Критические точки некоторых металлов, найденные на основе их связи с параметрами линии единичного фактора сжимаемости

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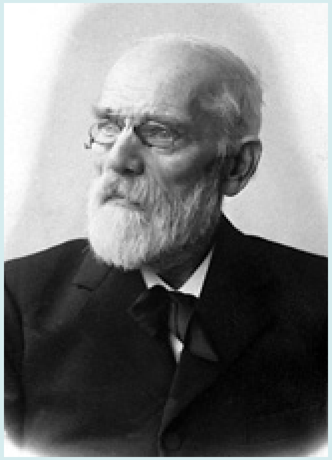
Линия единичного фактора сжимаемости (линия Бачинского, Z-line)



$$Z = \frac{P}{\rho T} = 1$$

Уравнение ван дер Ваальса

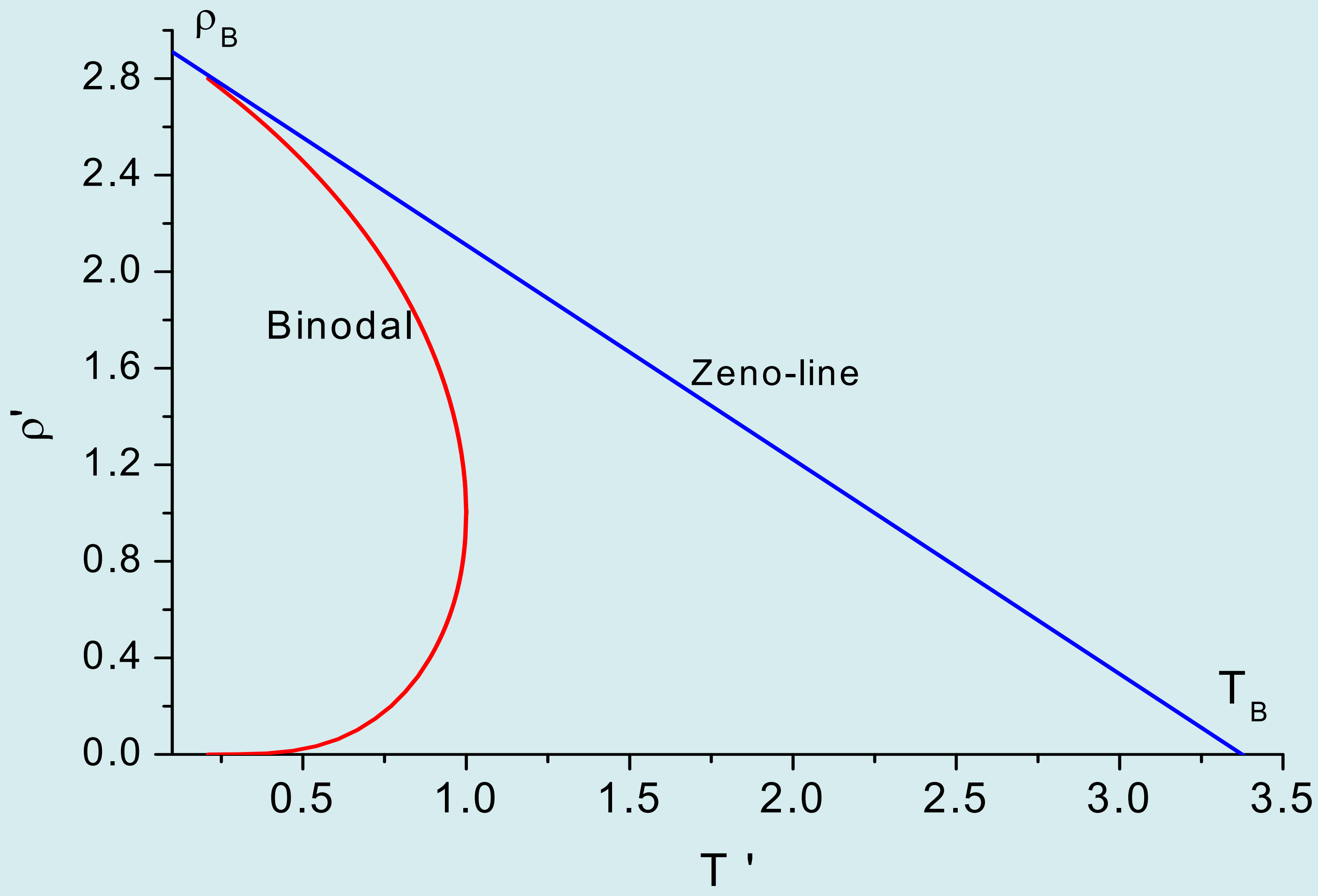
$$Z = \frac{P}{\rho T} = 1 + \frac{27\rho(\rho/3 + 8T/27 - 1)}{8T(3-\rho)}$$

Уравнение Z=1 линии

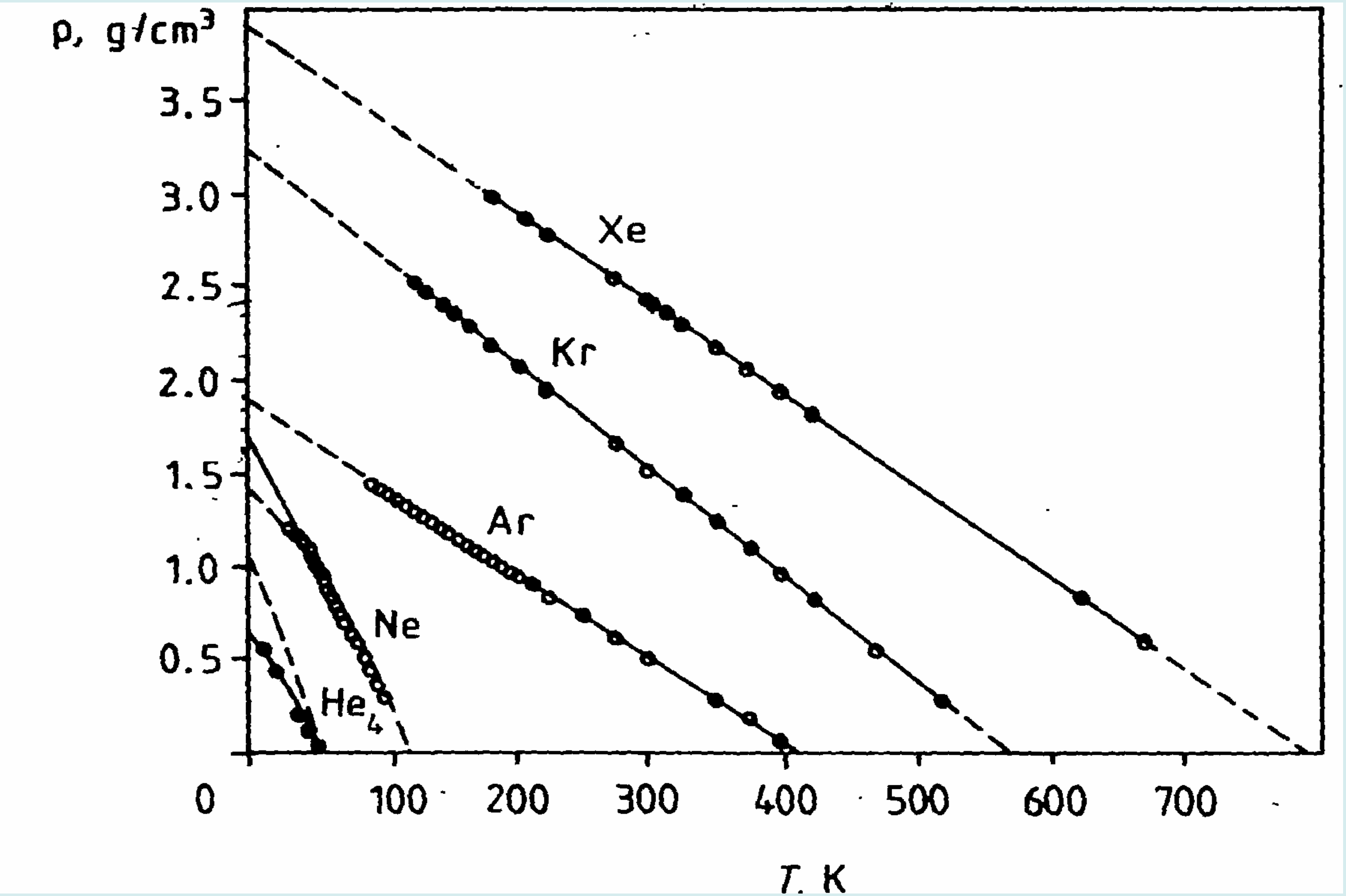
$$\frac{T}{T_B} + \frac{\rho}{\rho_B} = 1 \quad ; \quad T_B = 27/8 \quad ; \quad \rho_B = 3$$

