New theoretical approach describing the pressure effect on the melting temperature

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HISTORY

- The effect of pressure on the melting temperature was detected by Perkinson in 1826. Compressing acetic acid [CH_3COOH] to 1100 Atm. he found that the substance became crystallized.
- Ever since then numerous effort has been made to describe the effect of pressure on the melting temperature. The current standing of the research is outlined here.

THEORETICAL DESCRIPTIONS

- Clapyeron describes the dp/dT slope of co-existing gas-liquid phase in 1834
- Clausius extends to liquid-solid phase in 1850, which is know as the Clausius-Clapyeron relationship

$$\frac{dp}{dT} = \frac{\Delta H_f}{T\Delta V} = \frac{\Delta S}{\Delta V}$$

- The Lindemann melting formula (1910) is

$$T_m = cMa^2\theta_D^2$$

$$a = \sqrt[3]{\frac{V_{mol}}{N_A}}$$

$$T_m = cV_m^{\frac{2}{3}}\theta_D^2$$

Primarily is used for atmospheric pressure because it is difficult to determine V_m and θ_D at high pressure and temperature.

- Simon and Glatzel (1929) proposed the formula:

$$\frac{p_m - p_o}{a} = \left(\frac{T_m}{T_o}\right)^c - 1$$

Successfully describes the p-Tm curves of many substances.

Kennedy (1965) shown that the equation does not give satisfactory melting temperature when extrapolated to core pressure

- Kraut-Kennedy (1965)

$$T_m = T_m^o \left(1 + C \frac{\Delta V}{V_o}\right)$$

$\Delta V/V_o$ is the isothermal dilation

They claimed that in case of iron the linear relationship is valid up to compression of 0.5

- Gilvarry (1965); Vaidya and Gopal (1965)

Using the Lindemann melting criteria is has been shown that

$$C = 2\left(\gamma - \frac{1}{3}\right)$$

- Libby (1966); Mukherjee (1966)

Assuming constant bulk modulus the Kraut-Kennedy relationship can be derived from the Claussius-Clapeyron relationship

$$T_m - T_m^0 = \frac{\Delta V_m}{T_m \Delta S_m} T_m^0 K_0 \frac{\Delta V}{V_0}$$

- Wang (1999) proposed a model and introduced a critical temperature which is equivalent with the melting temperature

Using the EoS and conventional thermodynamic relationships the critical volume relating to the critical temperature is calculated

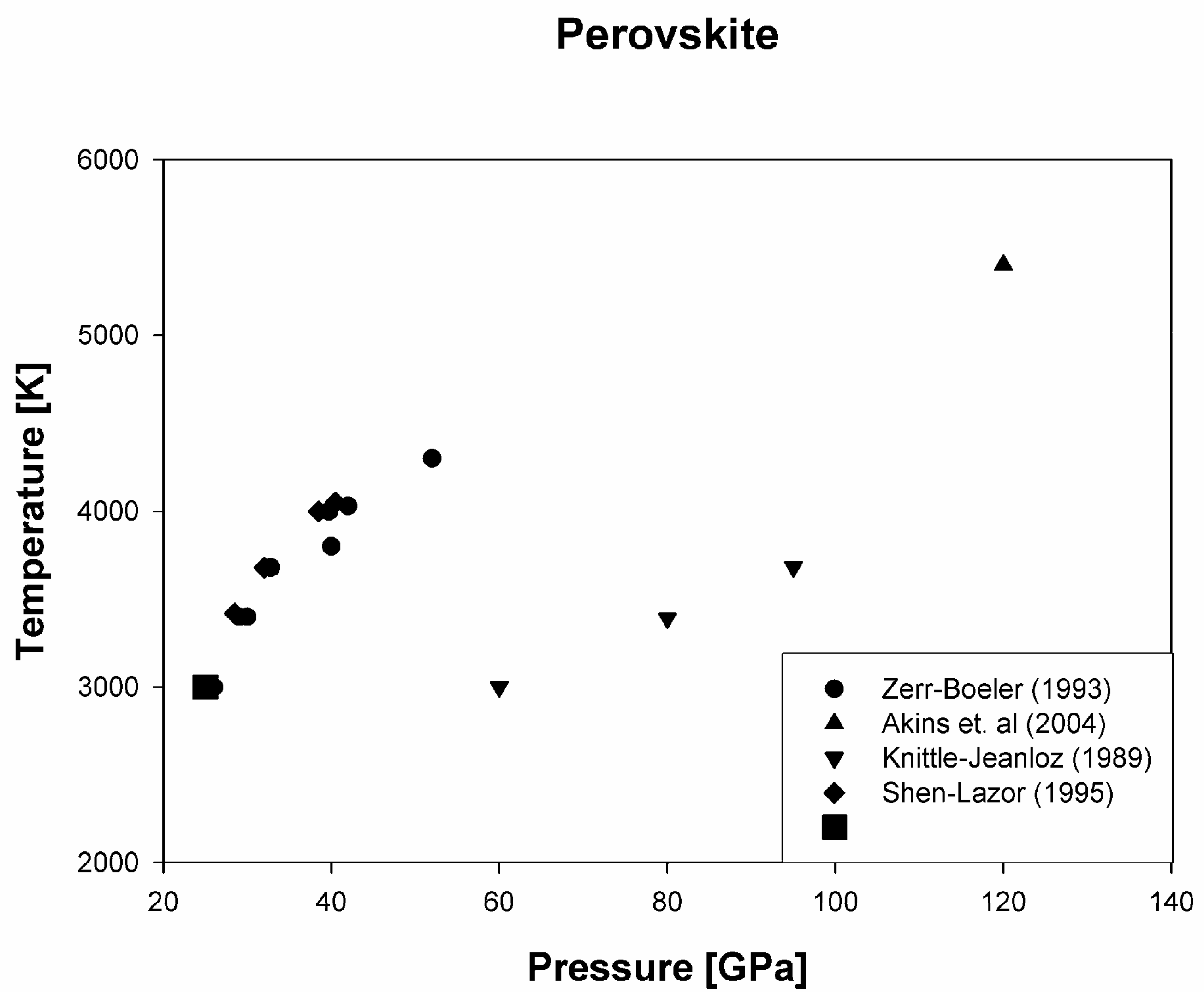
Deducting the thermal pressure from the actual pressure gives the pressure relating to the melting temperature

In all of the "theoretical" models the derived formulas contain a "fitting" parameter with no physical meaning.

