Phase transformations of ice and water at high pressures and temperatures

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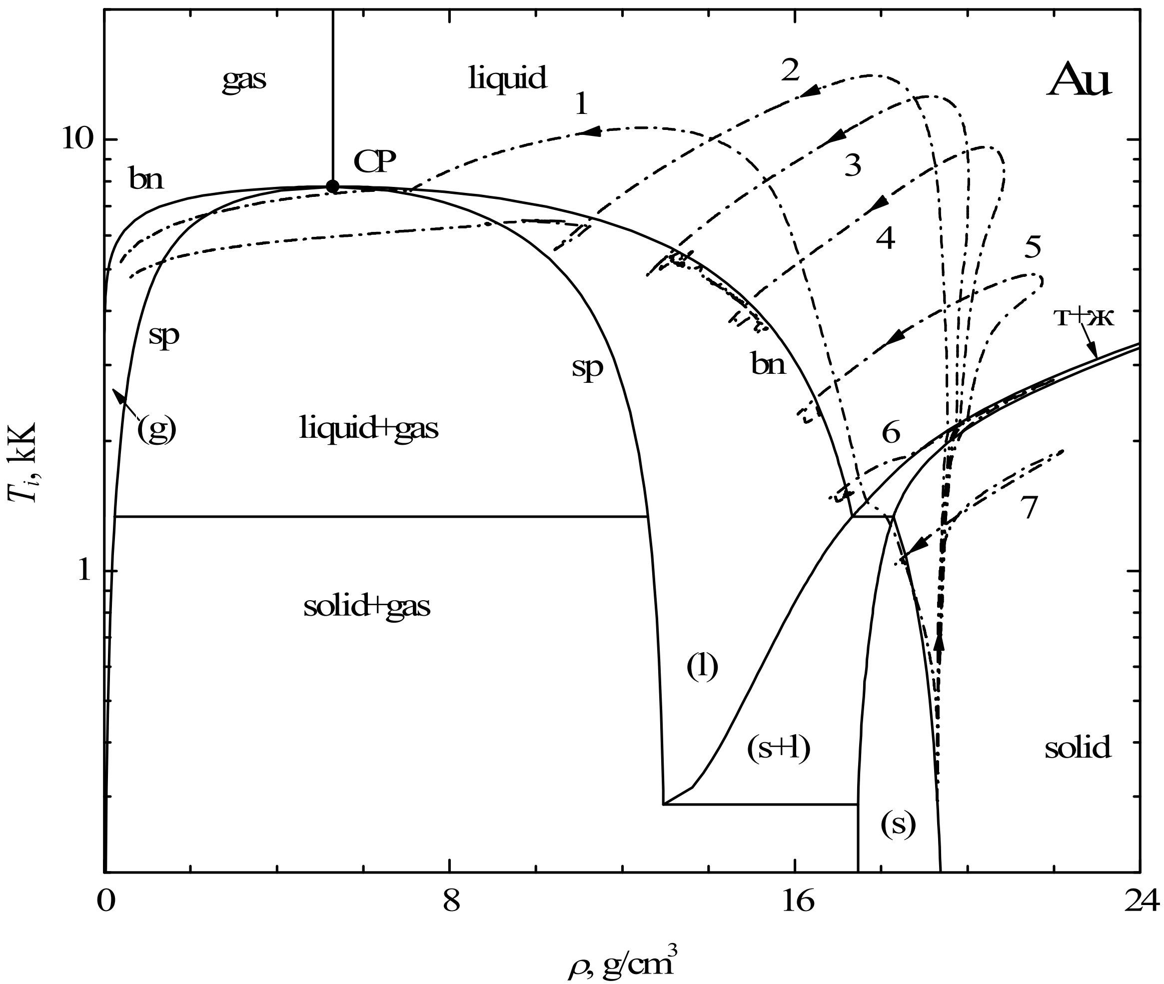
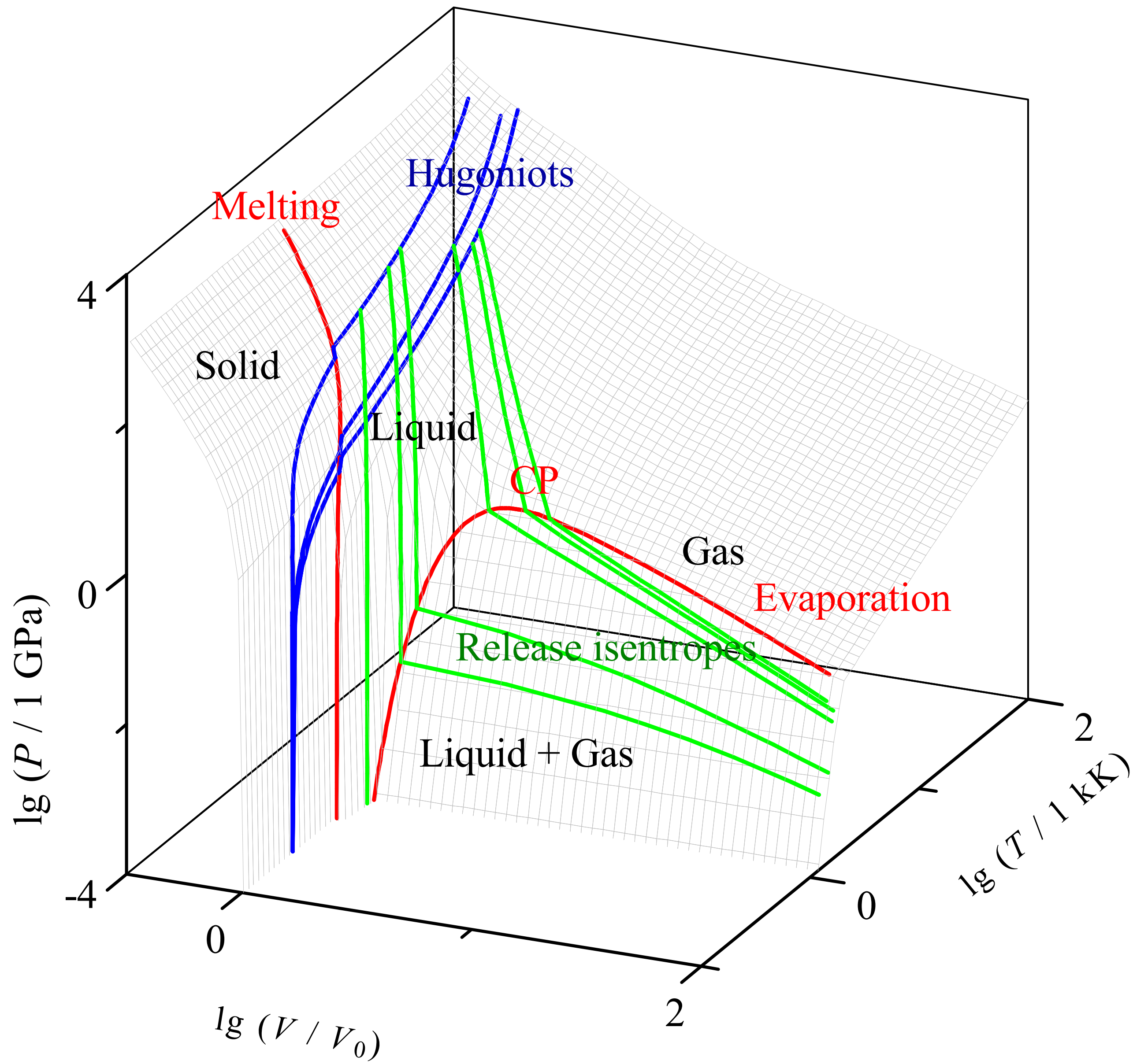
Phase diagram of a material under ultrashort laser irradiation