A. Bachinskii, Ann. Der Phys. (1906)

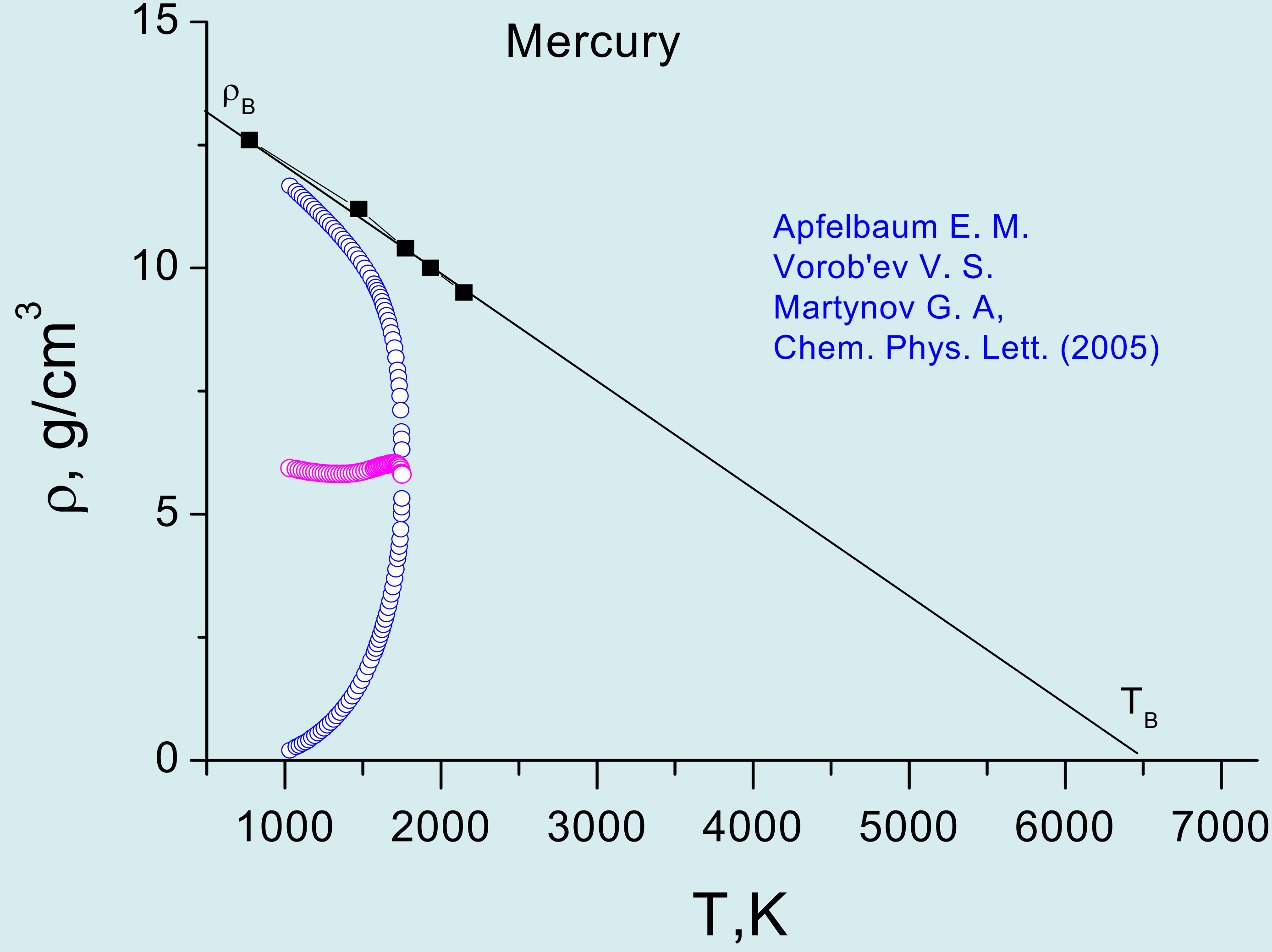
vdW binodal and Z-line

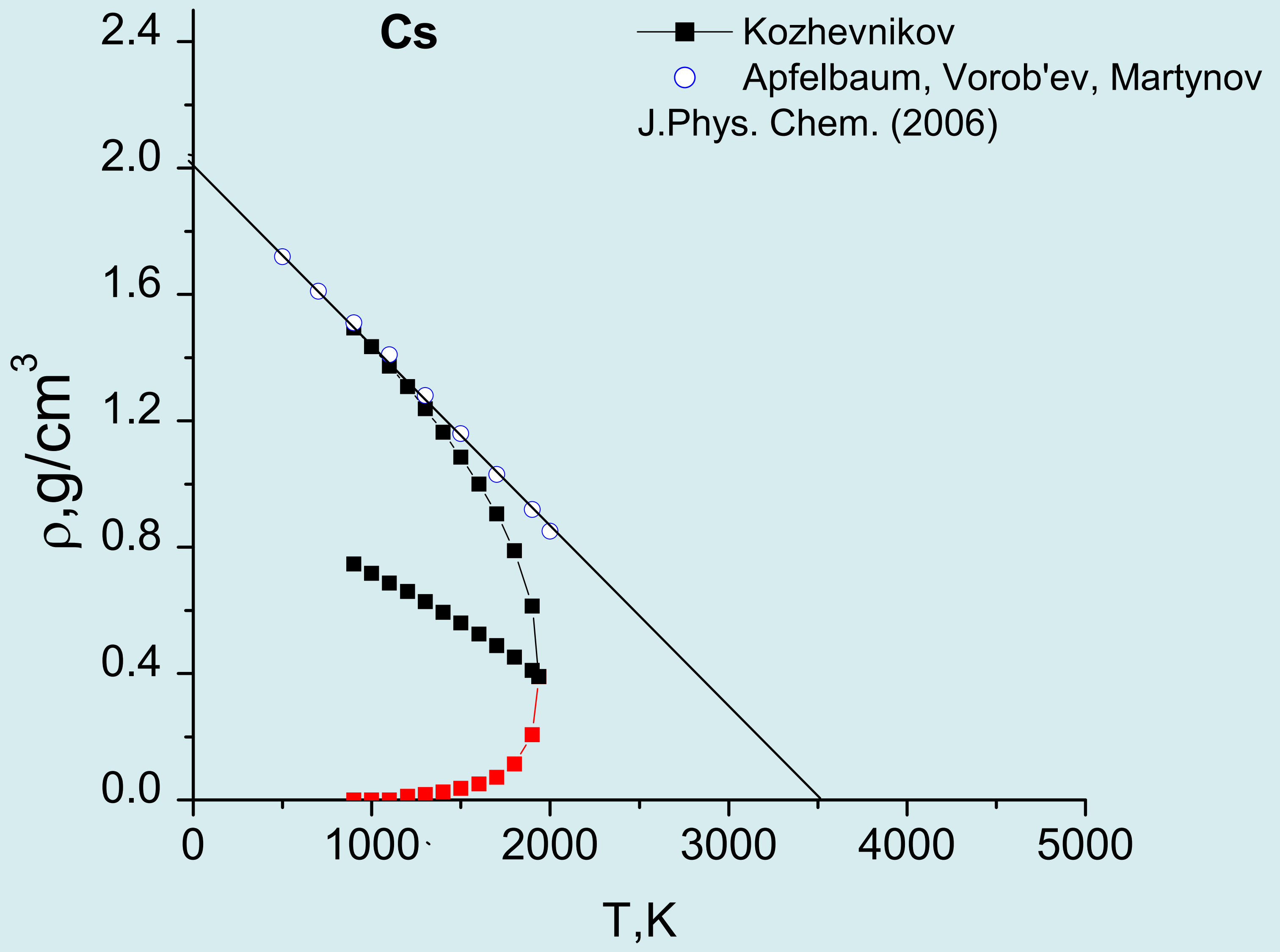


V. A. RABINOVICH. ET. AL., THERMOPHYSICAL PROPERTIES OF NEON, ARGON, KRYPTON AND XENON (HEMISPERE, BERLIN-NEW YORK, 1988).