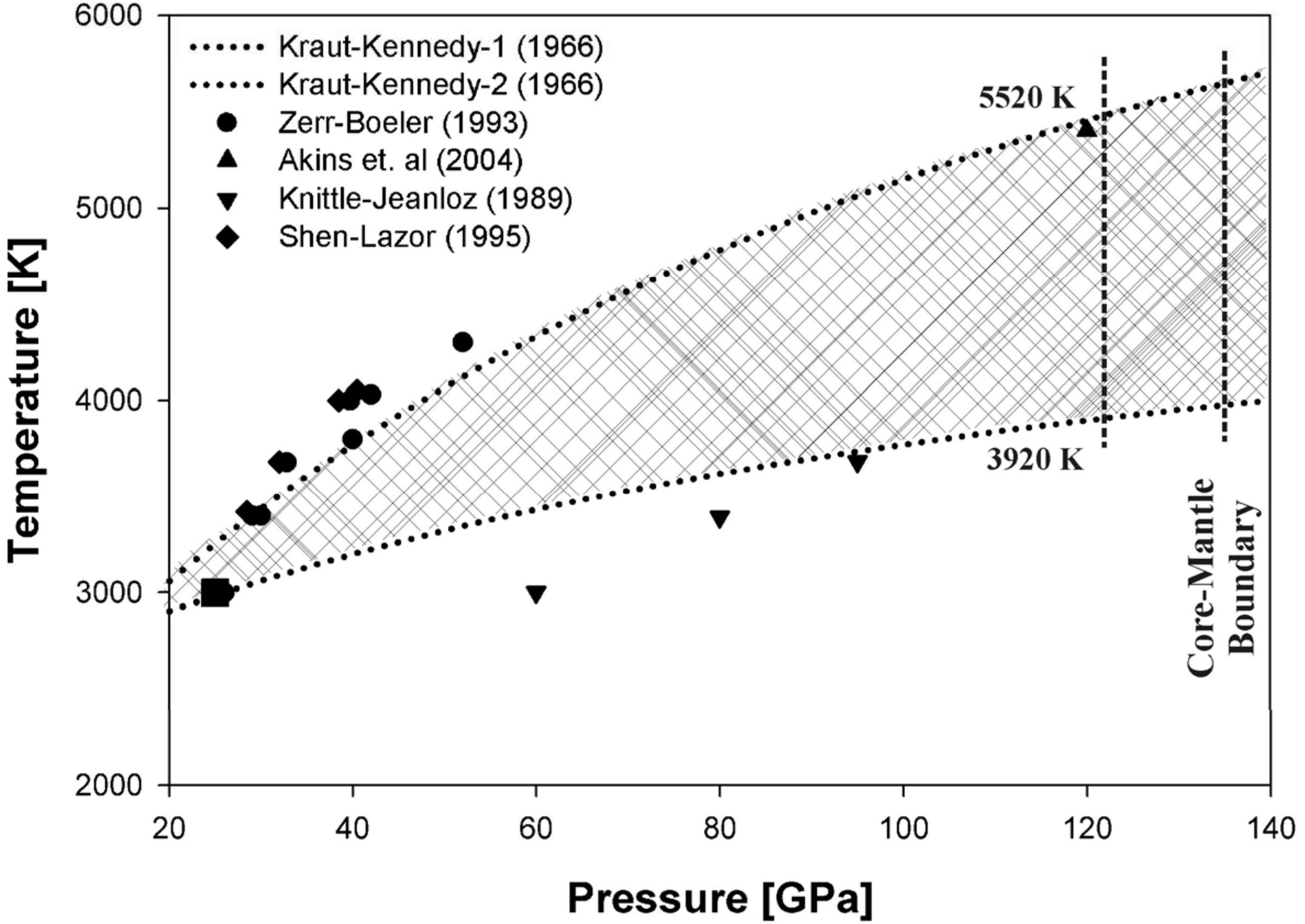
The descriptions therefore are semi empirical.

The uncertainties in the theoretical descriptions can be complemented by experiments.

Let’s do experiments!


Perovskite
Temperature [K]
Pressure [GPa]
6000
5000
4000
3000
2000
20
40
60
80
100
120
140
Zerr-Boeler (1993)
Akins et. al (2004)
Knittle-Jeanloz (1989)
Shen-Lazor (1995)

Perovskite



Kraut-Kennedy-1 (1966)
Kraut-Kennedy-2 (1966)
Zerr-Boeler (1993)
Akins et. al (2004)
Knittle-Jeanloz (1989)
Shen-Lazor (1995)
5520 K
3920 K
Core-Mantle Boundary
Temperature [K]
Pressure [GPa]
6000
5000
4000
3000
2000
20
40
60
80
100
120
140

