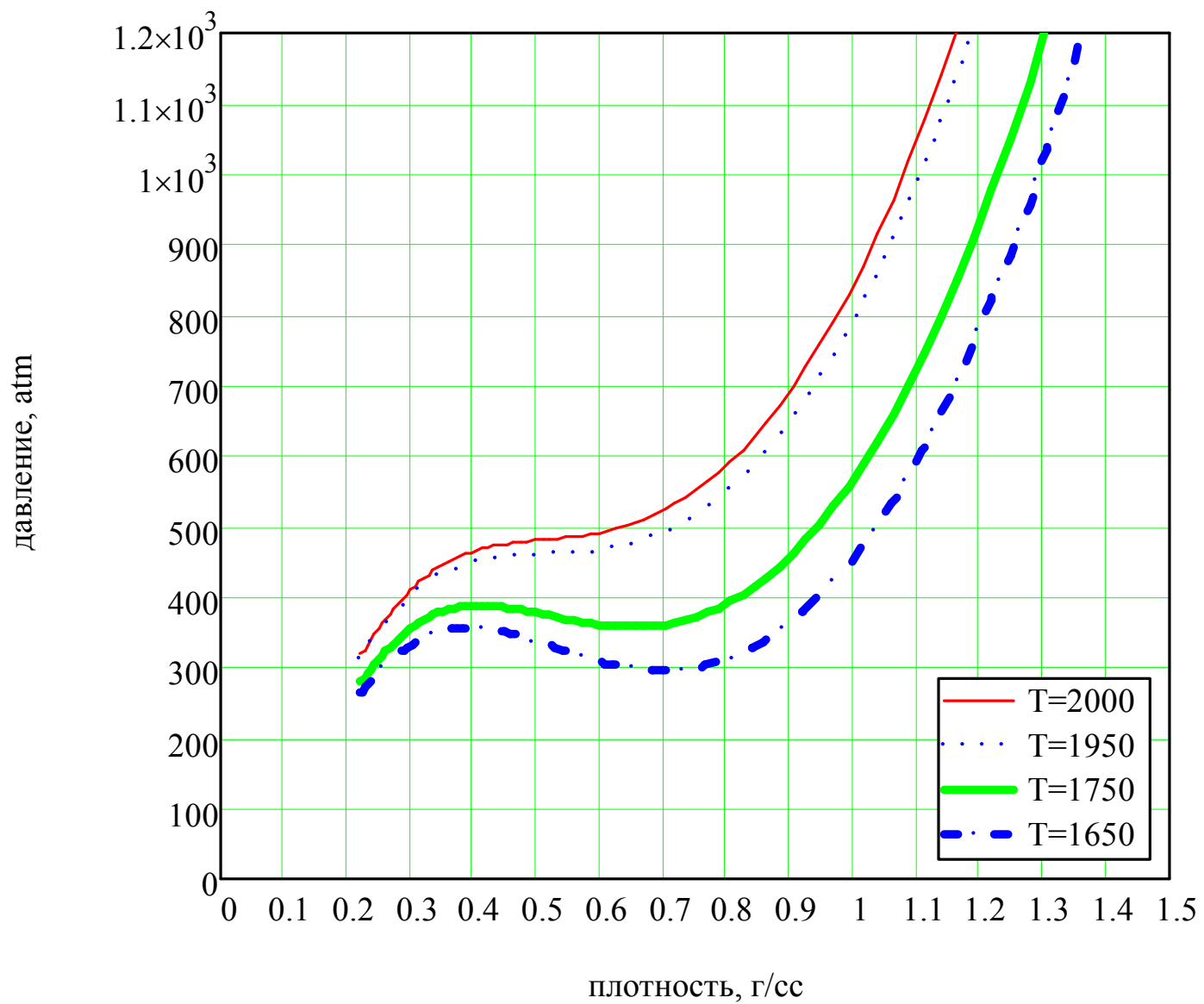
$$\eta = \frac{4}{3} \pi \left[\frac{N_a}{V} r_a^3 \right]$$