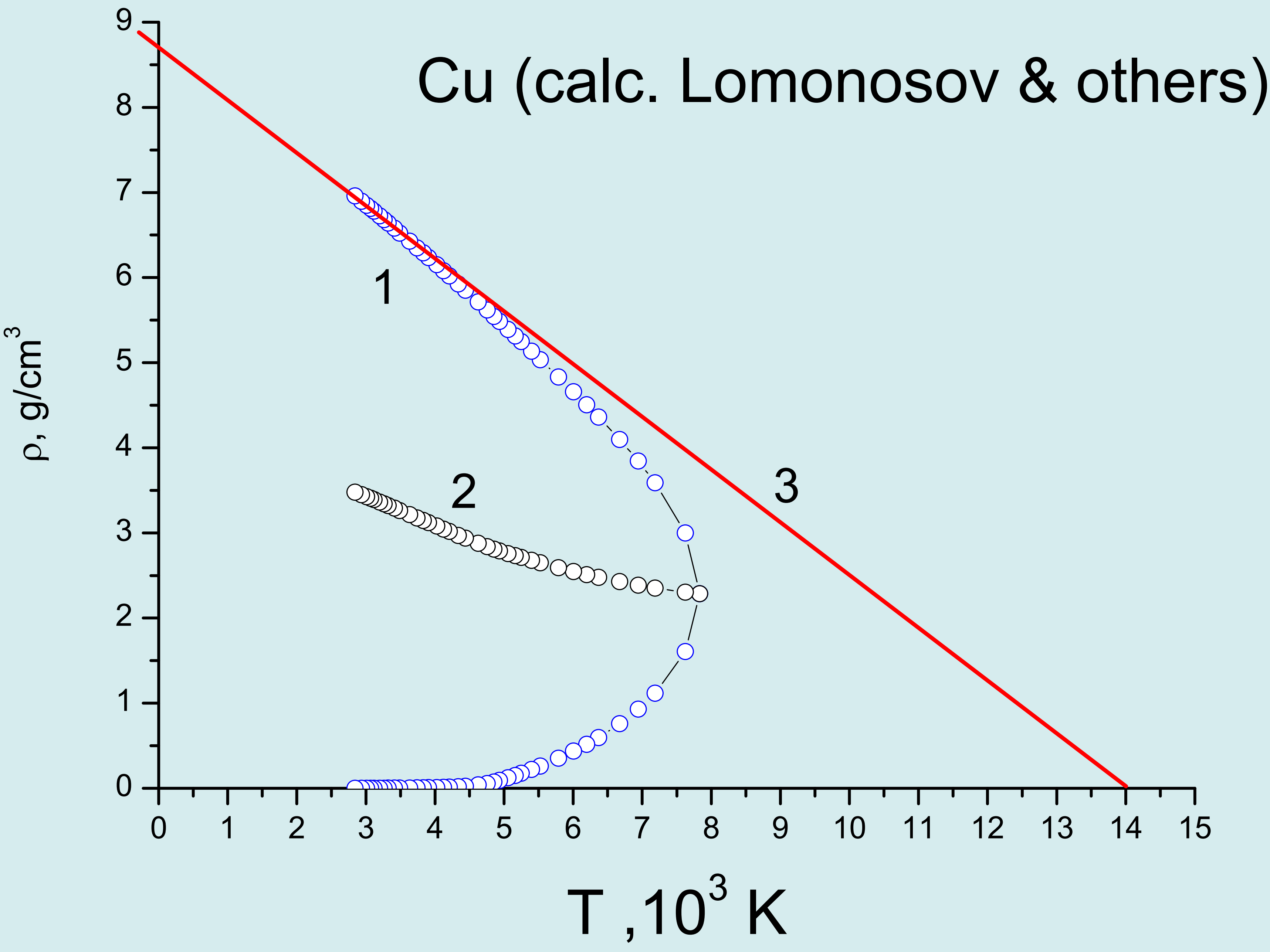


The linearity for Z-line has been confirm also HYDROCARBONS, WATER, CARBON DIOXIDE, METHANE and for many others

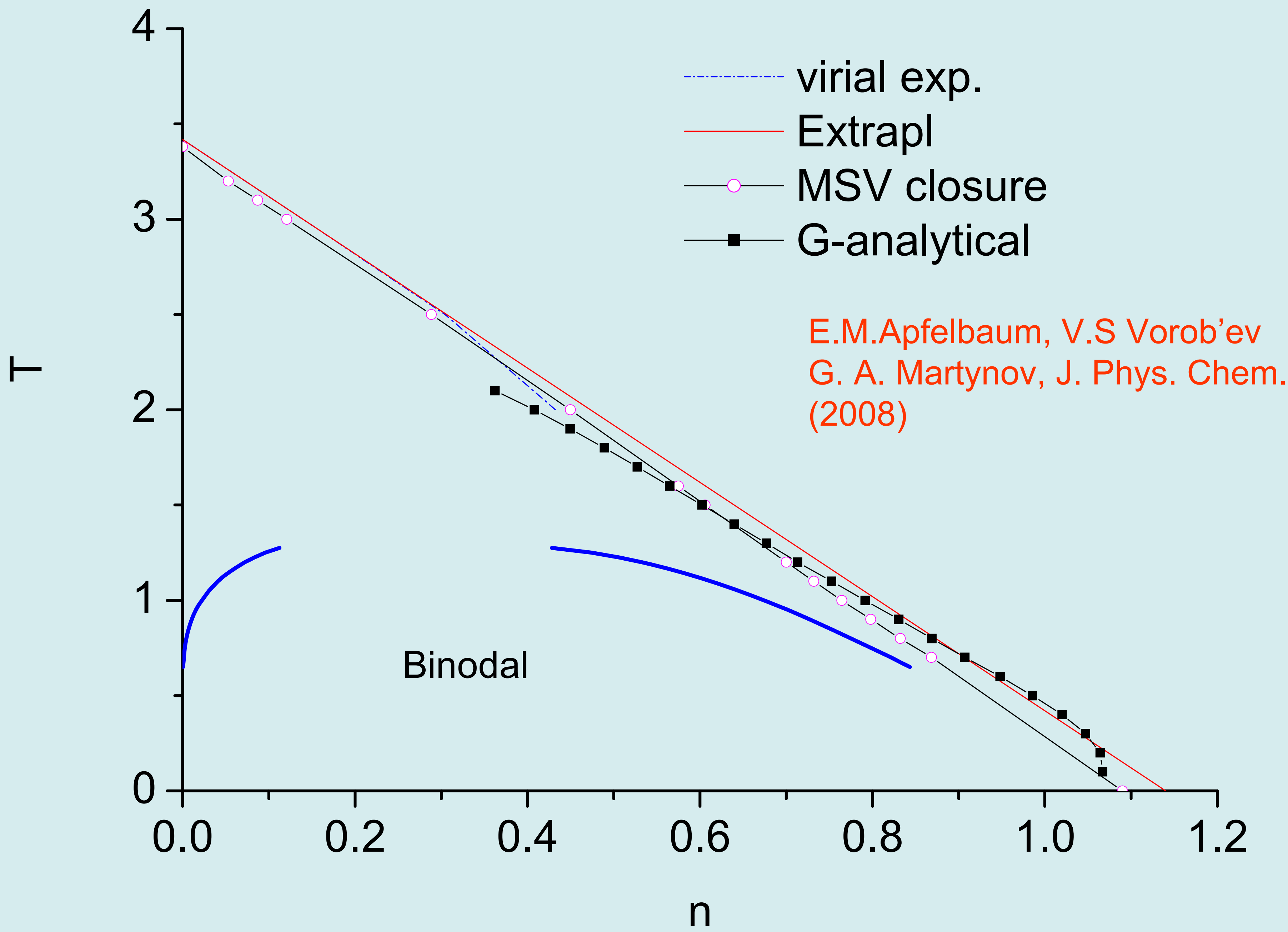




Cs
Kozhevnikov
Apfelbaum, Vorob'ev, Martynov
J.Phys. Chem. (2006)
ρ,g/cm3
T,K
0.0
0.4
0.8
1.2
1.6
2.0
2.4
0
1000
2000
3000
4000
5000



Cu (calc. Lomonosov & others)
1
2
3
ρ, g/cm3
T ,10^3 K
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15


virial exp.
Extrapl
MSV closure
G-analytical
E.M.Apfelbaum, V.S Vorob'ev
G. A. Martynov, J. Phys. Chem.
(2008)
Binodal
T
n
0
1
2
3
4
0.0
0.2
0.4
0.6
0.8
1.0
1.2

Liquid branch of binodal

$$\rho(T)=\rho_c+\alpha\tau+\beta\tau^{1/3} \qquad \tau=1-T/T_c$$

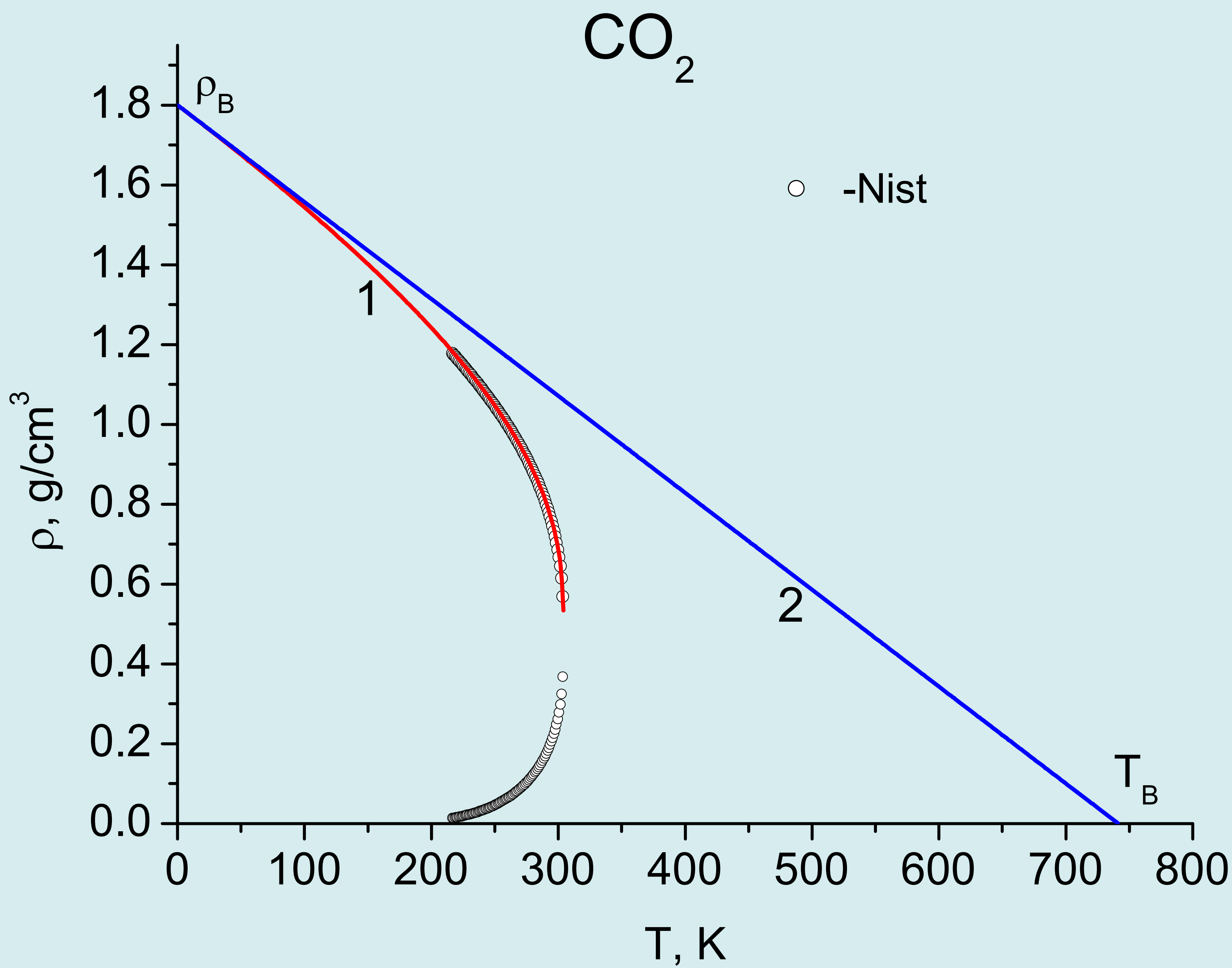
Guggenheim (1945), Reid (1977), Филиппов (1984)