Kavner & Jeanloz, 1998

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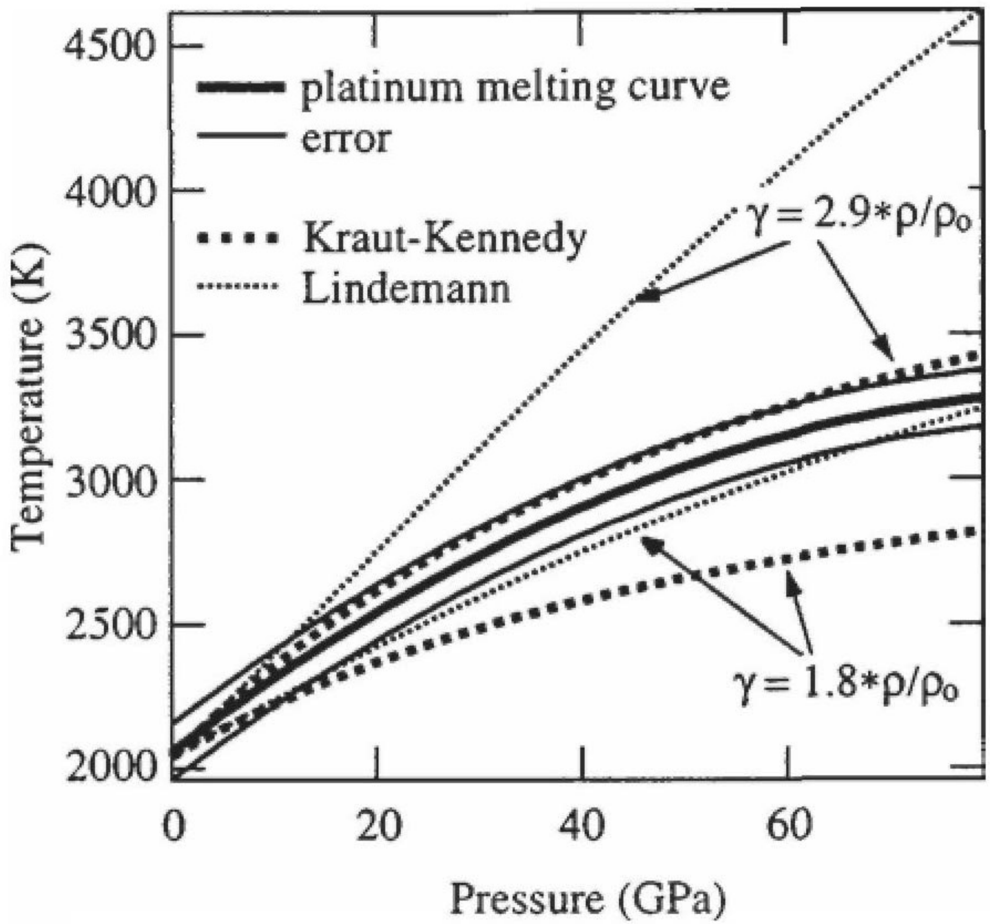
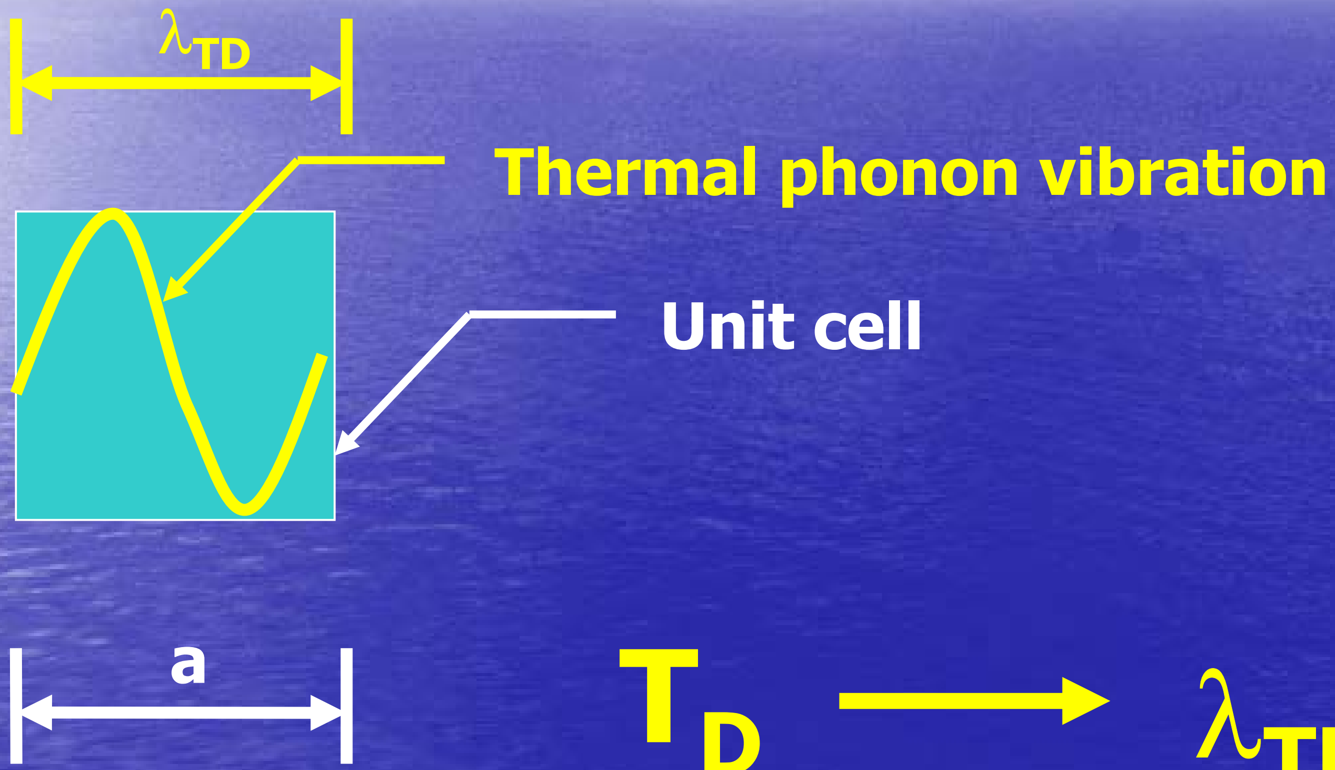


FIG. 6. Comparison of the melting curve determined here (bold solid line with solid line error envelope) with melting curves calculated using the Lindemann (narrow dotted line) and Kraut–Kennedy (bold dotted line) equations. Two curves for each are shown and are bounded by the experimentally determined range of values for the Grüneisen parameter, 1.8–2.9.

There is a need for a reliable theoretical model.

Background
of the proposed model

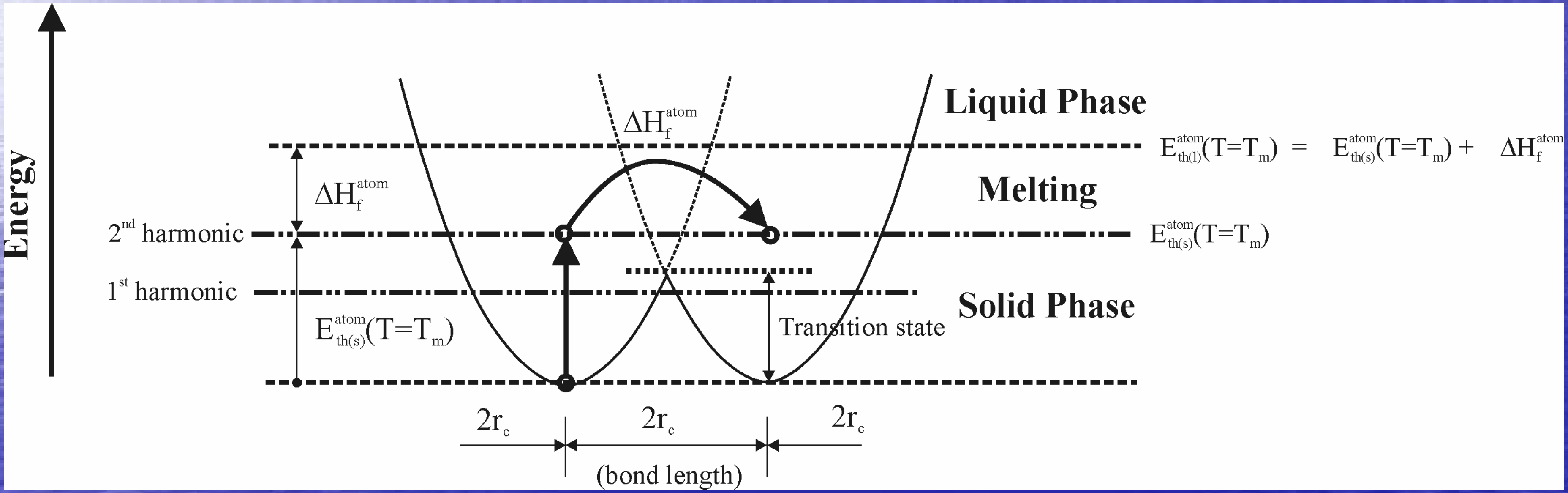
Physical explanation of the Debye temperature