Cs



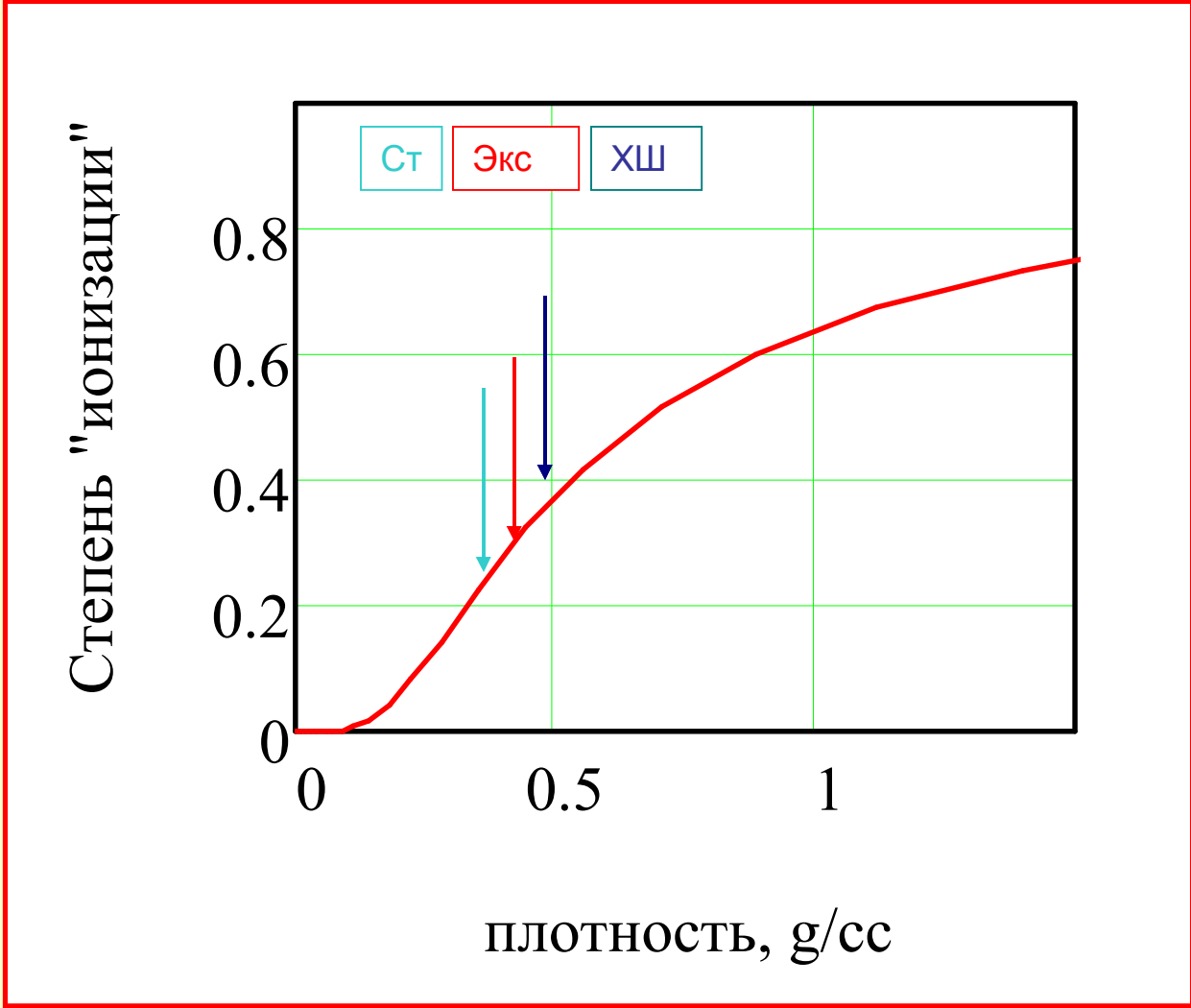
NPP-2011

Cs



NPP-2011

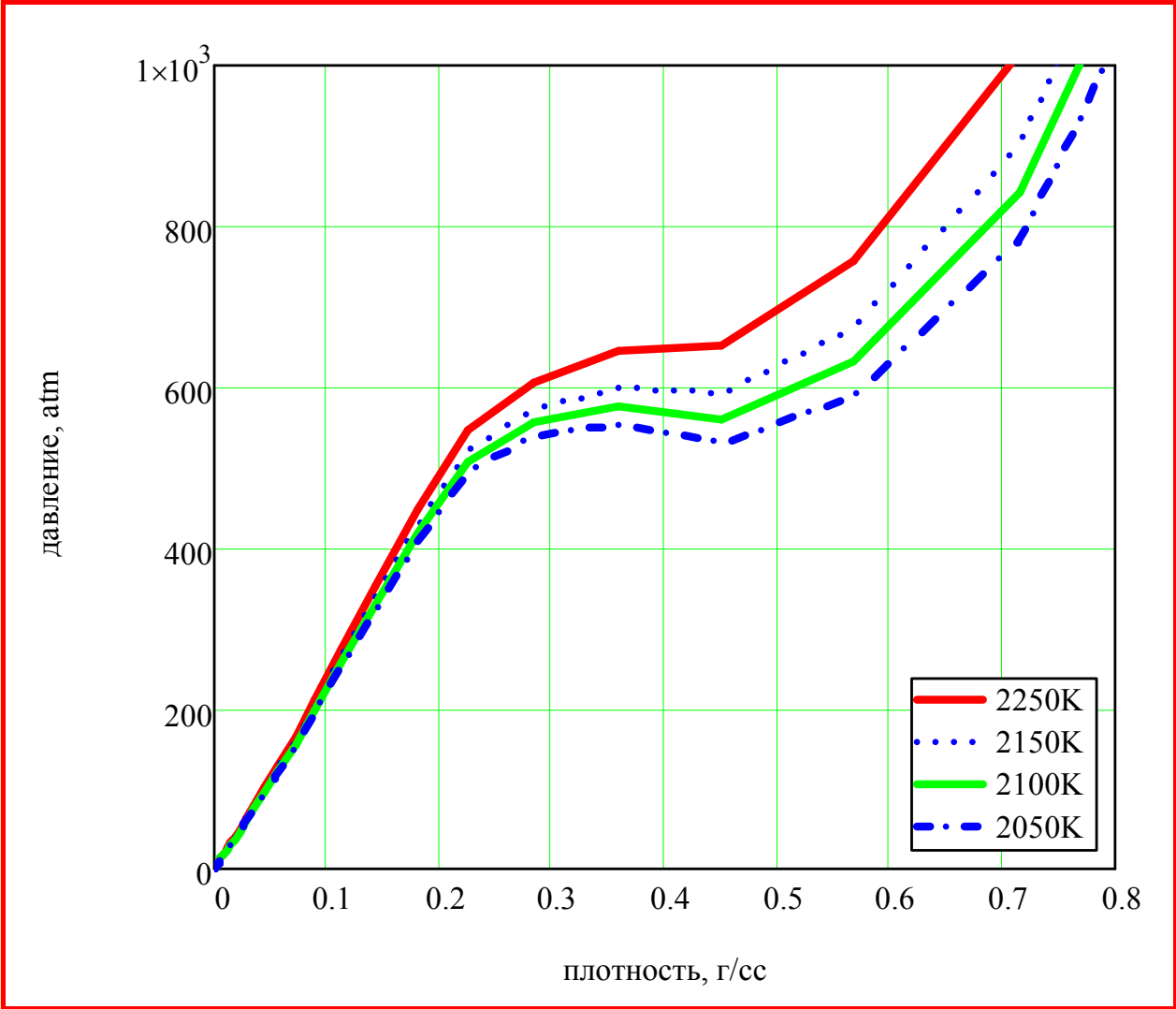
Cs

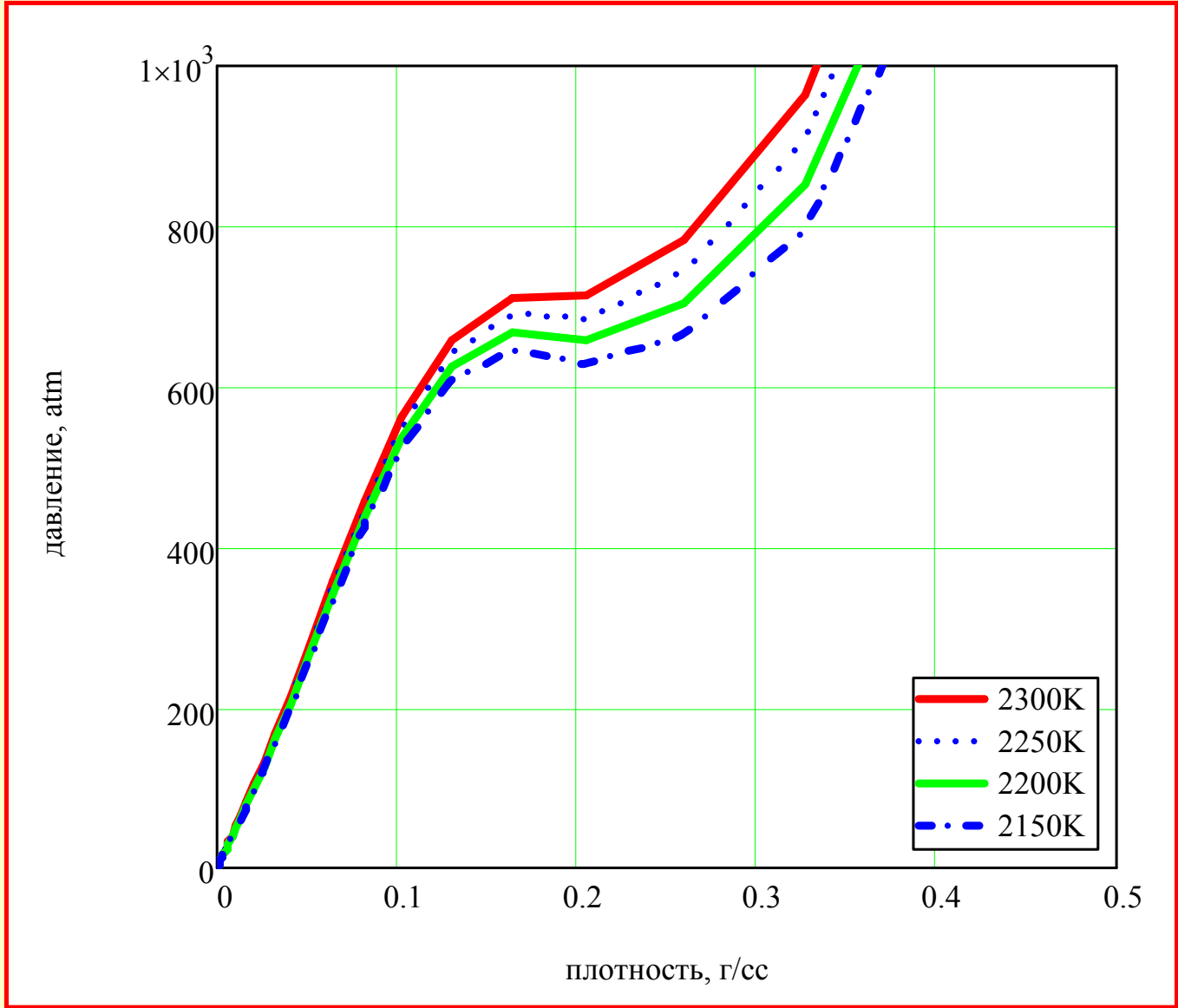


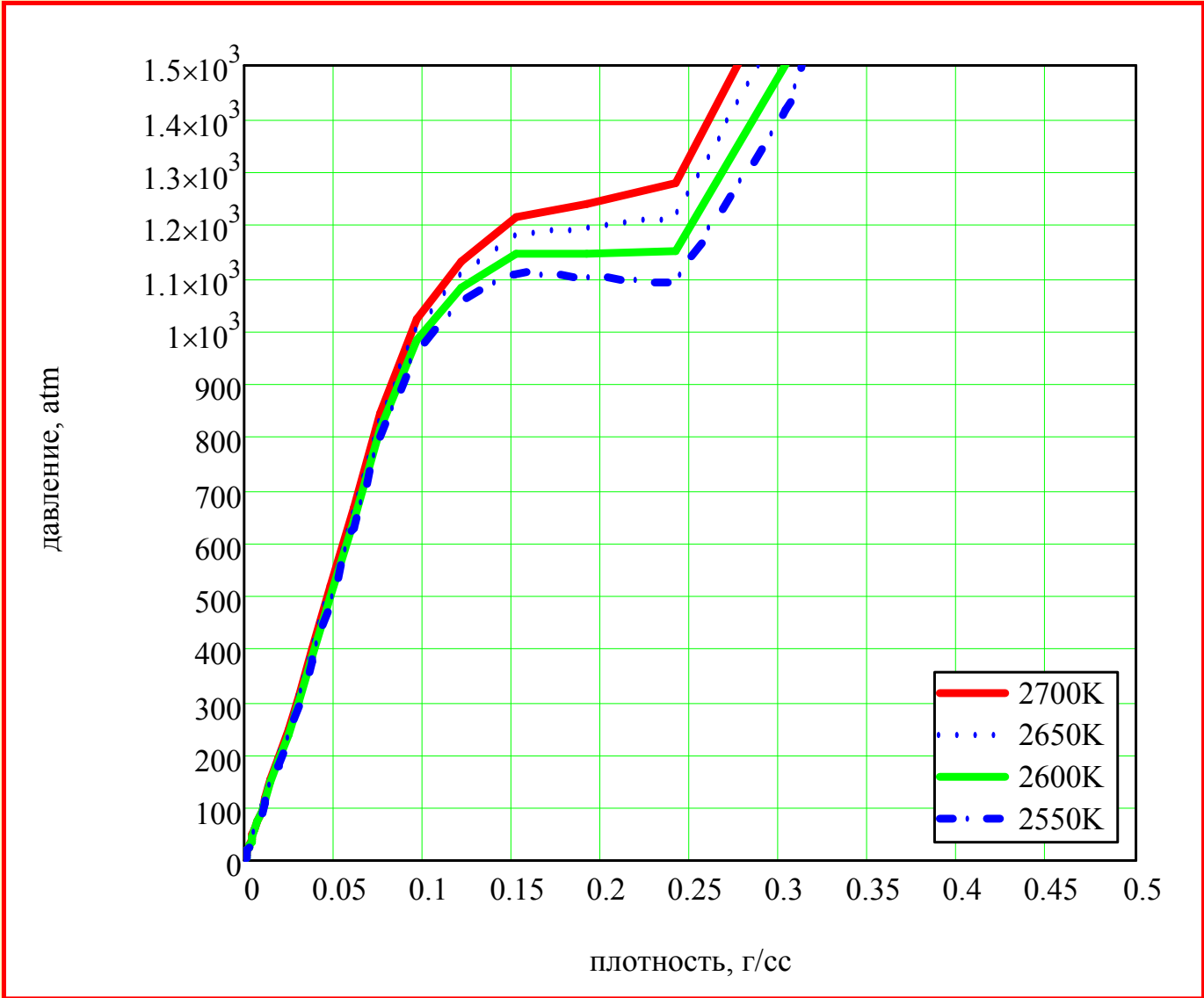
NPP-2011

NPP-2011

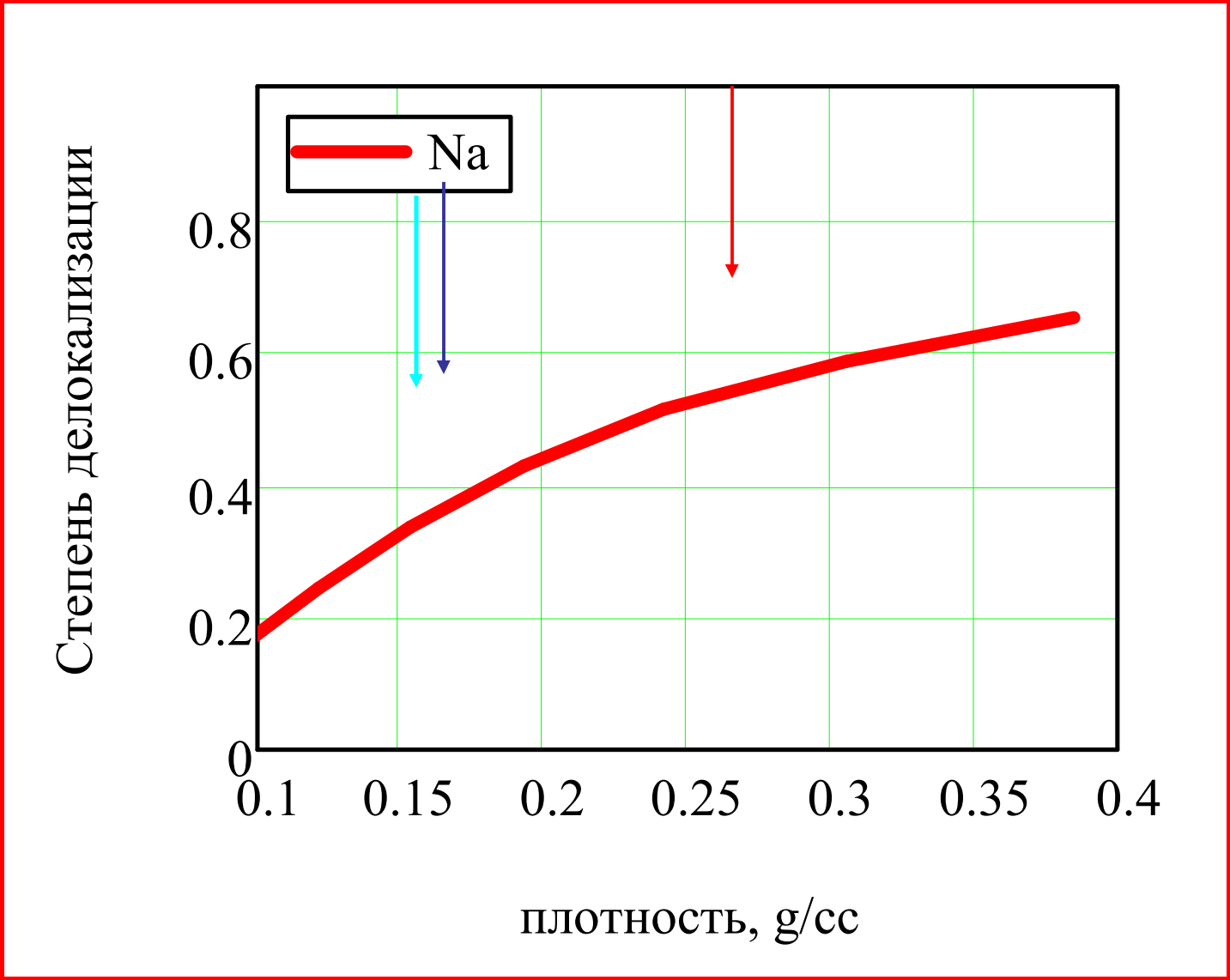