$$\rho(T)_{T\to 0}\to\rho_B\left(1-T/T_B\right)$$

Жидкая ветвь бинодали (Apfelbaum, Vorob’ev J. Phys. Chem.2008)

$$\rho(T)=\rho_c+\frac{1}{2}\left[\rho_c-\rho_B+3\rho_B\frac{T_c}{T_B}\right]\tau+\frac{3}{2}\left[\rho_B-\rho_c-\rho_B\frac{T_c}{T_B}\right]\tau^{1/3}$$

Thus, if T/Tc → 1 (critical point), then r = r_c, and, if T → 0, then r= r_B.
Besides, Eq.(2) transforms into Eq. (1) if T/Tc <<1
.



CO2
ρB
-Nist
1
2
TB
ρ, g/cm3
T, K
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
0
100
200
300
400
500
600
700
800

$Z_c = P_c m/\rho_B kT_B$ $P_c m/\rho_c kT_c$	*Critical parameters*				*Z-line parameters*		*Similary parameters*			
Model, Subs.	T_c, *K*	ρ_c, *g/cm*^{3}	P_c *,atm*	$Z_c = P_c m/\rho_c kT_c$	T_B, *K*	ρ_B, *g/cm*^{3}	S_2	$P_c m/\rho_B kT_B$	T_c/T_B	ρ_c/ρ_B
L-J[)]	1.305	0.314	0.127	0.308	3.418	1.14	0.076	0.033	0.383	0.285
vdW[1)]	1	1	1	3/8 = 0.375	27/8 = 3.375	3	5/81 =00. 061	1/27 = 0.037	0.296	0.333
Ar	150.7	0.536	48.63	0.286	392.84	1.87	0.078	0.031	0.383	0.286
Ne	44.49	0.482	26.79	0.3 0.34*[1)]	118.85	1.63	0.077	0.033	0.374	0.296
Kr	209.5	0.909	55.25	0.289	537.98	3.24	0.077	0.032	0.389	0.280
Xe	289.7	1.100	58.42	0.286	740.02	3.95	0.077	0.031	0.391	0.278
NH_3	405.4	0.225	113.30	0.251	935.92	0.95	0.076	0.026	0.433	0.236
CO_2	304.1	0.468	73.77	0.271	741.4	1.80	0.077	0.029	0.41	0.26
Ethane	305.3	0.207	48.72	0.275	779.35	0.74	0.079	0.03	0.39	0.28
Ethene	282.3	0.214	50.42	0.278	714.12	0.78	0.078	0.03	0.395	0.274
Fluorine	144.4	0.593	51.72	0.273	385.06	2.01	0.080	0.03	0.375	0.295
Hexane	507.8	0.233	30.34	0.263	1235.84	0.90	0.078	0.028	0.41	0.259
Methane	190.6	0.163	45.99	0.282	498.06	0.57	0.078	0.031	0.383	0.286
N_2	126.2	0.313	33.96	0.286	327.62	1.10	0.078	0.031	0.385	0.284
O_2	154.6	0.436	50.43	0.285	401.14	1.53	0.078	0.031	0.385	0.285
Propene	365.6	0.223	46.65	0.286	894.42	0.86	0.075	0.032	0.409	0.259
R13	302.0	0.583	38.79	0.277	763.31	2.13	0.078	0.03	0.395	0.274

	Critical parameters				*Z-line parameters*		*Similary parameters*			
Model, Subs.	T_c, *K*	ρ_c, *g/cm*^{3}	P_c ,*atm*	$Z_c = P_c m / \rho_c k T_c$	T_B, *K*	ρ_B, *g/cm*^{3}	S_2	$P_c m / \rho_B k T_B$	T_c/T_B	$\rho_c/\rho_{\mathbf{B}}$
R22	369.3	0.524	49.9	0.268	907.89	1.99	0.078	0.029	0.407	0.263
R32	351.3	0.424	57.82	0.243	823.92	1.74	0.079	0.025	0.426	0.244
Cs	1924	0.39	94	0.198	4114.47	1.96	0.075	0.018	0.468	0.199
Li	3223	0.120	689	0.17	7165.14	0.545	0.082	0.017	0.45	0.22
Rb	2017	0.29	124.5	0.22	4126.85	1.6	0.069	0.019	0.489	0.18
K	2178	0.18	148	0.178	4656.3	0.89	0.078	0.017	0.478	0.20
Na	2503	0.206	256	0.137	5394.40	1.0	0.083	0.013	0.464	0.206
Hg	1751	5.8	1650	0.387	6552.60	14.40	0.065	0.042	0.267	0.403
Water	647.3	0.32	221.2	0.228	1268.0	1.2	0.105	0.03	0.51	0.267
H_2	33.15	0.0312	12.964	0.30 0.37*	99.84	0.092	0.079	0.041	0.332	0.338
He^4	5.195	0.0696	2.2746	0.3 0.387*	19.46	0.173	0.071	0.03	0.257	0.407
He^3	3.34	0.0385	1.15	0.321 0.47*	18.55	0.078	0.06	0.03	0.18	0.49
Al	**6378**	**0.45**	**1074**	**0.12**	**12888**	**2.57**	**0.076**	**0.01**	**0.495**	**0.175**
Cu	**6000**	**1.8**	**2265**	**0.19**	**12740**	**9.05**	**0.061**	**0.025**	**0.471**	**0.186**
W	**12387**	**4.92**	**7448**	**0.27**	**29131**	**20.1**	**0.078**	**0.027**	**0.425**	**0.245**
U	**7000**	**3.3**	**1712**	**0.21**	**14030**	**19.3**	**0.077**	**0.02**	**0.499**	**0.170**
Zr	**15200**	**1**	**421**	**0.031**	**29330**	**6.58**	**0.073**	**0.024**	**0.52**	**0.15**

Empirical similarity relations

$$T_c / T_B + \rho_c / \rho_B = S_1 \approx 0.67$$

S_1, S_2, S_3 слабо зависят от вещества

$$S_2 = \frac{\rho_c T_c - P_c}{\rho_B T_B} \quad ; \quad S_3 = \frac{P_c}{\rho_B T_B} \quad \Rightarrow \quad P_c = \rho_c T_c - S_2 \rho_B T_B$$

$$x_1 = \rho_c / \rho_B \quad ; \quad x_2 = T_c / T_B$$

$$x_{1,2} = \frac{S_1}{2}\left[1 \pm \sqrt{1 - \frac{4S_2}{S_1^2(1 - Z_c)}}\right]$$