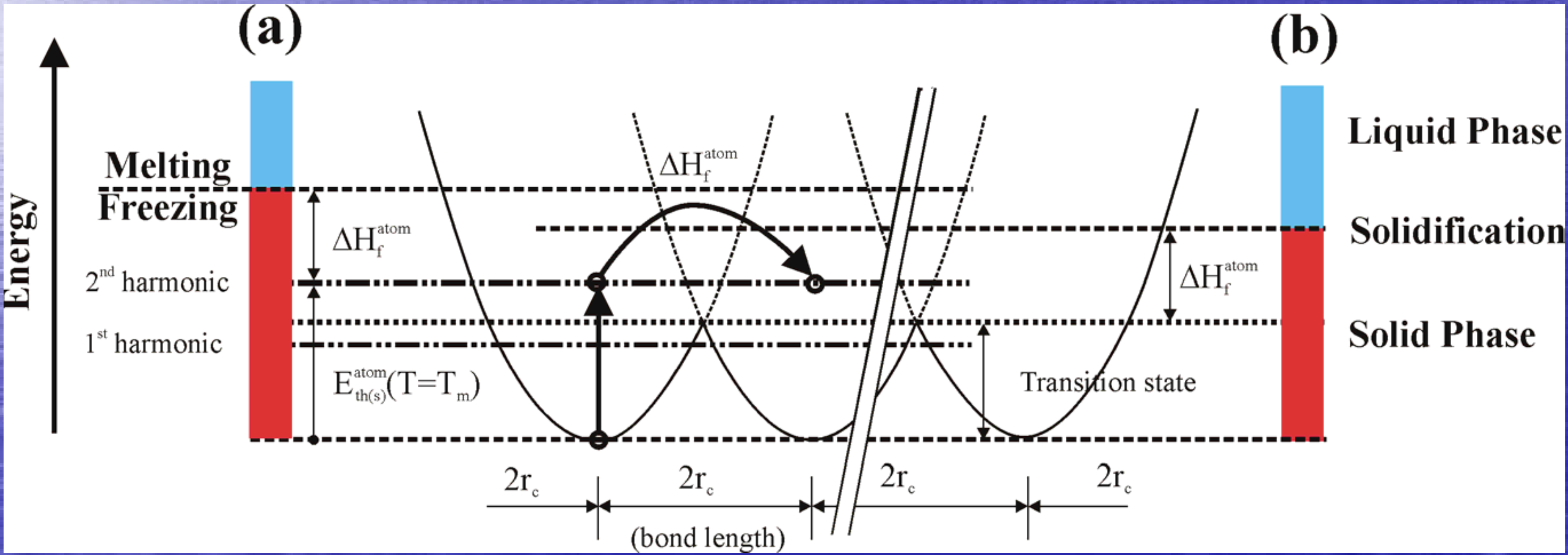


$$T_D \longrightarrow \lambda_{TD} = a$$

Element	Crystal Structure	Transverse Sound Velocity [$\times 10^3$ ms^{-1}]	Longitudinal Sound Velocity [$\times 10^3$ ms^{-1}]	Mean Sound Velocity [$\times 10^3$ ms^{-1}]	Debye Temperature [K]	Unit cell [Å]	Wavelength of the cut off frequency [Å]	Difference [%]
Ag	fcc	3.60	1.59	1.79	215	4.09[a]	4.01	2.1
Al	fcc	6.26	3.08	3.46	394	4.05[a]	4.21	4.0
Au	fcc	3.24	1.20	1.36	170	4.08[a]	3.84	5.7
Cu	fcc	4.70	2.26	2.54	315	3.61[a]	3.87	7.2
Ni	fcc	5.63	2.96	3.31	375	3.52[a]	4.24	20.3
Pb	fcc	2.16	0.70	0.80	88	4.05[a]	4.34	7.3
Pt	fcc	3.96	1.67	1.89	230	3.92[a]	3.94	0.5
Be	hcp	12.55	8.83	9.58	1031	3.58[c]	4.46	24.5
Mg	hcp	5.78	3.05	3.41	330	5.19[c]	4.96	4.5
Ti	hcp	6.33	3.11	3.49	380	4.68[c]	4.41	5.8
Zn	hcp	4.17	2.41	2.68	234	3.82[c]	5.49	43.6