Mikhail E. Povarnitsyn, Pavel R. Levashov, and Konstantin V. Khishchenko, Implementation of kinetics of phase transitions into hydrocode for simulation of laser ablation, Proceedings of SPIE 7005 (2008)

Pressure versus volume and temperature for zinc



Equation of State Modeling

Equation of State Model

General form

$$F(V,T) = F_c(V) + F_a(V,T) + F_e(V,T)$$

Solid phase. Elastic component (EOS at *T* = 0 K)

at $V < V_{0c}$:

$$F_c(V) = 3V_{0c}\sum_{i=1}^{2}\frac{a_i}{i}\left(\sigma_c^{i/3} - 1\right) - 3V_{0c}\sum_{i=1}^{3}\frac{b_i}{i}\left(\sigma_c^{-i/3} - 1\right) + b_0 V_{0c}\ln\sigma_c$$

at $V > V_{0c}$:

$$F_c(V) = V_{0c}\left[A\left(\sigma_c^m/m - \sigma_c^n/n\right) + B\left(\sigma_c^l/l - \sigma_c^n/n\right)\right] + E_{sub}$$

at $V = V_{0c}$:

$$\sigma_c = V_{0c}/V$$

$$F_c(V_{0c}) = F_{0c}$$

$$P_c(V_{0c}) = -dF_c/dV = 0$$

$$B_c(V_{0c}) = -VdP_c/dV = B_{0c}$$

$$B_c'(V_{0c}) = dB_c/dP_c = B_{0c}'$$

$$B_c''(V_{0c}) = -d(V\,dB_c/dV)/dB_c = B_{0c}''$$

Equation of State Model

General form

$$F(V,T) = F_c(V) + F_a(V,T) + F_e(V,T)$$

Solid phase. Thermal lattice components

$$F_a(V,T) = F_a^{acst}(V,T) + \sum_{\alpha=1}^{3(\nu-1)} F_{a\alpha}^{opt}(V,T)$$

$$F_a^{acst}(V,T) = \frac{RT}{\nu}\left[3\ln\left(1 - e^{-\theta^{acst}/T}\right) - D\left(\theta^{acst}/T\right)\right] - \beta_{acst}\frac{T^2/\theta^{acst}}{e^{\theta^{acst}/T} - 1}$$

$$F_{a\alpha}^{opt}(V,T) = \frac{RT}{\nu}\ln\left(1 - e^{-\theta_\alpha^{opt}/T}\right) - \beta_{opt\alpha}\frac{T^2/\theta_\alpha^{opt}}{e^{\theta_\alpha^{opt}/T} - 1}$$

$$D(x) = \frac{3}{x^3}\int_0^x \frac{t^3 dt}{e^t - 1}$$

$$\frac{\theta^{acst}(V)}{\theta_0^{acst}} = \frac{\theta_\alpha^{opt}(V)}{\theta_{0\alpha}^{opt}} = \sigma^{2/3}\exp\left\{(\gamma_0 - 2/3)\frac{\sigma_n^2 + \ln^2\sigma_m}{\sigma_n}\,\mathrm{arctg}\left[\frac{\sigma_n \ln\sigma}{\sigma_n^2 - \ln(\sigma/\sigma_m)\ln\sigma_m}\right]\right\}$$

Equation of State Model

General form

$$F(V,T) = F_c(V) + F_a(V,T) + F_e(V,T)$$

Fluid phase. Elastic component (EOS at *T* = 0 K)

at $V < V_{m0}$:

$$F_c^{(l)}(V) = F_c^{(s)}(V) + 3RT_{m0}\frac{2\sigma_m^2}{1+\sigma_m^3}\left[\frac{3A_m}{5}\left(\sigma_m^{5/3}-1\right)+C_m\right]$$

at $V_{m0} < V < V_{cr}$:

$$F_c^{(l)}(V) = F_c^{(s)}(V) + V_{m0}\sum_{i=1}^{7}\frac{a_{mi}}{\alpha_{mi}}\left(\sigma_m^{\alpha_{mi}}-1\right)+E_{m0}$$

$$\sigma_m = V_{m0}/V$$

at $V_{cr} < V$:

$$F_c^{(l)}(V) = F_c^{(s)}(V) + 3V_{cr}\sigma_V\sum_{i=1}^{3}\frac{b_{mi}}{i}\left(\sigma_V^{i/3}-1\right)$$

$$\sigma_V = V_{cr}/V$$

Equation of State Model

General form

$$F(V,T) = F_c(V) + F_a(V,T) + F_e(V,T)$$

Fluid phase. Thermal atomic components

$$F_a(V,T) = C_a(V,T)T\ \ln\left(1 - e^{-\theta^{liq}/T}\right) + 3RT\,\frac{B_m}{D_m + \left(\theta^{liq}/T\right)^{\alpha_m}}$$