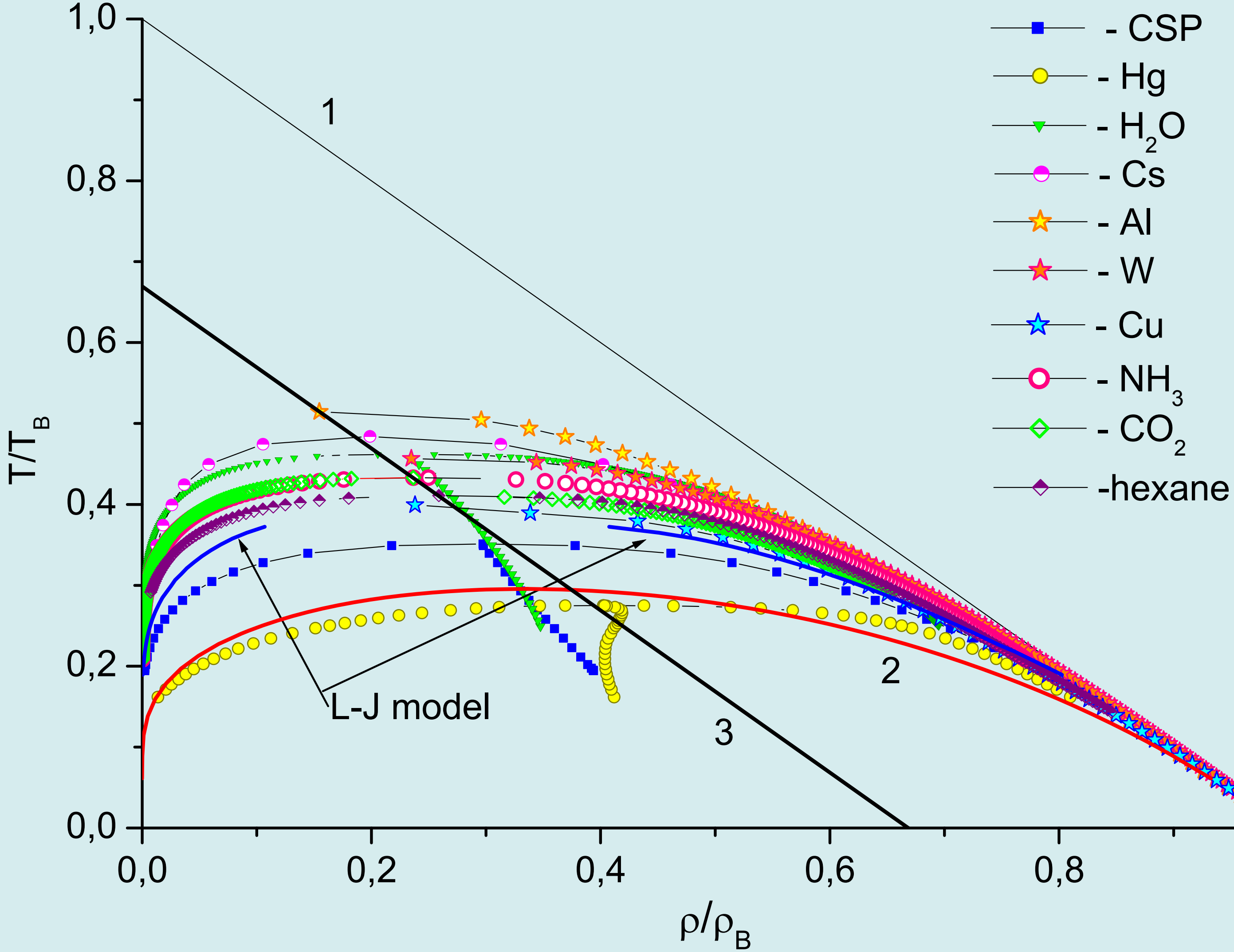
$$Z_c \le 0.32$$

Все классические вещества

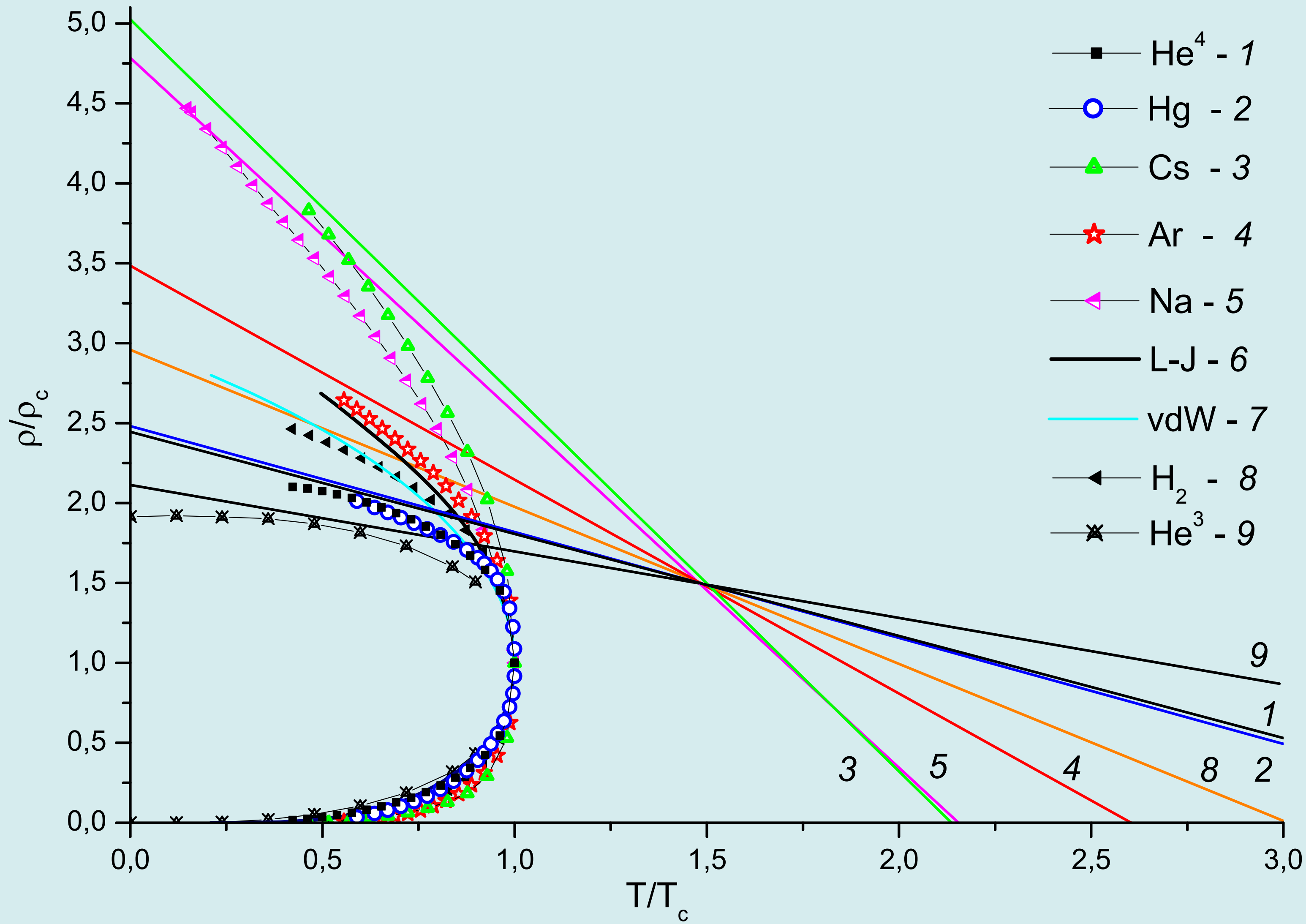
$$x_{1,2} = \frac{S_1}{2}\left[1 \pm \sqrt{1 - \frac{4S_3}{S_1^2 Z_c}}\right]$$

$$Z_c \text{ or } Z^* \ge 0.37$$

Ртуть и квантовые жидкости



1,0
0,8
0,6
0,4
0,2
0,0
T/T_B
0,0
0,2
0,4
0,6
0,8
1,0
ρ/ρ_B
1
2
3
L-J model
- CSP
- Hg
- H_2O
- Cs
- Al
- W
- Cu
- NH_3
- CO_2
-hexane



ρ/ρc
T/Tc
He4 - 1
Hg - 2
Cs - 3
Ar - 4
Na - 5
L-J - 6
vdW - 7
H2 - 8
He3 - 9
5,0
4,5
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0,0
0,5
1,0
1,5
2,0
2,5
3,0
9
1
3
5
4
8
2

Quantum Liquids

$$d_c = \left(T_c / P_c\right)^{1/3}$$ характерная длина

$$Z_c = P_c / \rho_c T_c = 1/\left(\rho_c d_c^3\right)$$

В квантовом случае

$$d_c^* \Rightarrow \left(\frac{T_c}{P_c\left(1+aB\right)}\right)^{1/3}$$

(Garrabos, J. Physique,1985)