Rb

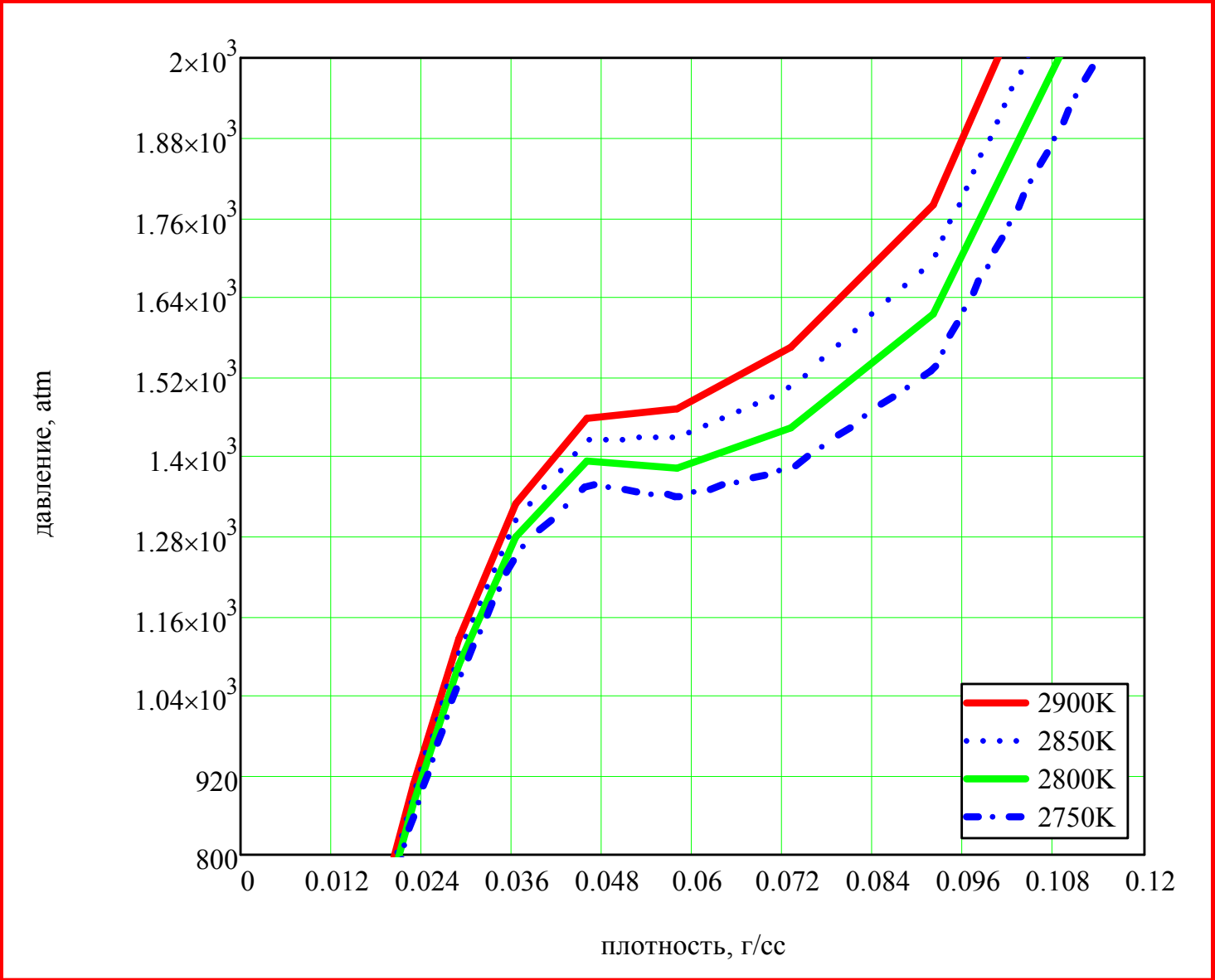




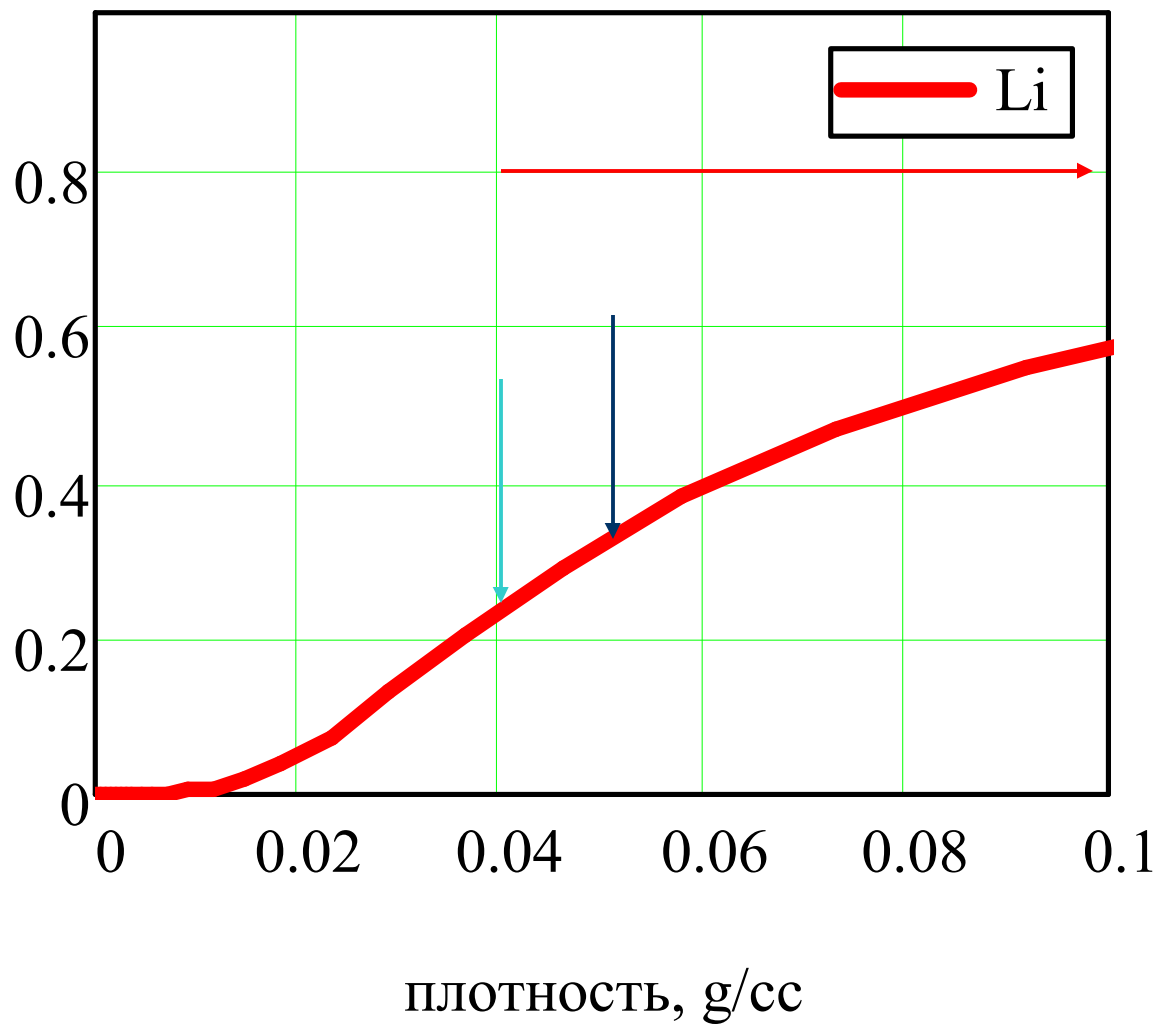


NPP-2011





Степень делокализации



NPP-2010

	T_c , K	ρ_c , g/cc	P_c , atm	Z_c	α_c
Cs	1950 <i>1924</i>	0.5 <i>0.38</i>	450 <i>92.5</i>	0.75	0.38
Rb	2250 <i>2017</i>	0.4 <i>0.29</i>	650 <i>124</i>	0.75	0.38
K	2300 <i>2178</i>	0.18 <i>0.17</i>	700 <i>150</i>	0.76	0.38
Na	2700 <i>2485</i>	0.15 <i>0.3</i>	1200 <i>248</i>	0.85	0.32
Li	2900 <i>?</i>	0.05 <i>0.1</i>	1400 <i>?</i>	0.85	0.32

Переход Мотта. Проводимость!!!