$$C_a(V,T) = \frac{3}{2}R\left[2 - \frac{1}{1 + \theta^{liq}/T}\right]$$

$$\theta^{liq}(V,T) = T_{sa}\sigma^{2/3}\left[\theta_l(V) + \frac{1 - \theta_l(V)}{1 + \sqrt{T_{ca}\sigma_m^{2/3}/T}}\right]$$

$$\frac{\theta_l(V)}{\theta_{0l}} = \exp\left\{(\gamma_{0l} - 2/3)\frac{B_l^2 + D_l^2}{B_l}\operatorname{arctg}\left(\frac{B_l \ln\sigma}{B_l^2 + D_l(\ln\sigma + D_l)}\right)\right\}$$

Equation of State Model

General form

$$F(V,T) = F_c(V) + F_a(V,T) + F_e(V,T)$$

Thermal electron component is from Ref. [A. V. Bushman, V. E. Fortov, G. I. Kanel', A. L. Ni, *Intense Dynamic Loading of Condensed Matter* (Taylor & Francis, Washington, 1993).]

$$F_e(V,T) = -C_e(V,T)T\ln\left\{1 + \frac{B_e(T)T}{2C_{ei}}\sigma^{-\gamma_e(V,T)}\right\}$$

$$C_e(V,T) = \frac{3R}{2}\left\{Z + \frac{\sigma_Z T_Z^2(1-Z)}{(\sigma+\sigma_Z)\left(T^2+T_Z^2\right)}\right\}\exp(-\tau_i(V)/T) \qquad C_{ei} = \frac{3RZ}{2}$$

$$B_e(T) = \frac{2}{T^2}\int\int_0^T \beta(\tau)d\tau dT \qquad \beta(T) = \beta_i + (\beta_0 - \beta_i + \beta_m T/T_b)\exp(-T/T_b)$$

$$\tau_i(V) = T_i\exp(-\sigma_i/\sigma) \qquad \gamma_e(V,T) = \gamma_{ei} + (\gamma_{e0} - \gamma_{ei} + \gamma_m T/T_g)\exp(-T/T_g)$$

Phase Equilibration

- Phase equilibrium boundary at given temperature T is determined by conditions

$$G^{(1)}(V_1, T) = G^{(2)}(V_2, T)$$
$$P^{(1)}(V_1, T) = P^{(2)}(V_2, T)$$

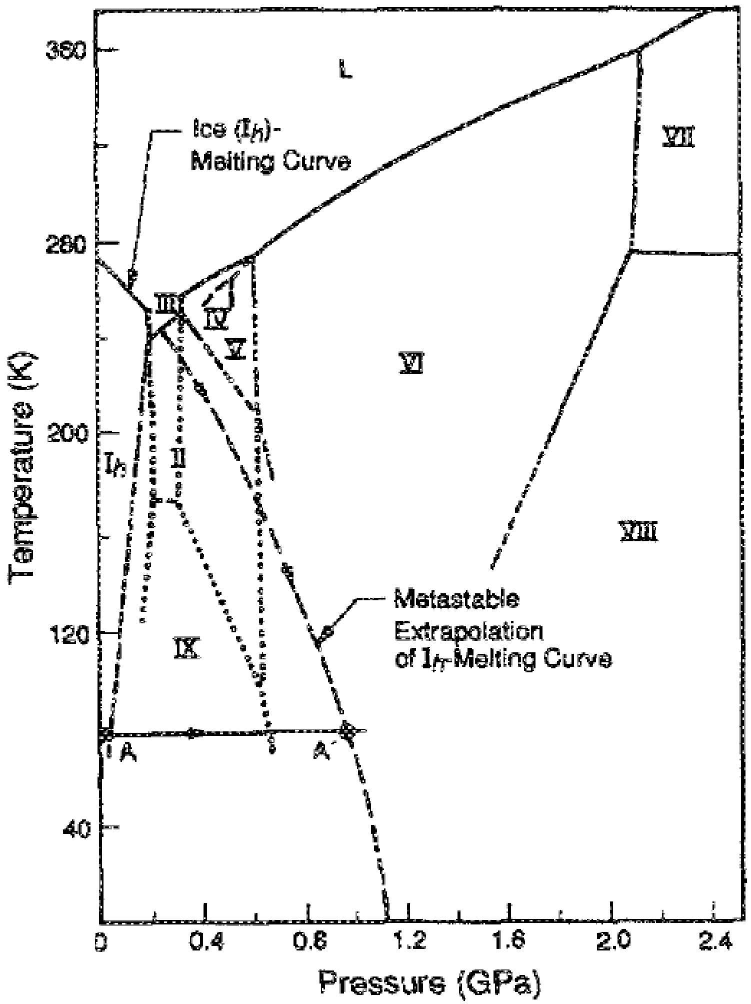
where $G^{(i)}$ and $P^{(i)}$ are the Gibbs energy and pressure functions defined by EOS of phase i = 1 and 2;
V_1 and V_2 are specific volumes of competitive phases 1 and 2