De Boer parameter

$$B = h / \sigma\sqrt{2\pi m D}$$

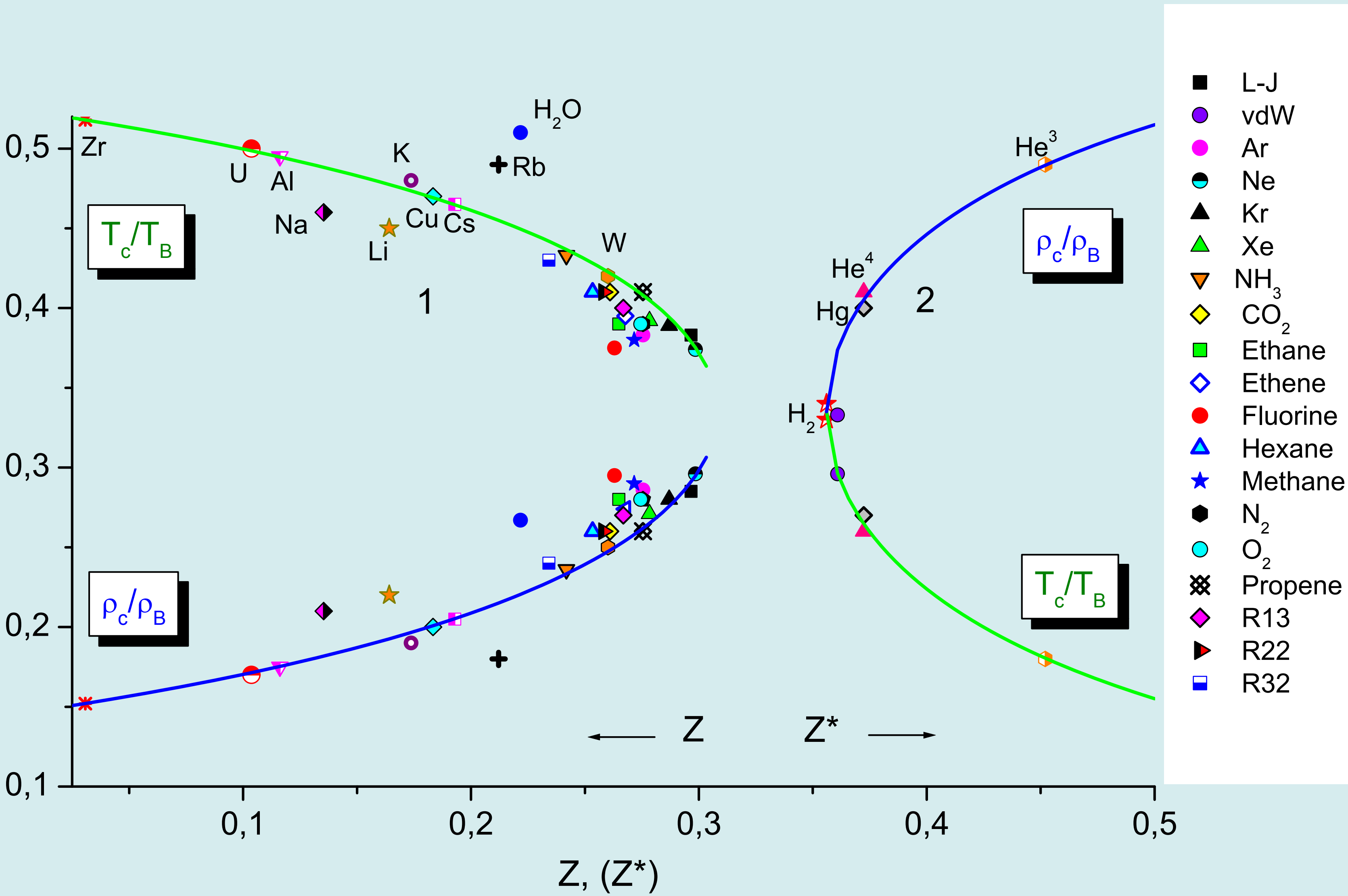
Quantum Liquids

De Boer parameter $B = h/\sigma\sqrt{2\pi m D}$

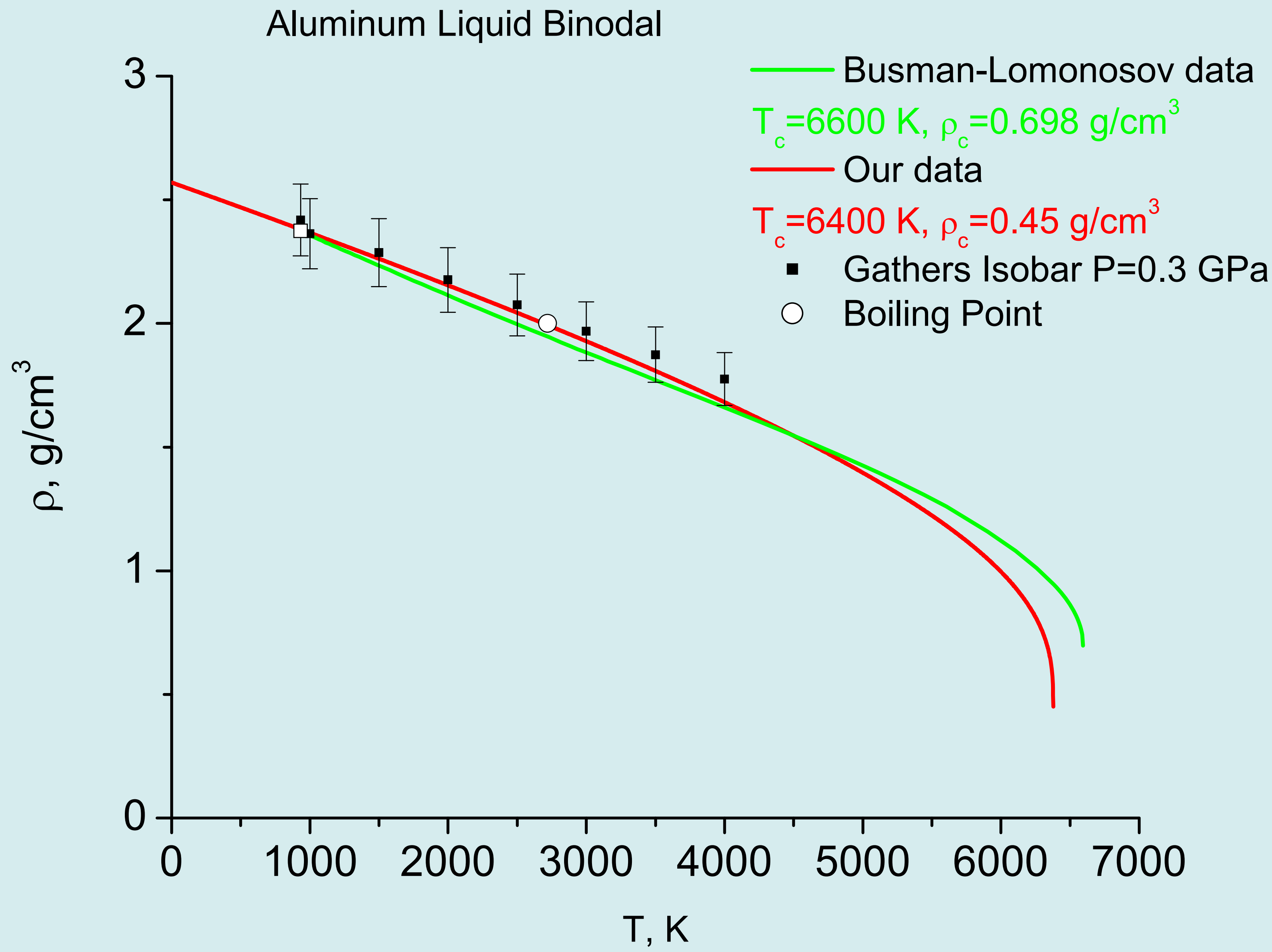
	Ar	Ne	D_2	H_2	He^4	He^3
B	0.069	0.217	0.452	0.78	0.99	1.76
Z_c	0.289	0.3	0.3	0.3	0.3	0.321
Z^*	0.293	0.319	0.34	0.37	0.386	0.48

Effective factor compressibility $Z^* = Z_c(1 + aB)$

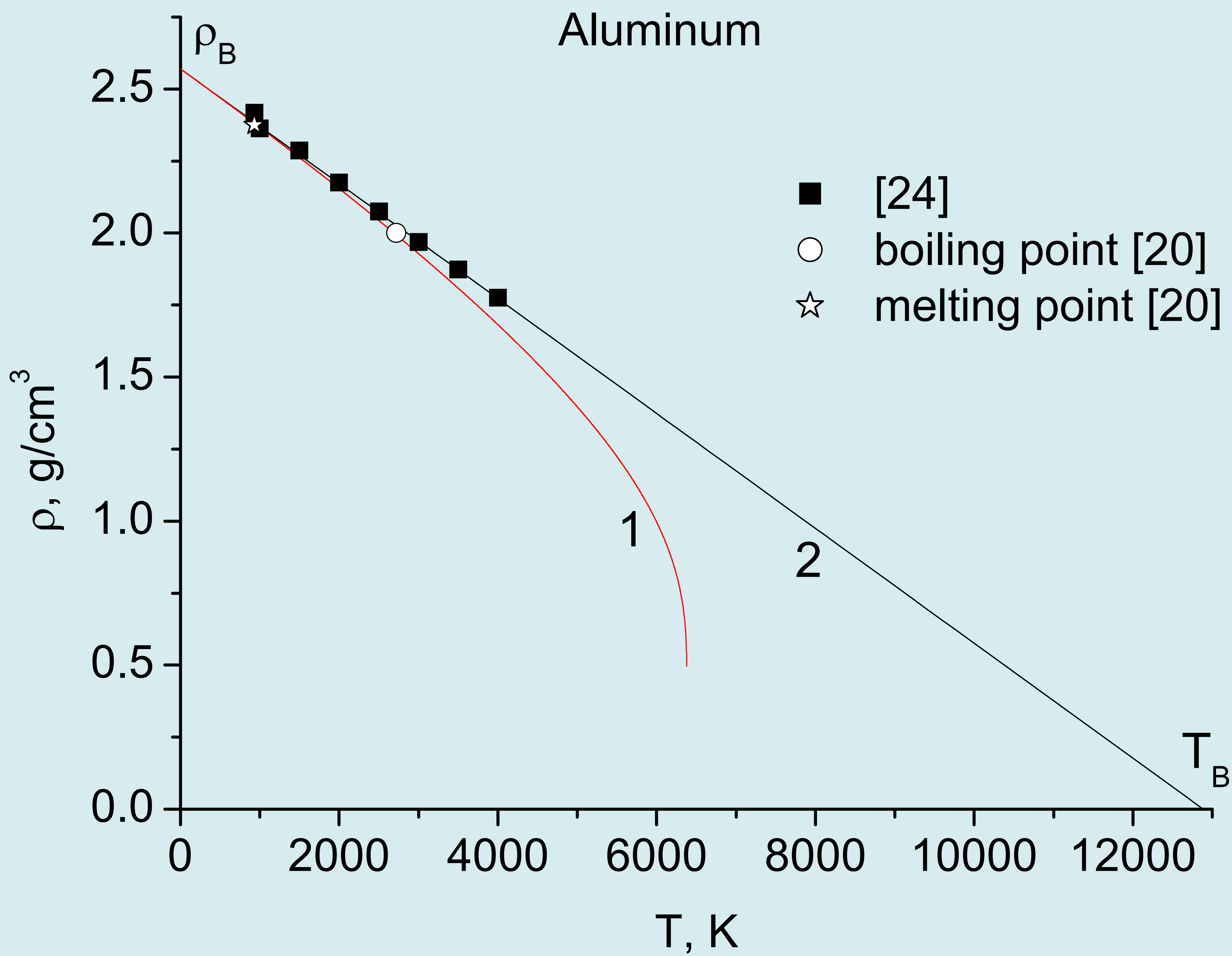
$Z_c(Hg) = Z^*(He^4)$.