Минимальная проводимость металлизированного газа

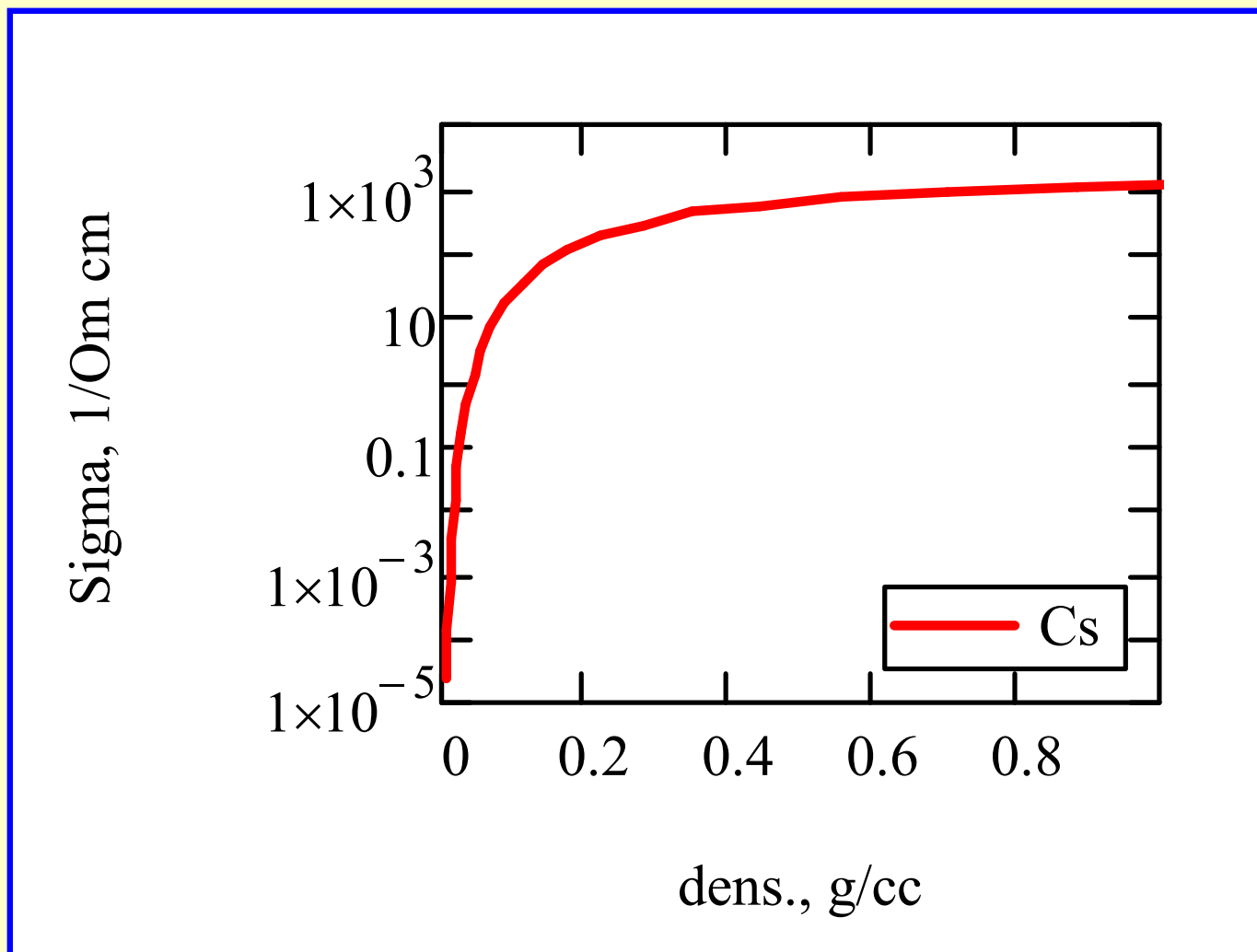
$$\sigma = n_e^f \frac{e^2}{m_e^f} \tau_e$$