- Phase equilibrium boundary at given pressure P is determined by conditions

$$G^{(1)}(V_1, T) = G^{(2)}(V_2, T)$$
$$P^{(1)}(V_1, T) = P$$
$$P^{(2)}(V_2, T) = P$$

where $G^{(i)}$ and $P^{(i)}$ are the Gibbs energy and pressure functions defined by EOS of phase i = 1 and 2;
V_1 and V_2 are specific volumes of competitive phases 1 and 2;
T is the temperature of phase equilibrium

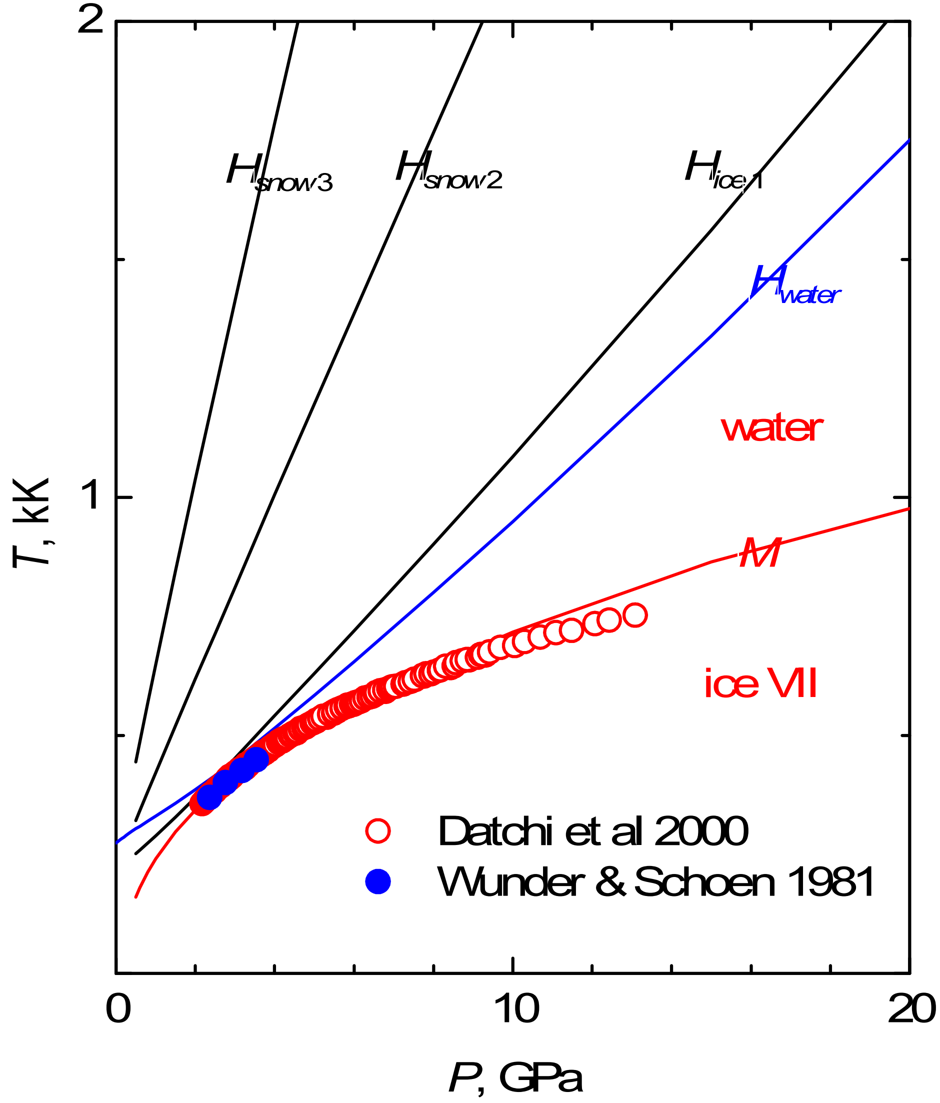
Phase Diagram of Water



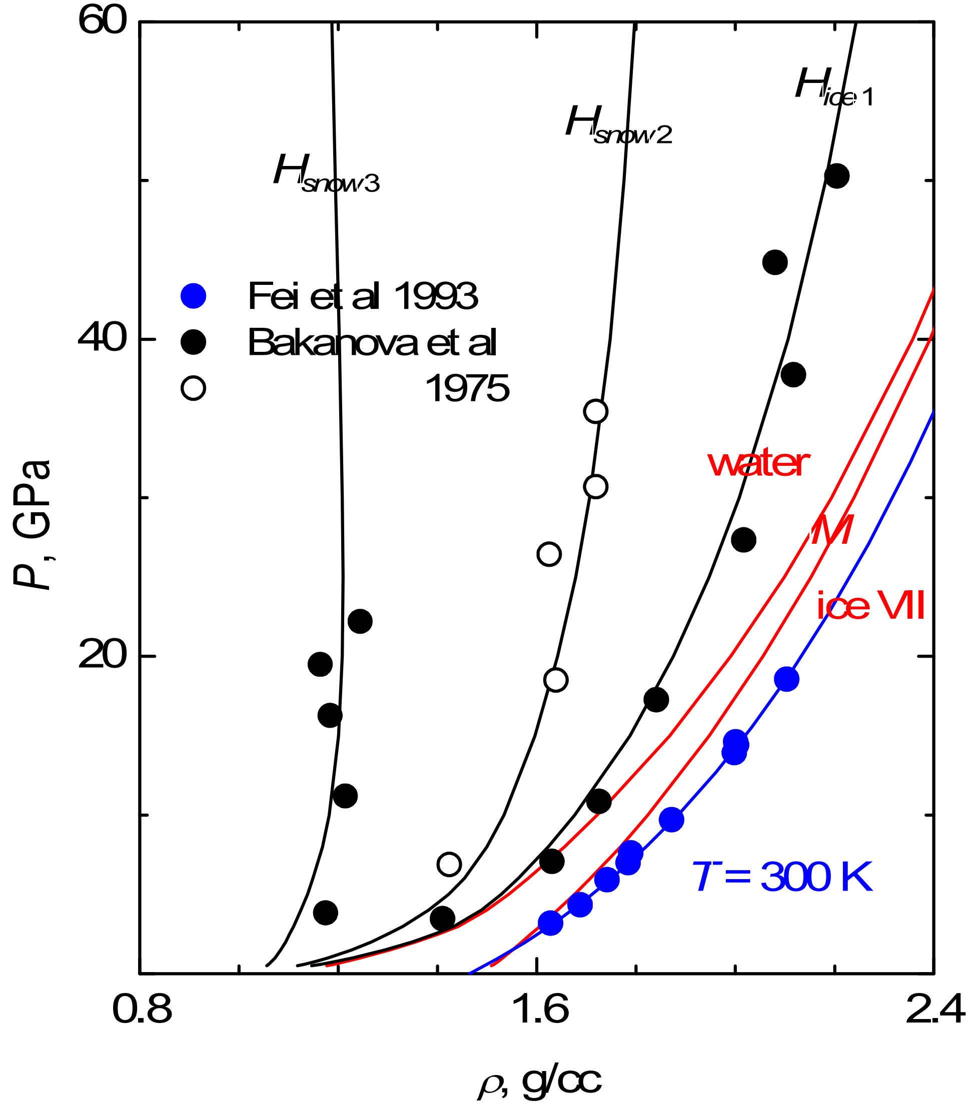
Tan H., Ahrens T. J.,
J. Appl. Phys. 67(1), 217 (1989)