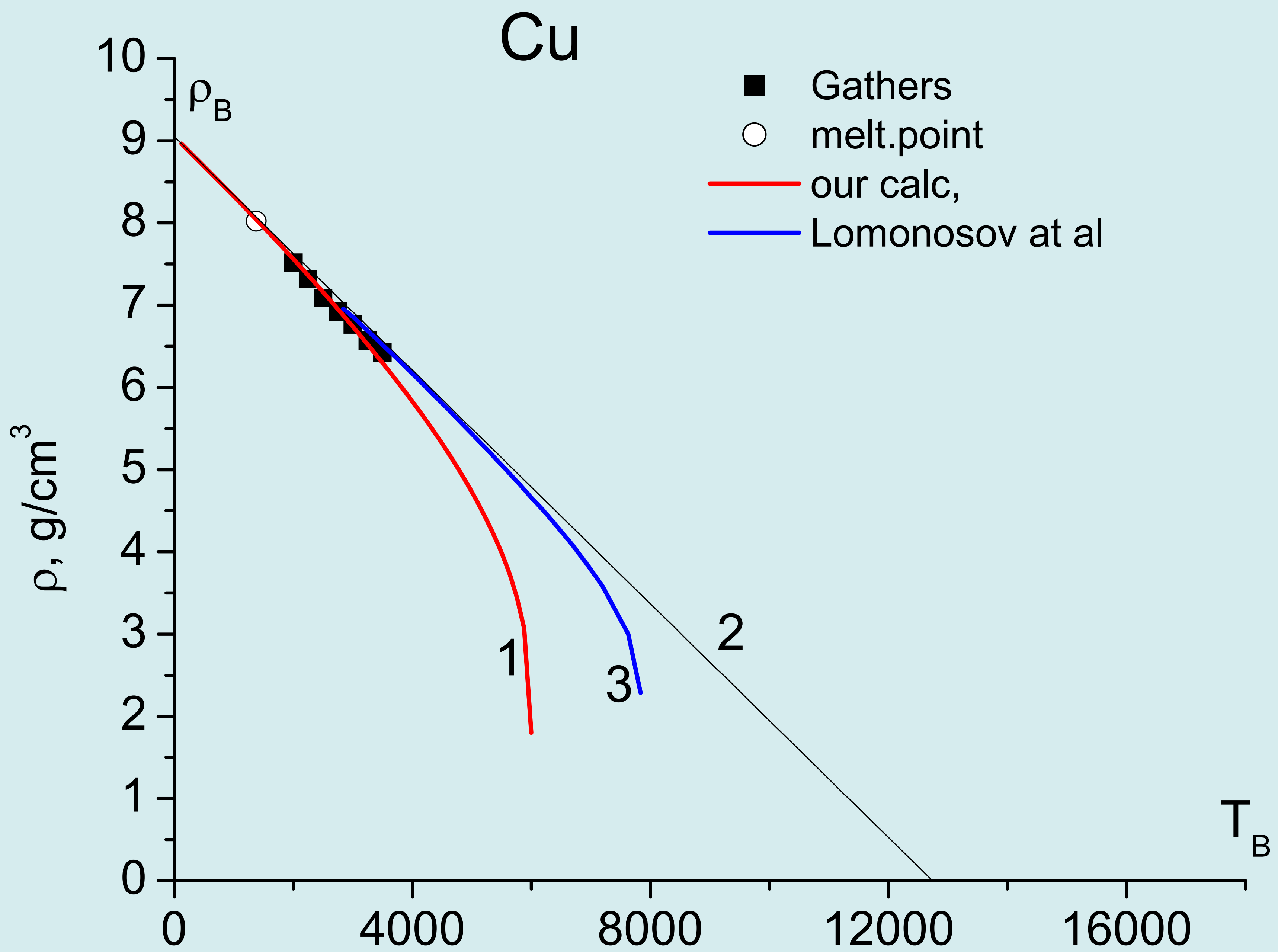
H2O
K
Rb
Zr
U
Al
Na
Cu
Cs
Li
W
1
2
He3
He4
Hg
H2
Tc/TB
ρc/ρB
ρc/ρB
Tc/TB
Z
Z*
0,1
0,2
0,3
0,4
0,5
Z, (Z*)
L-J
vdW
Ar
Ne
Kr
Xe
NH3
CO2
Ethane
Ethene
Fluorine
Hexane
Methane
N2
O2
Propene
R13
R22
R32



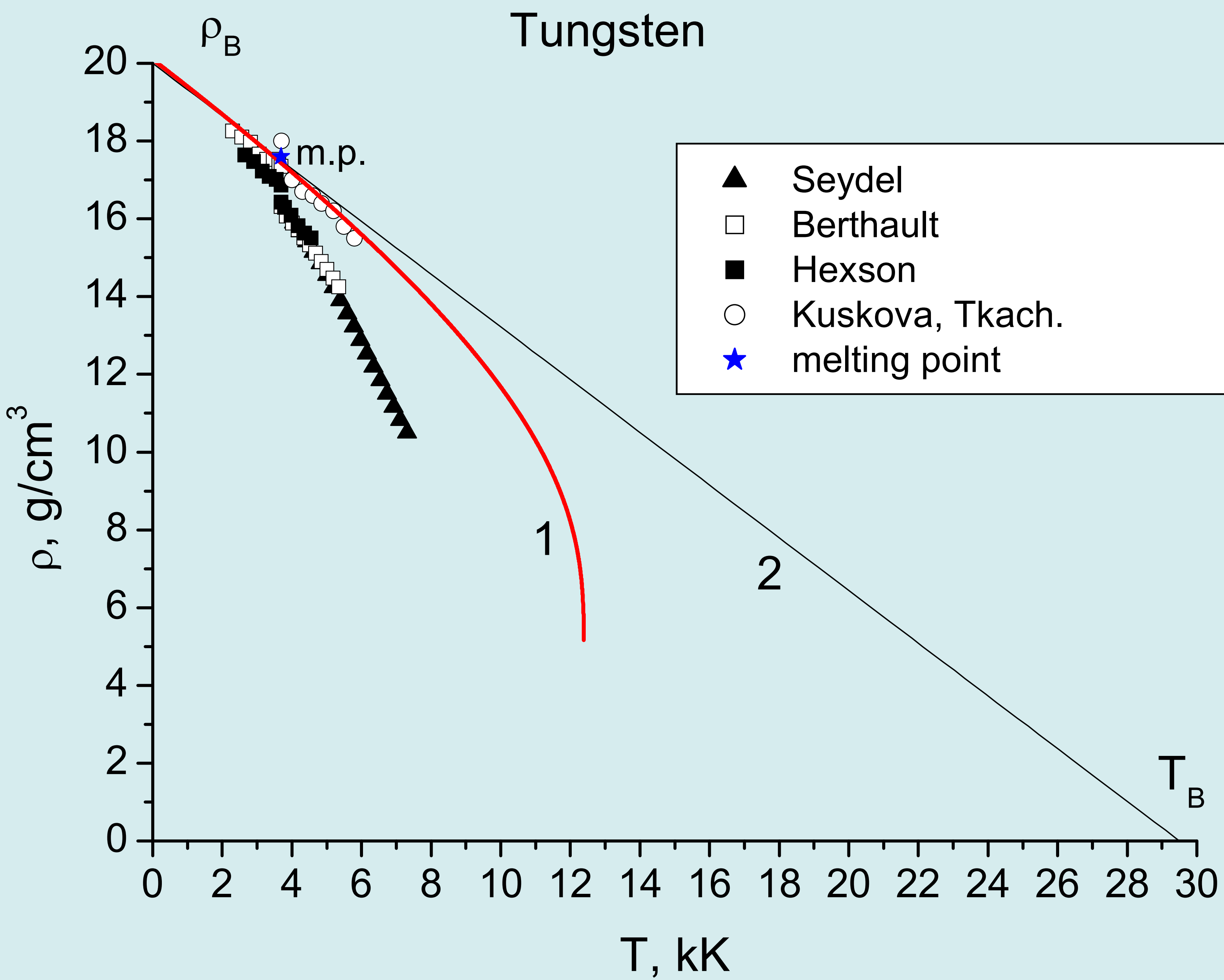
Aluminum Liquid Binodal
Busman-Lomonosov data
T_c=6600 K, ρ_c=0.698 g/cm^3
Our data
T_c=6400 K, ρ_c=0.45 g/cm^3
Gathers Isobar P=0.3 GPa
Boiling Point
ρ, g/cm^3
T, K
0
1
2
3
0
1000
2000
3000
4000
5000
6000
7000