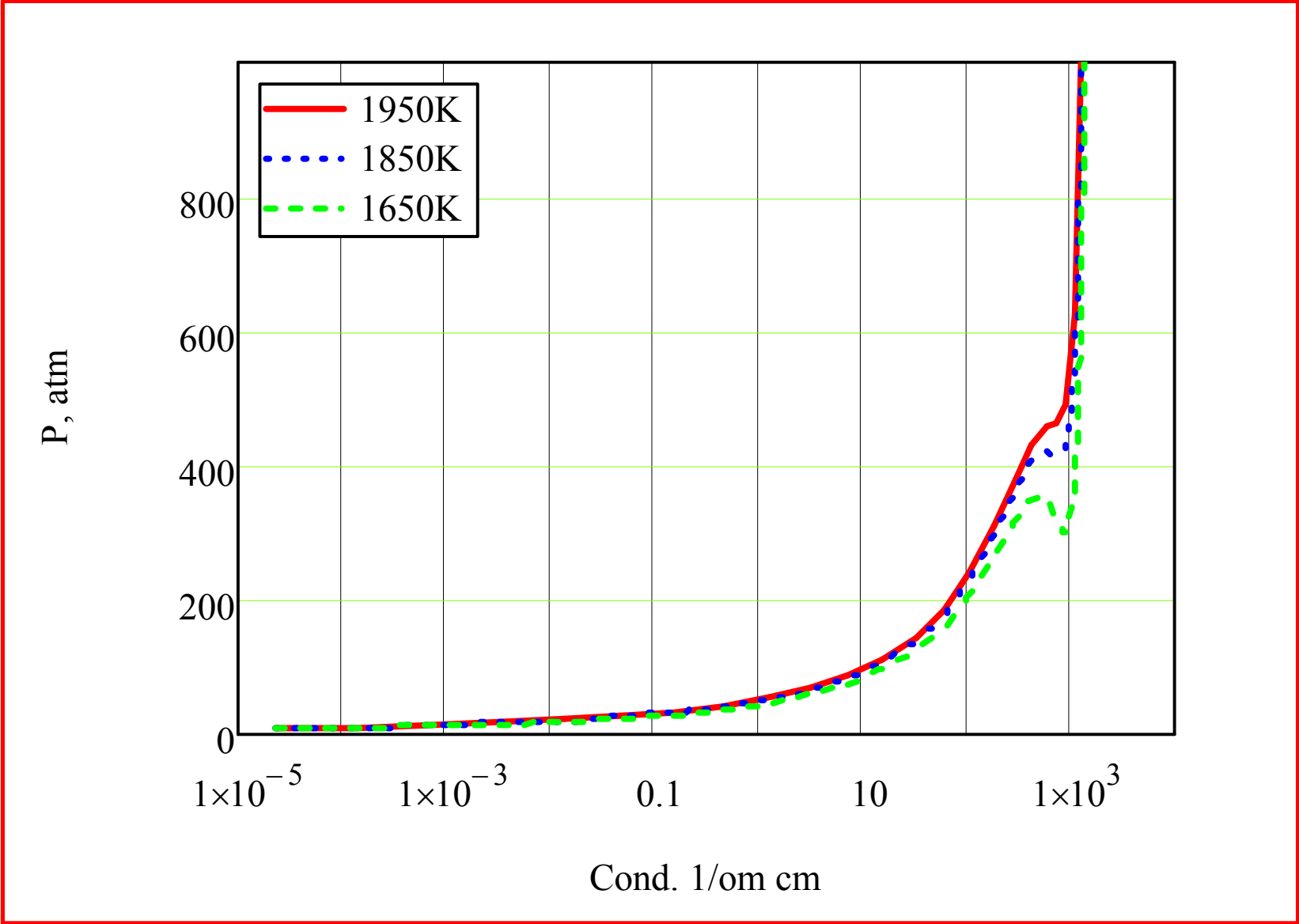
$$n_e^f = n \alpha_{del}(n, I)$$

$$\frac{\tau_e}{m_e^f} = \frac{2r_c(n)}{p_F}$$

$$p_F = \left(3\pi^2 n_e^f\right)^{1/3} \hbar$$

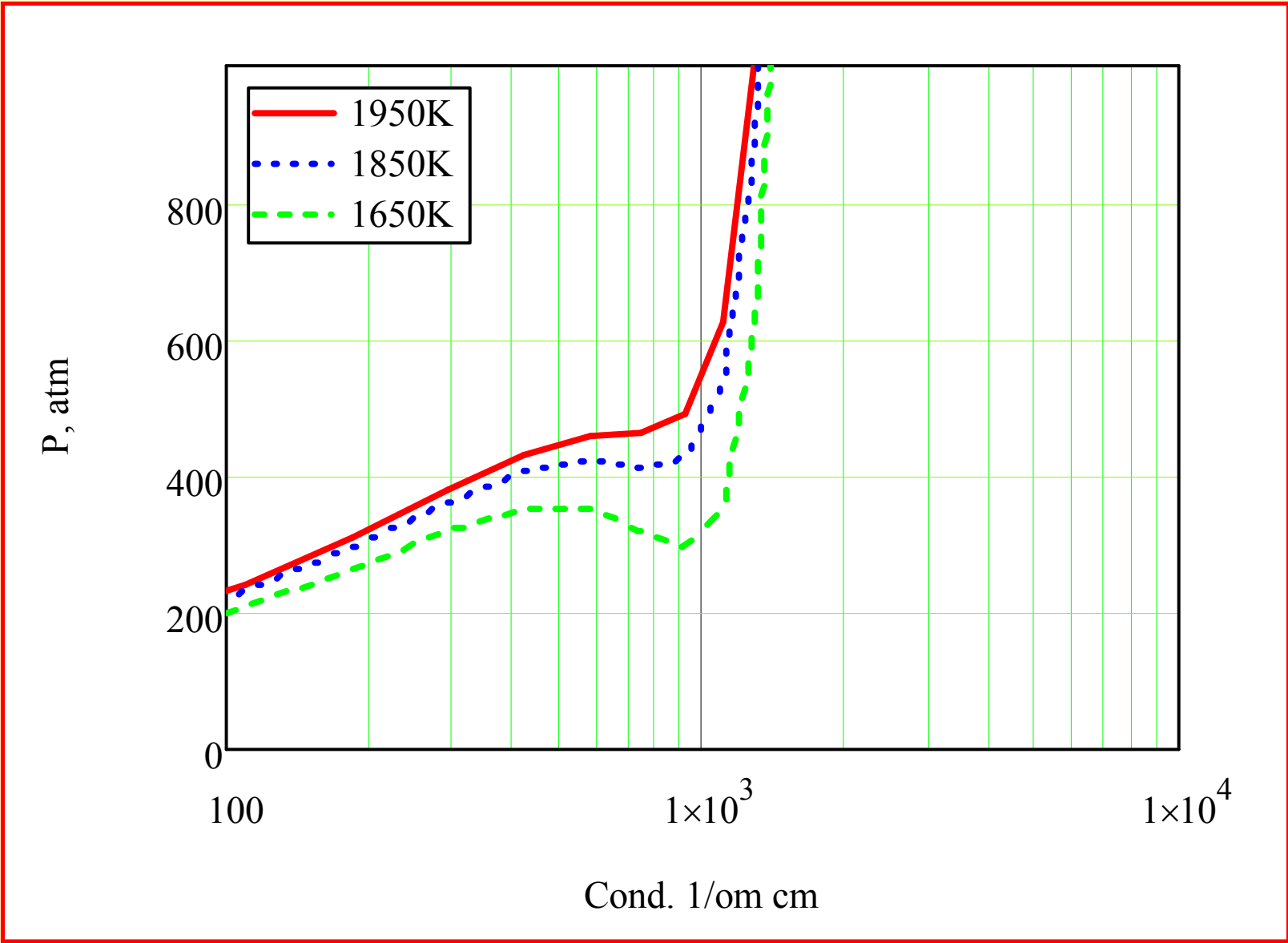
Минимальная проводимость металлизированного газа





NPP-2010

Cs



NPP-2011

ВЫВОДЫ

1. Создана простая физическая модель, описывающая основные закономерности поведения паров щелочных металлов в окрестности критической точки.
2. Рассчитанные околокритические изотермы демонстрируют наличие фазового перехода:
металлизированный пар – жидкий металл
3. Рассчитана степень делокализации (металлизации) паров в критической точке.
4. Оценена проводимость паров до и после бинодали
5. Переход Мотта в модели совпадает с переходом пар - жидкость

НЕКОТОРЫЕ ПРОБЛЕМЫ НА БУДУЩЕЕ:

- 1. ТЕРМИЧЕСКАЯ ИОНИЗАЦИЯ И ПЕРЕХОД
К ПЛАЗМЕННОЙ ПРОВОДИМОСТИ**
- 2. РАЗМЕР КВАЗИАТОМОВ**
- 3. ТЕРМОДИНАМИКА**
- 4. УЧЕТ МОЛЕКУЛ**

NPP-2011

*ВСЕМ ПРИСУТСТВУЮЩИМ
НА ЗАСЕДАНИИ*

СПАСИБО ЗА ВНИМАНИЕ !!!