Calculation Results

Phase Diagram of Water



Water Diagram of States



Equation of State for Water

Principal Hugoniot

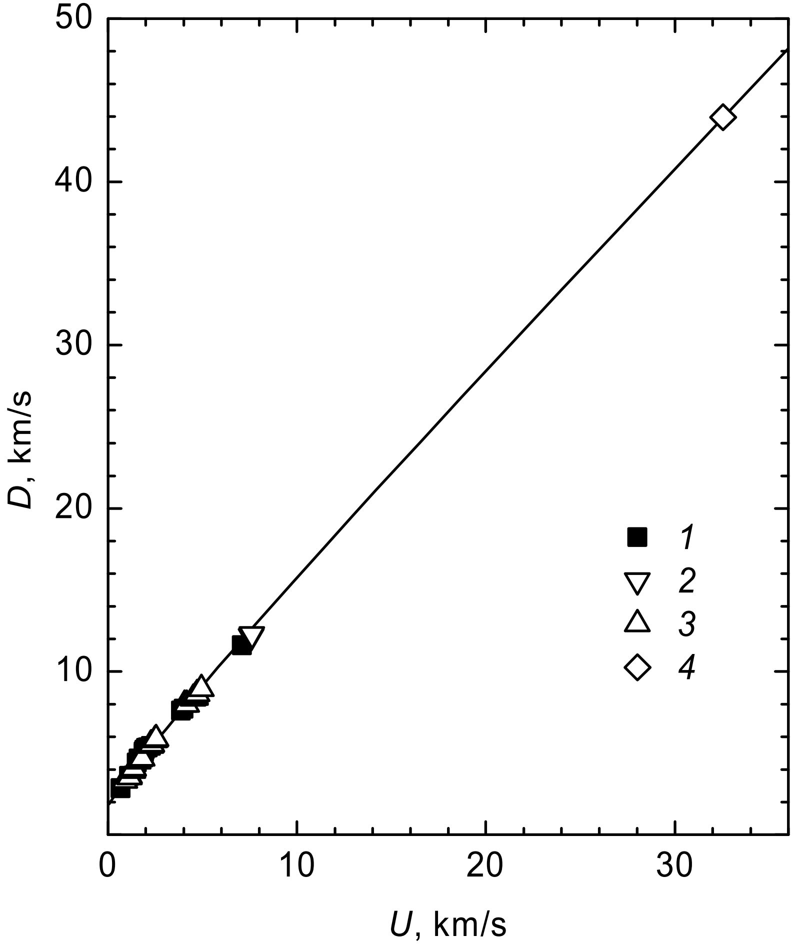
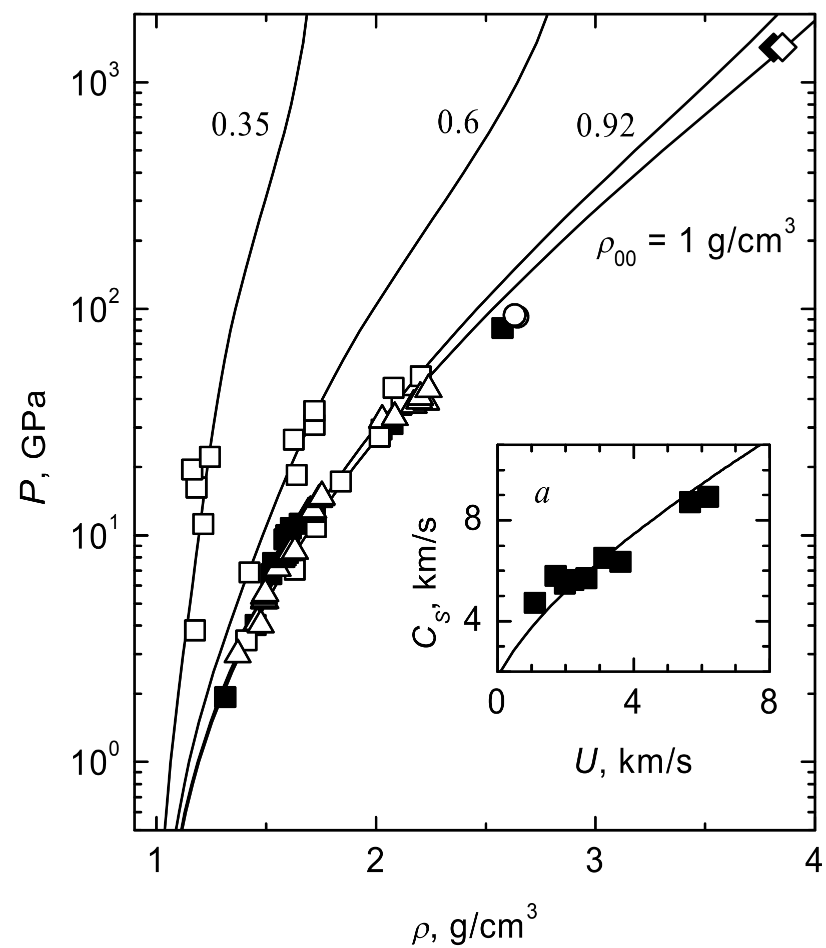
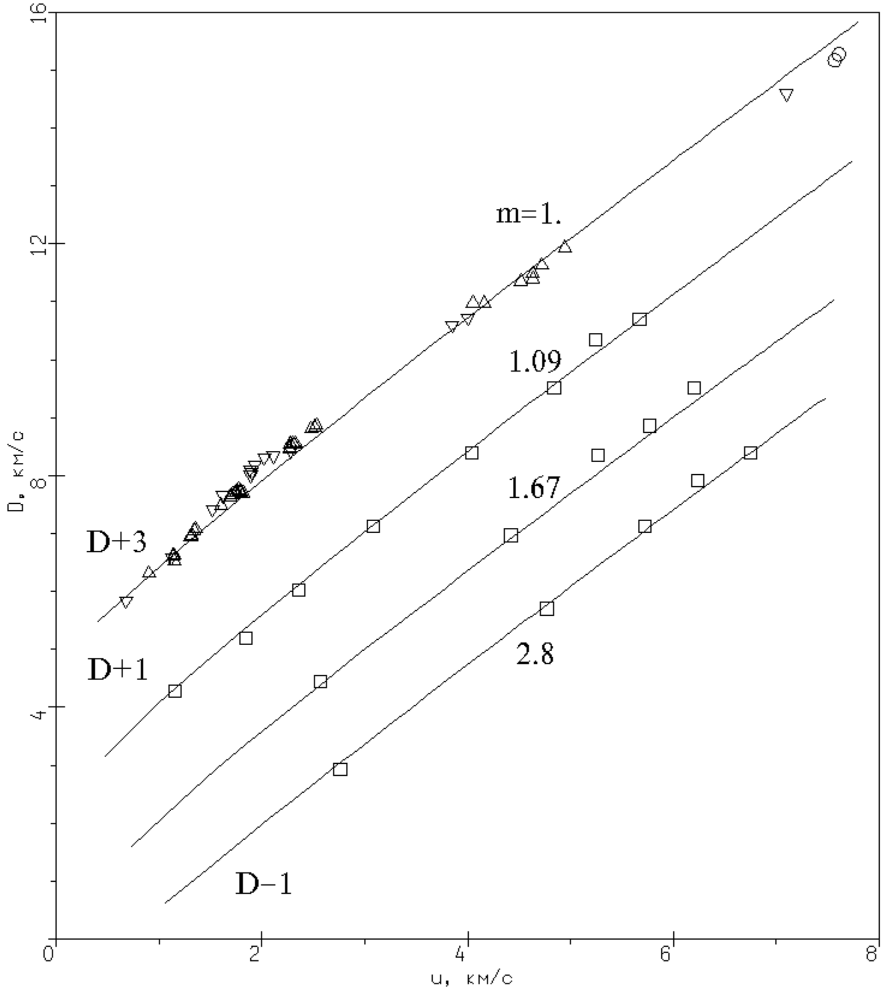


Diagram of States



Shock Hugoniots of Water, Ice, and Snow



$m_p = \rho_0/\rho_{00}$ is initial porosity

Conclusions

- A thermodynamic approach is proposed for modeling of equation of state of structural materials over a broad region of the phase diagram.
- Multiphase equation of state for water is developed with taking into account melting and crystallization. The equations of state are in a good agreement with experimental data.
- Obtained equation of sate can be used in numerical simulations of processes in matter under extreme conditions of high temperatures and high pressures.

Thank you