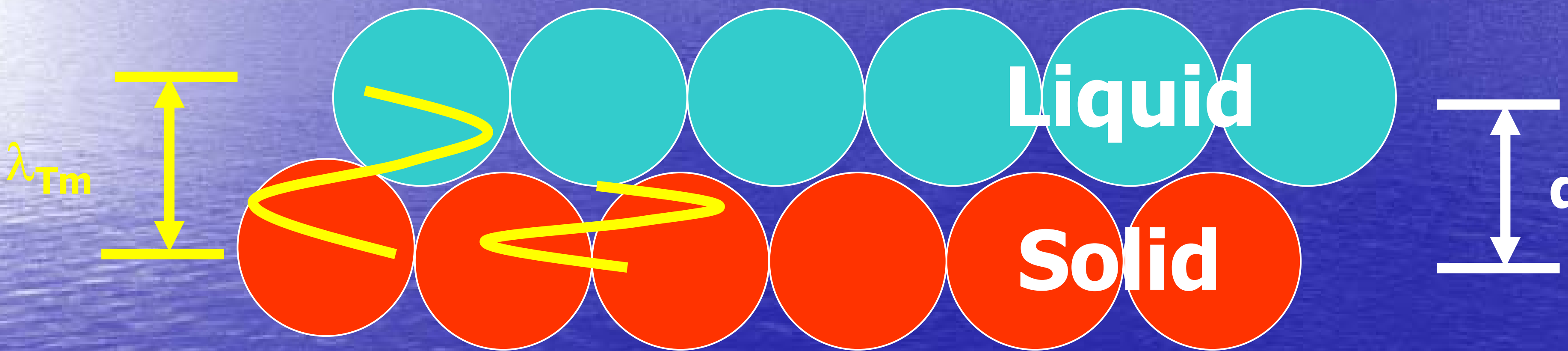
Physical explanation of melting

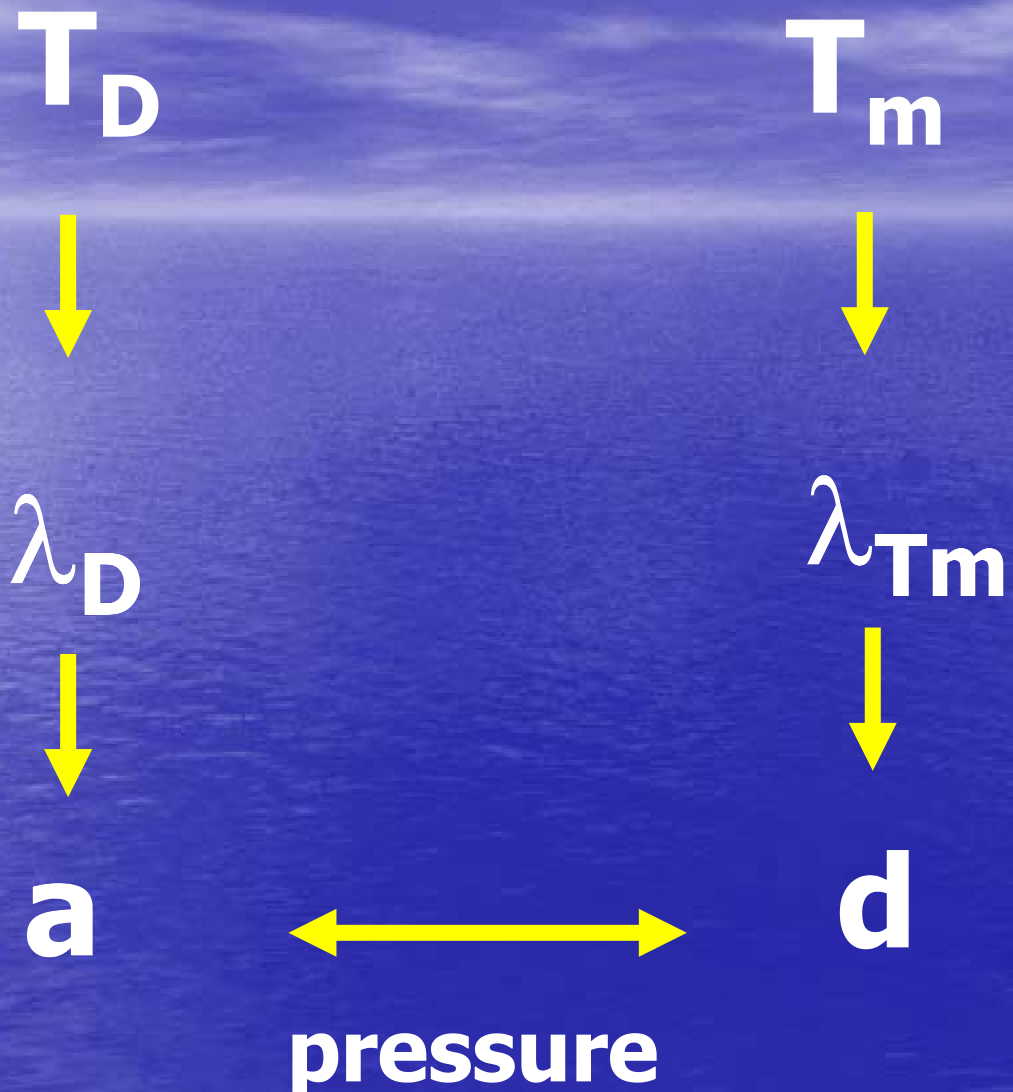




(a)
(b)
Energy
Melting
Freezing
2nd harmonic
1st harmonic
ΔH_f^atom
ΔH_f^atom
ΔH_f^atom
E_th(s)^atom(T=T_m)
Liquid Phase
Solidification
Solid Phase
Transition state
2r_c
2r_c
2r_c
2r_c
(bond length)

$$T_m \longrightarrow n\lambda_{Tm} = d$$





T_D
T_m
λ_D
λ_{Tm}
a
d
pressure

$$a/d = \text{const}$$

$$\lambda_D/\lambda_{Tm} = \text{const}$$

$$T_D/T_m = \text{const}$$

$$\downarrow$$

$$T_m = c\,T_D$$

Calculation

$$T_D = \frac{h}{k_B}\left[\frac{3n_A}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{\frac{1}{3}} v_B = 251.2\left(V_{Tm}\right)^{-\left(\frac{1}{3}\right)} v_{B(Tm)}$$

$$V = nV_o^m e^{\frac{-p}{ap+bp^2+K_o}+\left(\alpha_o+cp+dp^2\right)T+\left(1+\frac{cp+dp^2}{\alpha_o}\right)^f gT^2}$$

$$v_{B(Tm)} = \sqrt{\frac{V_{Tm}K_{Tm}(p)}{M_{mol}}}$$

$$p = \frac{3K_{0T}}{2}\left[\left(\frac{V_{0T}}{V}\right)^{\frac{7}{3}} - \left(\frac{V_{0T}}{V}\right)^{\frac{5}{3}}\right]\left\{1 + \frac{3}{4}\left(K_0^{'} - 4\right)\left[\left(\frac{V_{0T}}{V}\right)^{\frac{2}{3}} - 1\right]\right\}$$

$$V_{0T} = V_o e^{(\alpha_o + \alpha_1 T)T}$$

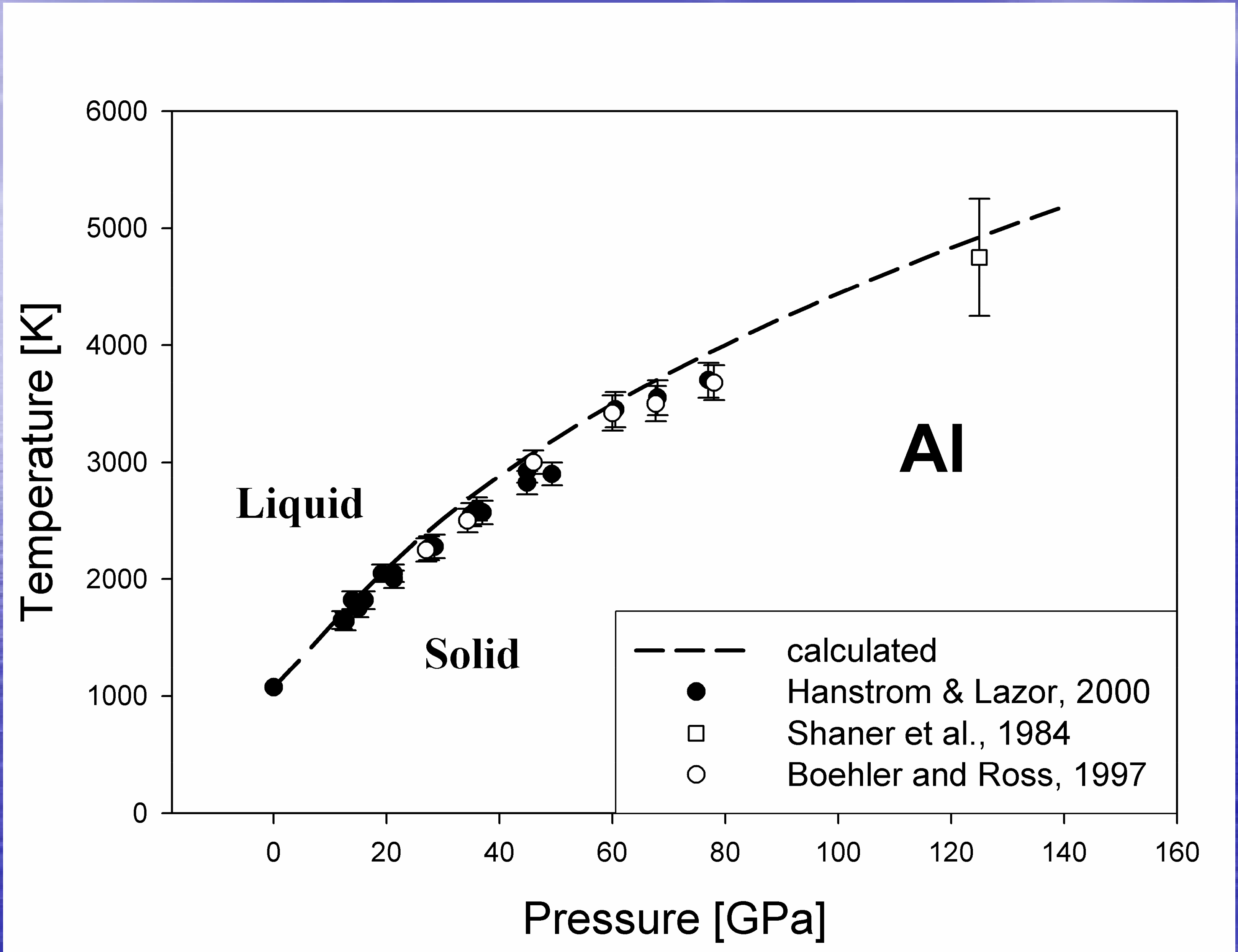
$$K_{0T} = K_o e^{-\int_{T=0}^{T=T} \alpha(T)\delta dT} \cong K_o e^{-(\alpha o + \alpha_1 T)\delta T}$$