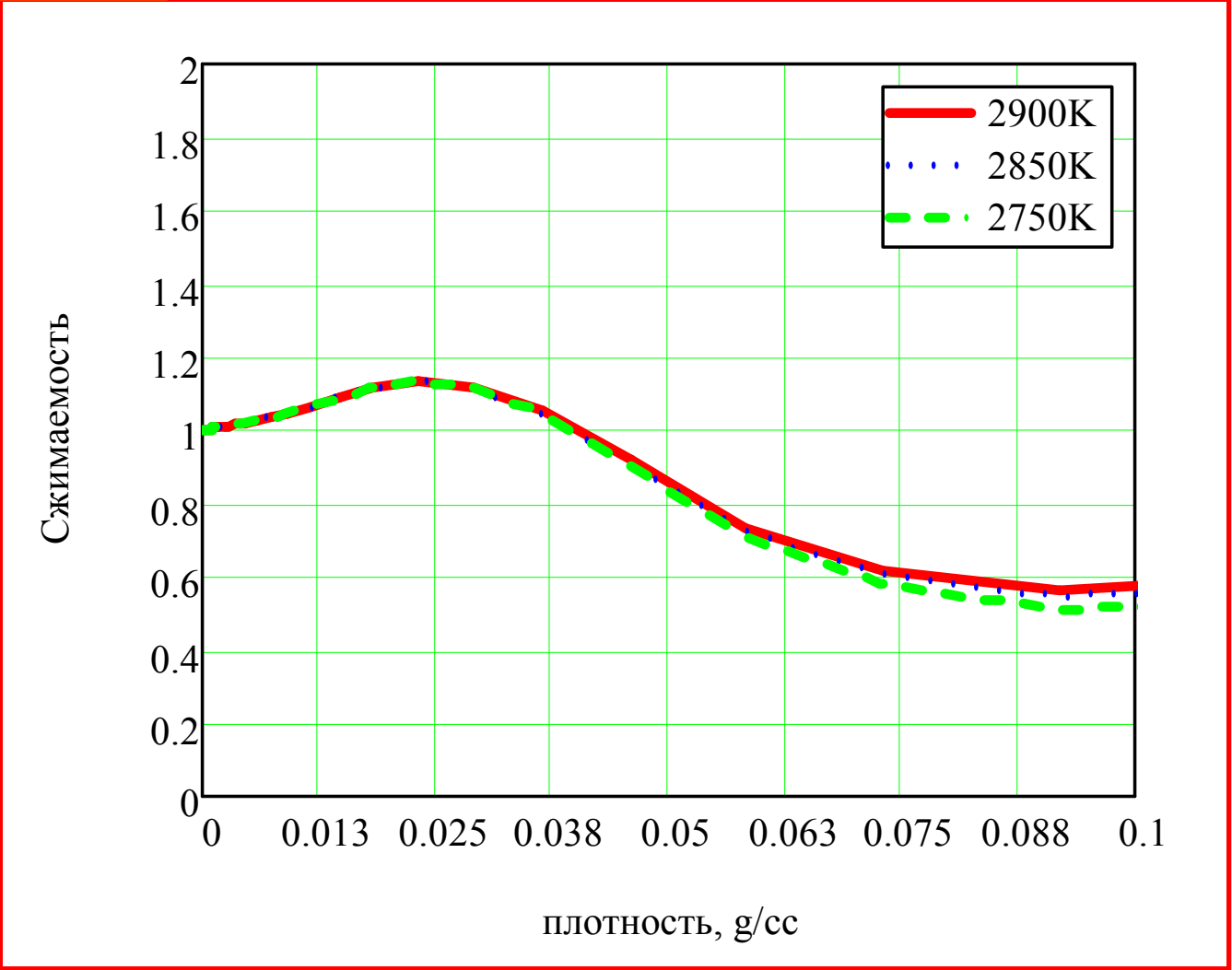
$$E_a = E_0 + \alpha \frac{3}{5} E_F$$

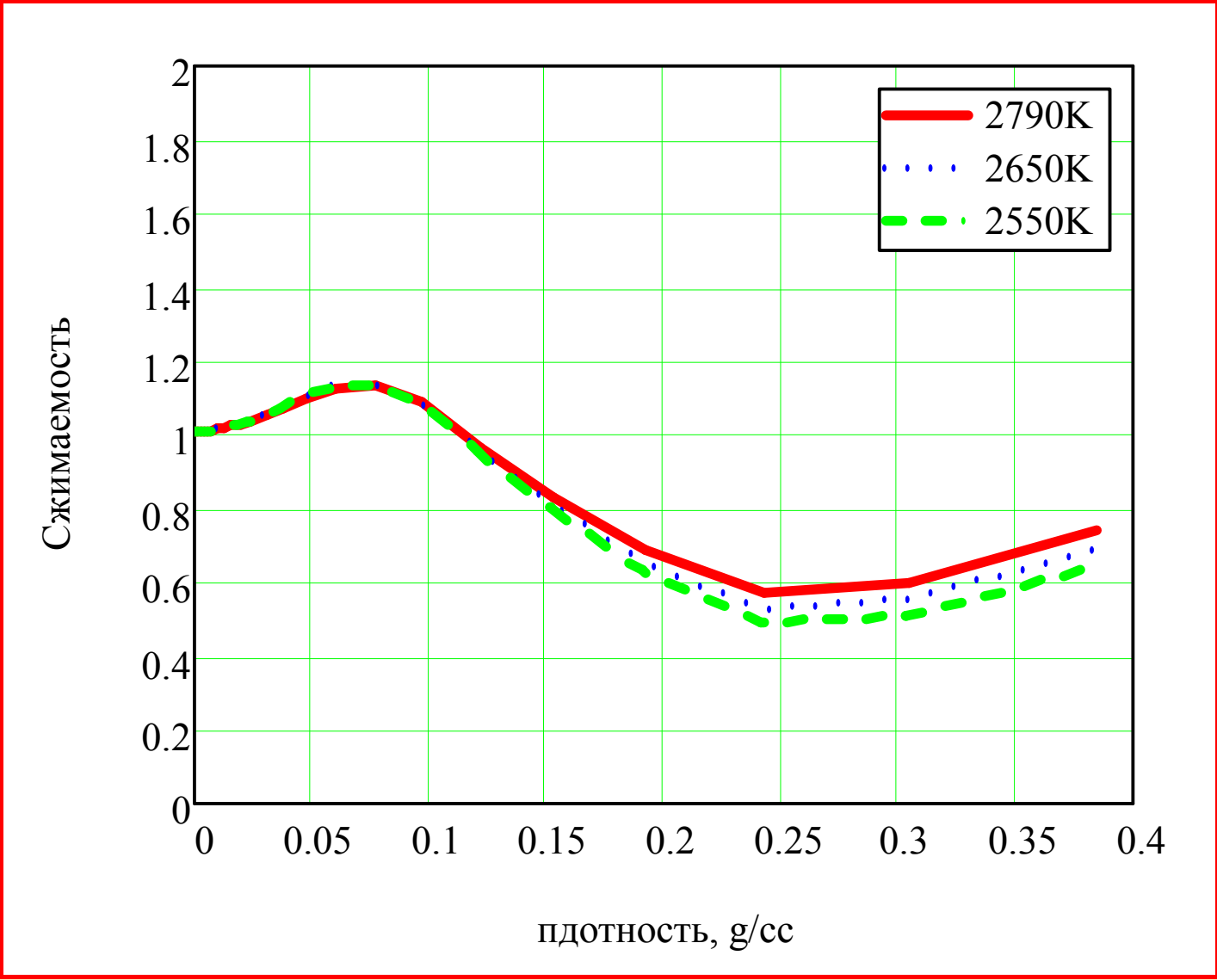
$$E_{coh} = E_a + Ry$$

$$\alpha = \left[\frac{4\pi}{3} R_0^3(r_c) \right] \left[\frac{r}{R_1(r)} \frac{dR_1(r)}{dr} \right]_{r=r_c}$$

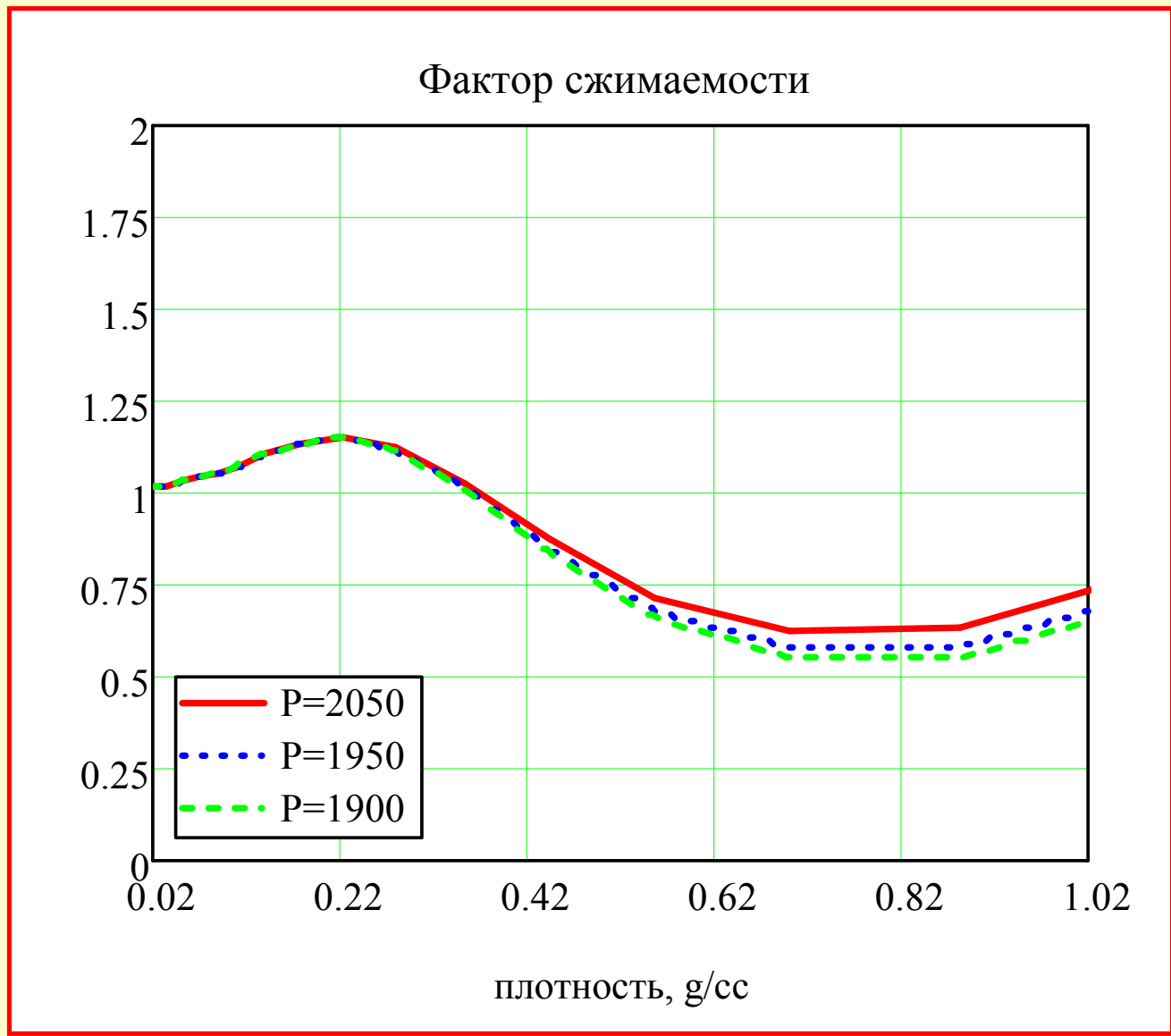
NPP-2010

Li





Cs



NPP-2011

NPP-2011

Модель изолированного щелочного атома

Потенциал взаимодействия электрона и иона?

Влияние кора!!!