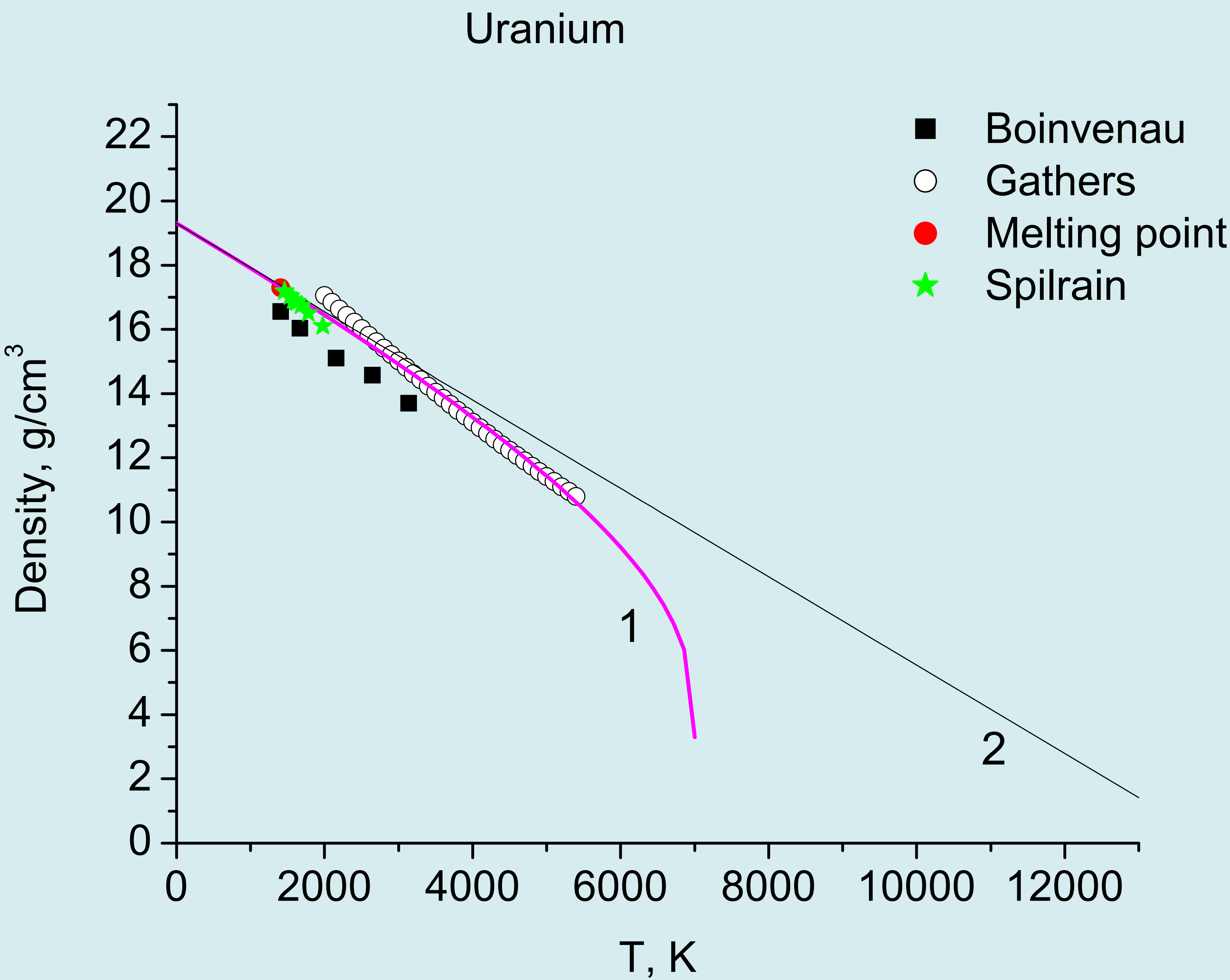
Aluminum
ρB
2.5
2.0
1.5
1.0
0.5
0.0
ρ, g/cm3
[24]
boiling point [20]
melting point [20]
1
2
TB
0
2000
4000
6000
8000
10000
12000
T, K

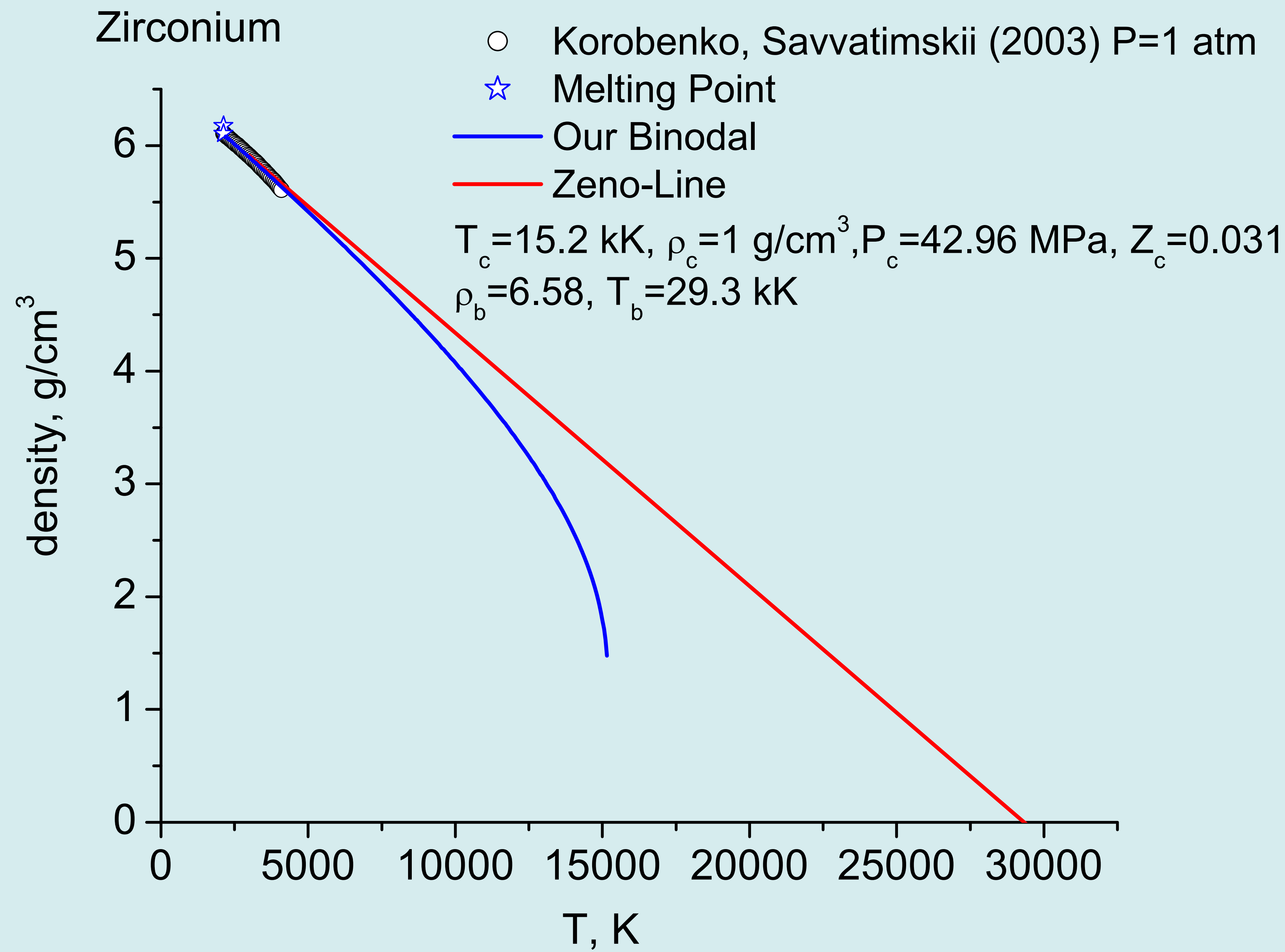


Cu
Gathers
melt.point
our calc,
Lomonosov at al
ρ_B
ρ, g/cm^3
T_B
1
2
3
0
1
2
3
4
5
6
7
8
9
10
0
4000
8000
12000
16000



Tungsten
ρ_B
m.p.
Seydel
Berthault
Hexson
Kuskova, Tkach.
melting point
1
2
T_B
ρ, g/cm^3
T, kK
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30


Uranium
Boinvenau
Gathers
Melting point
Spilrain
Density, g/cm^3
T, K
1
2
0
2
4
6
8
10
12
14
16
18
20
22
0
2000
4000
6000
8000
10000
12000


Zirconium
Korobenko, Savvatimskii (2003) P=1 atm
Melting Point
Our Binodal
Zeno-Line
T_c=15.2 kK, ρ_c=1 g/cm^3,P_c=42.96 MPa, Z_c=0.031
ρ_b=6.58, T_b=29.3 kK
density, g/cm^3
0
1
2
3
4
5
6
0
5000
10000
15000
20000
25000
30000
T, K

Metal	T_c, K	ρ_c, g/cm^3	Method	Ref.	T_B, K	ρ_B, g/cm^3	P_c, *atm*	Z_c
Al	**6378** 8860 8000	**0.45** 0.28 0.64	**this work** scaling Extrapol.	- Lik Fort.	**12890**	**2.57**	**1074** 4680 4470	**0.12** 0.60 0.28
Cu	**7093** 7620 8390	**1.95** 1.4 2.4	**this work** scaling extrapol	- Lik Fort.	**15600**	**8.6**	**4500** 5770 7460	**0.19** 0.39 0.28
W	**12390** 12500 14000	**4.92** 4.52 4.71	**this work** estimate estimate	- Boin. Seyd.	**29130**	**20.1**	**7450** 1100 5000	**0.27** 0.43 0.13
U	**7000** 9000 11630	**3.3** 2.6 5.3	this work estimate extrapol	 Lik. Fort	**14030**	**19.3**	**1710** 5000 6100	**0.11** 0.60 0.28
Zr	**15200**	**1**	**this work**		**29330**	**6.58**	**421**	**0.031**

Спасибо за внимание