$$K_{p,T} = K_o e^{-(\alpha_o + \alpha_1 T)\delta T} + K_o^{'} p$$

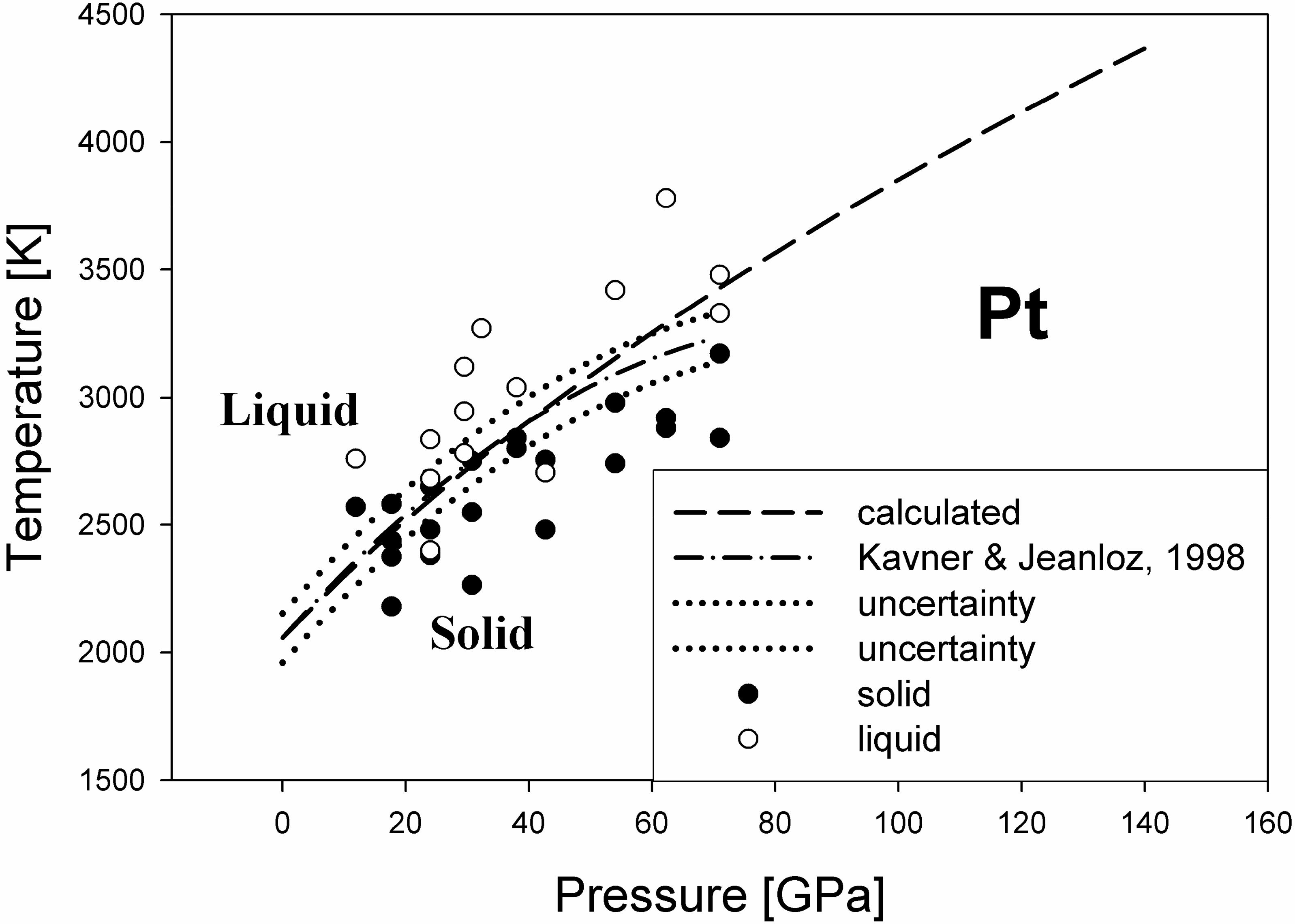
ThermalVolume	V_o [cm^3]	K_o [GPa]	α_o $[\times 10^{-5} K^{-1}]$	a	b $[\times 10^{-3}]$	c $[\times 10^{-7}]$	d $[\times 10^{-10}]$	g $[\times 10^{-9}]$	f
Al	9.804	100.00	1.184	1.983	-3.145	-0.820	0	10.24	44.5
Pt	9.041	282.42	1.554	2.234	-3.375	-0.283	0	8.631	38.2
MgO	11.149	164.95	2.737	1.717	-2.126	-1.502	2.00	7.901	12.0
$MgSiO_3$	24.287	272.5	1.96	1.384	1.430	-1.08	0	0.614	1.0
εFe	6.701	171.05	4.029	1.847	-1.276	-0.621	0	-5.087	0.49

Bulk Modulus	K_o [GPa]	K_o'	α_o x10^{-5}	α_1 x10^{-9}	δ
Al	91.00	3.70	7.650	37.657	12.39
Pt	254.65	6.030	1.750	5.520	4.737
MgO	154.70	4.212	3.317	6.705	3.549
$MgSiO_3$	206.79	4.160	2.591	-0.802	3.149
εFe	155.41	5.577	5.577	0	2.623