Потенциалы:

Прокофьева

Ашкрофта

Аборенкова

Твердая стенка- Апфельбаум

$$\beta\mu_a = \beta\mu_a^0 + \beta\Delta\mu_a$$

$$\beta\mu_a^0 = -\ln\left(\frac{Vg_a\Sigma_a}{N_a\lambda_a^3}\right), \quad \Sigma_a = 1$$

$$\beta\Delta\mu_a = \frac{4\eta - 3\eta^2}{(1-\eta)^2} + \eta \frac{4-2\eta}{(1-\eta)^3} + \frac{\beta E_{coh}}{2} \left(1 - \frac{y}{3E_{coh}} \frac{\partial E_{coh}}{\partial y}\right)$$

NPP-2011

$$U_{\text{mod}} = \alpha e^2 n^{4/3}$$

$$\alpha_{\text{ocp}} = 1.78$$

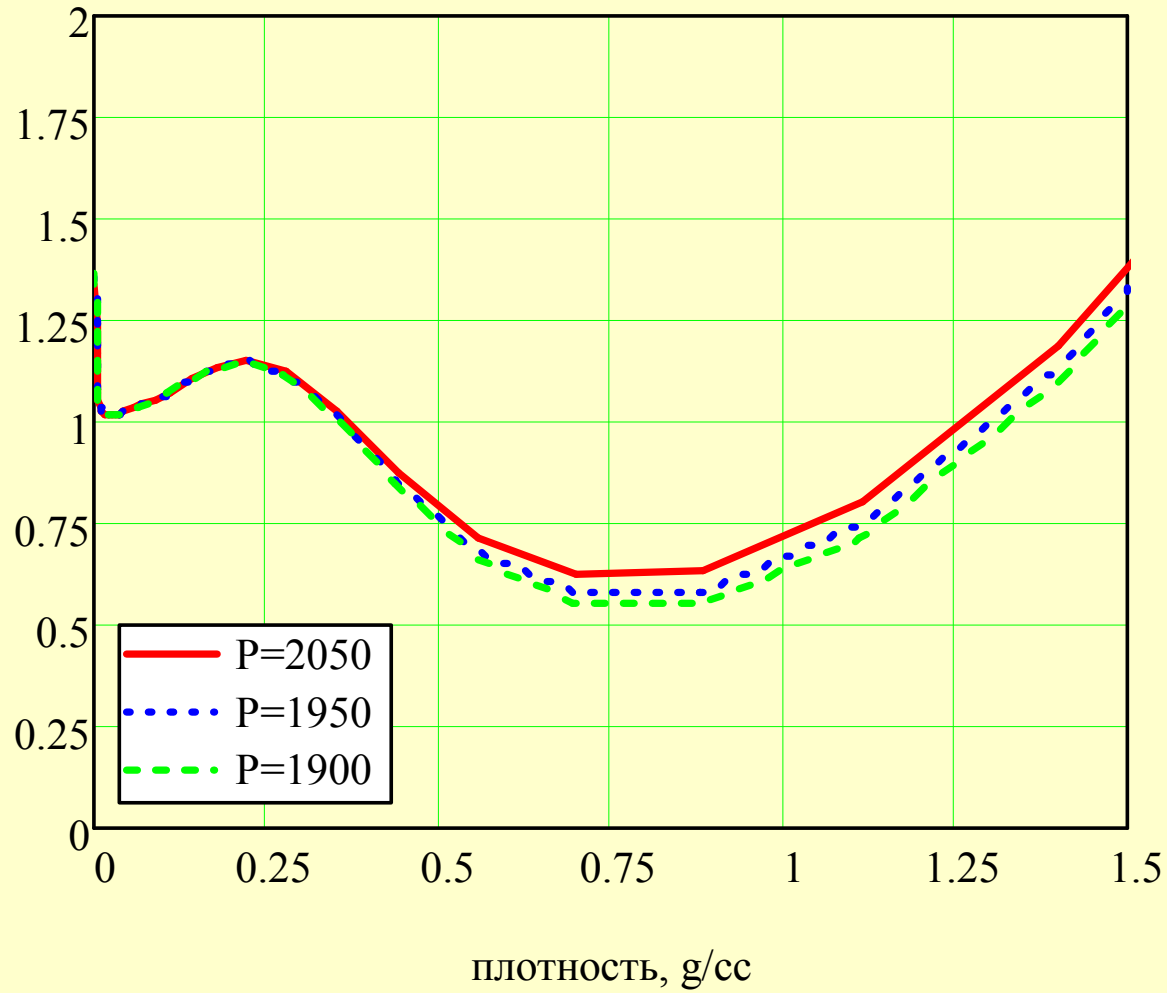
$$\alpha_{\text{Lik}} = \frac{1}{4} = 0.25$$

$$e_{\text{eff}} = e\alpha_{\text{del}}$$

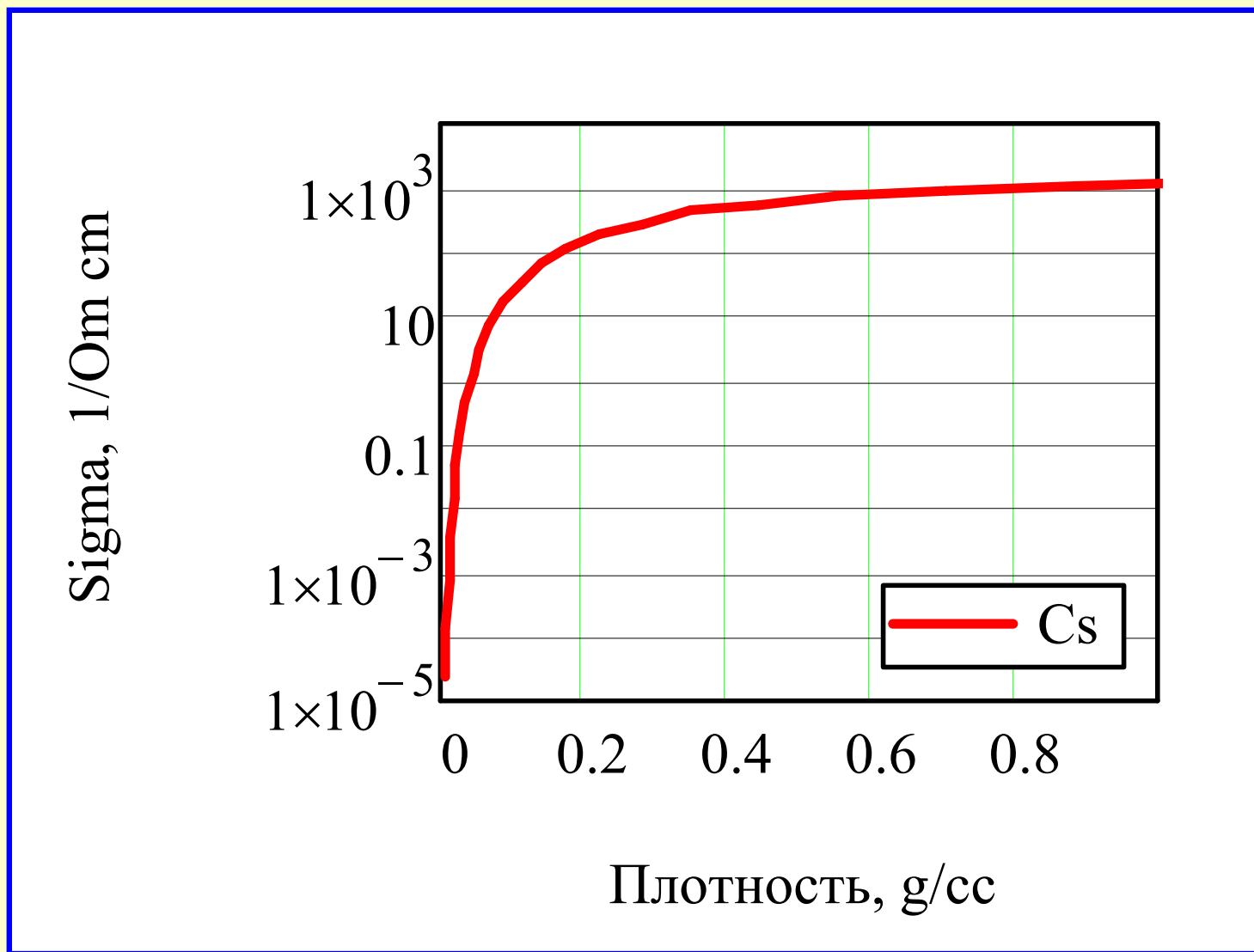
$$\alpha_{\text{KS}} = 1.78\alpha_{\text{del}}^2 = 0.257$$

Фактор сжимаемости

Cs



Минимальная проводимость металлизированного газа



Cs