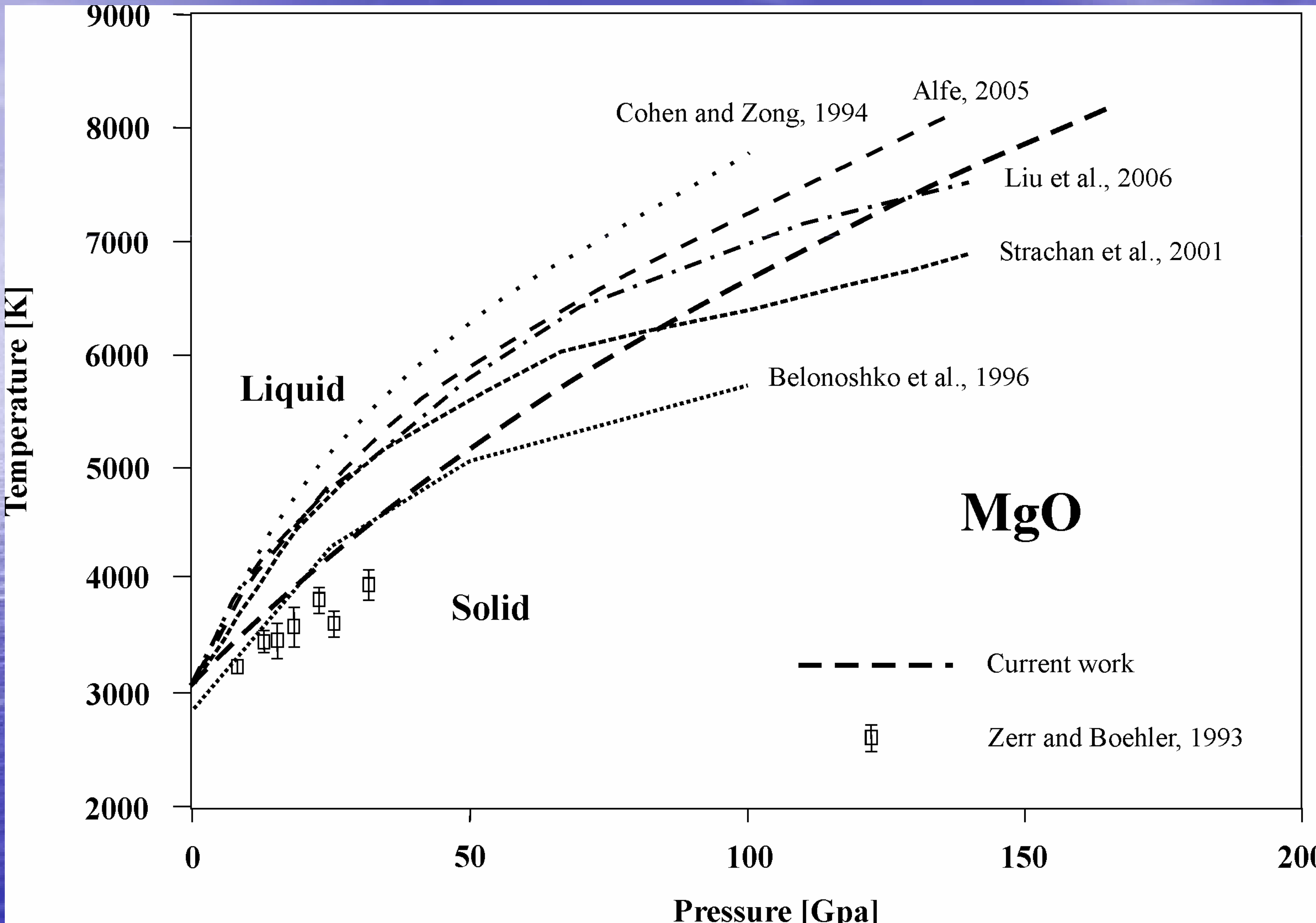
Results

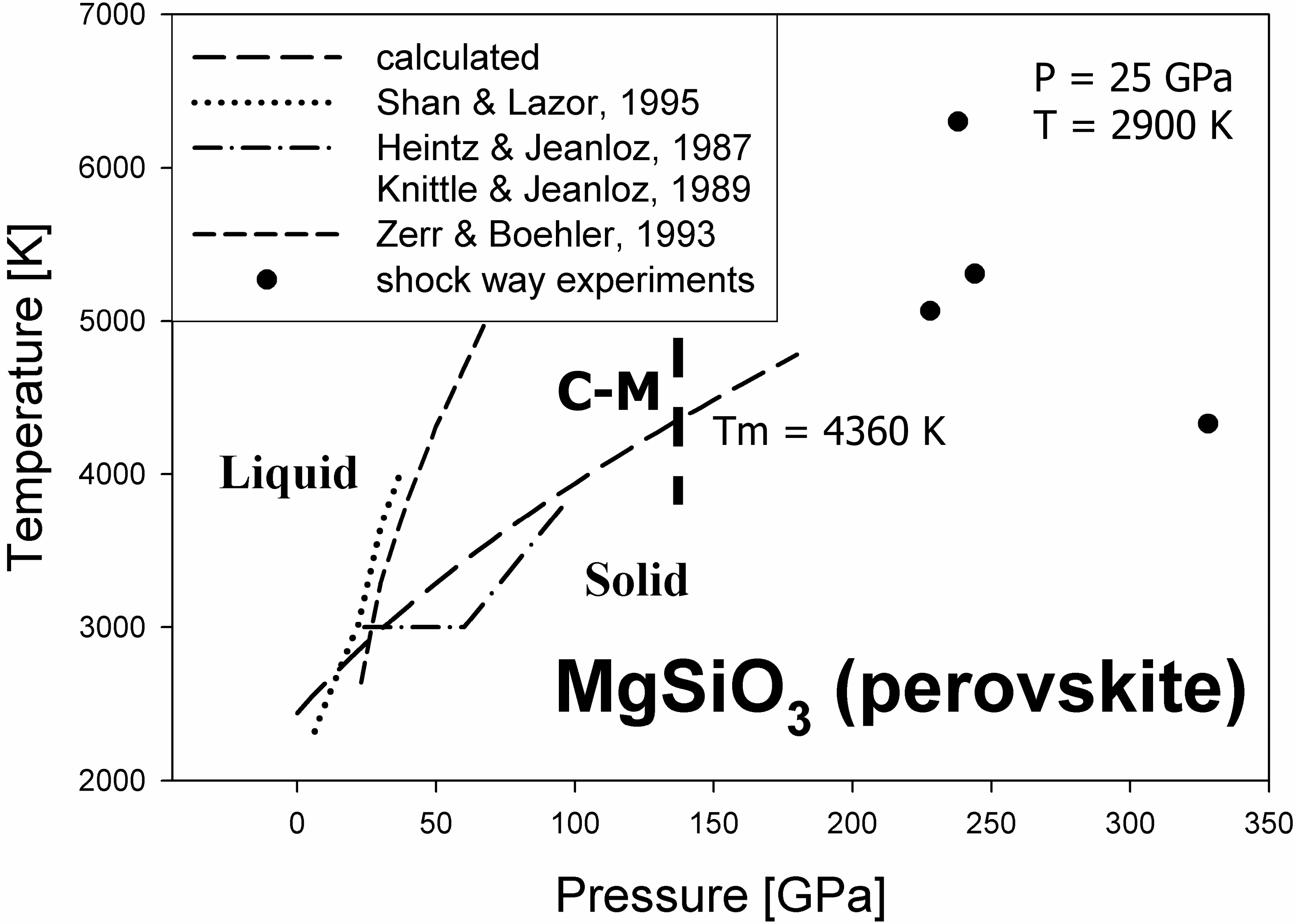


6000
5000
4000
3000
2000
1000
0
Temperature [K]
0
20
40
60
80
100
120
140
160
Pressure [GPa]
Liquid
Solid
Al
calculated
Hanstrom & Lazor, 2000
Shaner et al., 1984
Boehler and Ross, 1997

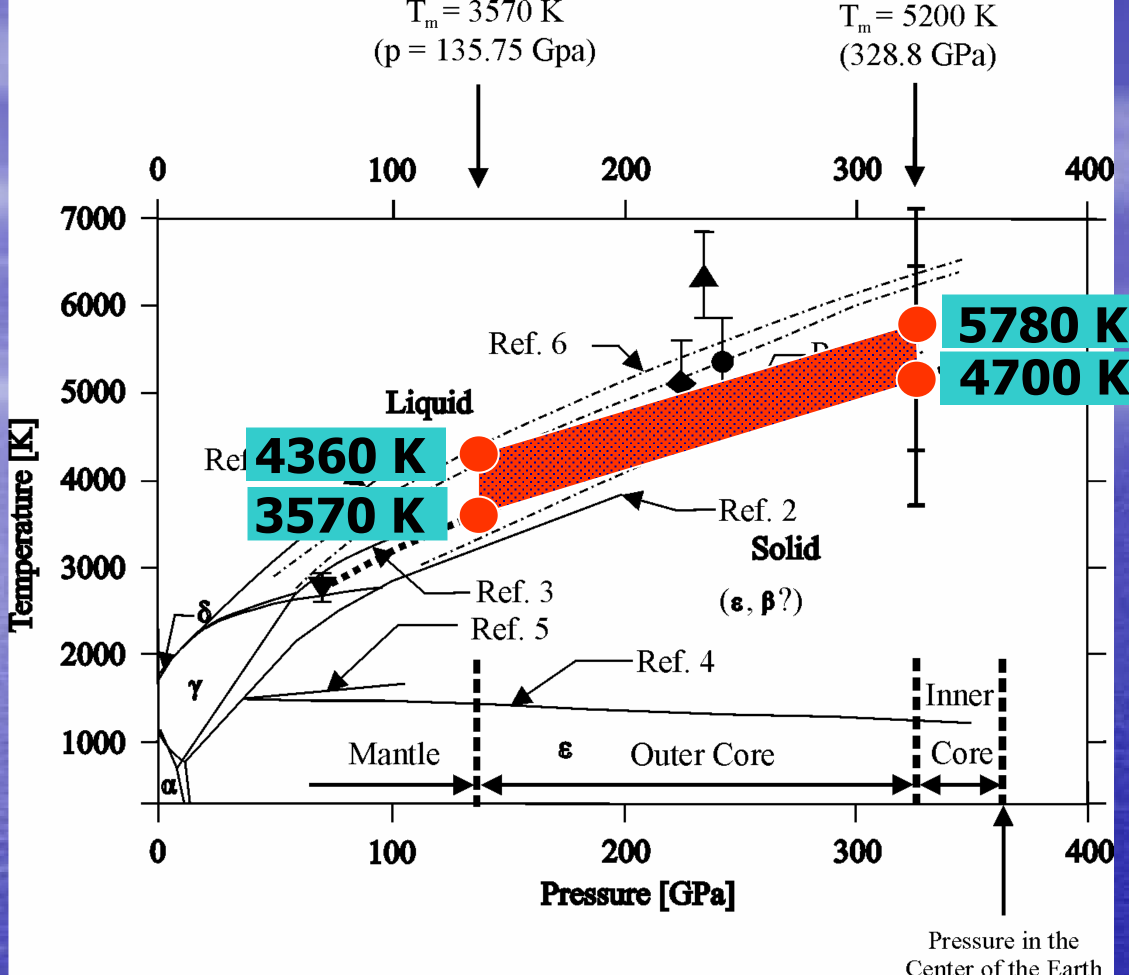


Pt
Liquid
Solid
Temperature [K]
Pressure [GPa]
4500
4000
3500
3000
2500
2000
1500
0
20
40
60
80
100
120
140
160
calculated
Kavner & Jeanloz, 1998
uncertainty
uncertainty
solid
liquid


9000
8000
7000
6000
5000
4000
3000
2000
Temperature [K]
0
50
100
150
200
Pressure [Gpa]
Cohen and Zong, 1994
Alfe, 2005
Liu et al., 2006
Strachan et al., 2001
Belonoshko et al., 1996
Liquid
Solid
MgO
Current work
Zerr and Boehler, 1993



calculated
Shan & Lazor, 1995
Heintz & Jeanloz, 1987
Knittle & Jeanloz, 1989
Zerr & Boehler, 1993
shock way experiments
P = 25 GPa
T = 2900 K
C-M
Tm = 4360 K
Liquid
Solid
MgSiO3 (perovskite)
Temperature [K]
7000
6000
5000
4000
3000
2000
0
50
100
150
200
250
300
350
Pressure [GPa]



Solid lines DAC experiments, dashed curves are calculated.
1 Williems et. Al. (1987)
2 Boehler (1993)
3 Shen et al. (1998)
4 Saxena-Dubrovinsky (2000)
5 Andrault et al. (2000)
6 Alfe et al. (2002)
7 Laio et al. (2000)
Triangle Yoo et al. (1995)
Circle Brown-McQueen (1986)
Reverse Triangle Ahrens et al. (2002)
Diamond Nguyen-Holmes (2005)
Open circles temperature from EoS

P = 72 GPa

T = 2800 K

Conclusions

- First principle theoretical description of the pressure-melting temperature relationship is proposed.
- Assuming that the ratio of the thermal phonon wavelength at the melting and Debye temperature is constant and using the conventional thermodynamic relationships, equation describing the pressure effect on the melting temperature, is derived.
- The equation is tested against the experiments of Al, Pt, MgO, MgSiO3 and epsilon Fe with positive results.
- If the boundary conditions are known and the EoS of the substance is available then the p-Tm curve can be calculated.
- From the melting temperatures and EoSs the proposed constrains on the geotherm are:

  CMB: 3570-4360 K and ICB: 4700-5780 K.

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