

Dynamics of metastable states in volumetrically heated foils

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The lifetime of the superheated liquid state within the quasi-static expansion of volumetrically heated foils was calculated. For this purpose an equation-of-state model for homogeneous mixtures of elements based on the model QEOS and the corresponding code MPQeos with an improved cold curve and liquid-vapor phase coexistence data routine was developed. Besides their general importance the calculations were done in order to plan an experiment with a novel ion-beam target scheme based on a stack of thin foils.

Description of the experiment

- Aim: use ion-beam heated matter for EOS measurements
- The proposed targets are based on quasi-static heating of thin foils [1] which insures constant ρ , T , and p in space.
- Quasi-static expansion:
 - Characterized by a small density change $\Delta\rho/\rho \ll 1$ within the time of sound propagation $t_s = l/c_s$
 - l : thickness of the foil; c_s : speed of sound
 - Condition fulfilled for sufficiently thin target foils
 - Expansion velocity of the heated foil: $u_l = \alpha l q / 2$
 - q : ion-beam heating rate
 - $\alpha = (\partial p / \partial E)_\rho (\partial p / \partial \ln \rho)_E^{-1}$
- Obtained thermodynamical quantities:
 - Measure position of expanding surface $\Rightarrow \rho$
 - Measure temperature at target surface and determine q
 - \Rightarrow Thermal/caloric exp. coef. α_p / α_p^* ; heat capacity C_p
- Stack target (Fig. 1a) with n foils:
 - Measure temperature and time t_x when the foils merge $\Rightarrow \alpha_p, \alpha_p^*, C_p$ obtained; ρ = initial mean stack density
 - Detect t_x by measuring the surface velocity (Fig. 1b):
 - * $t < t_x$: The foils expand quasi-statically.
 - * $t = t_x$: Weak shocks are generated.
 - * $t > t_x$: velocity determined by shock hydrodynamics

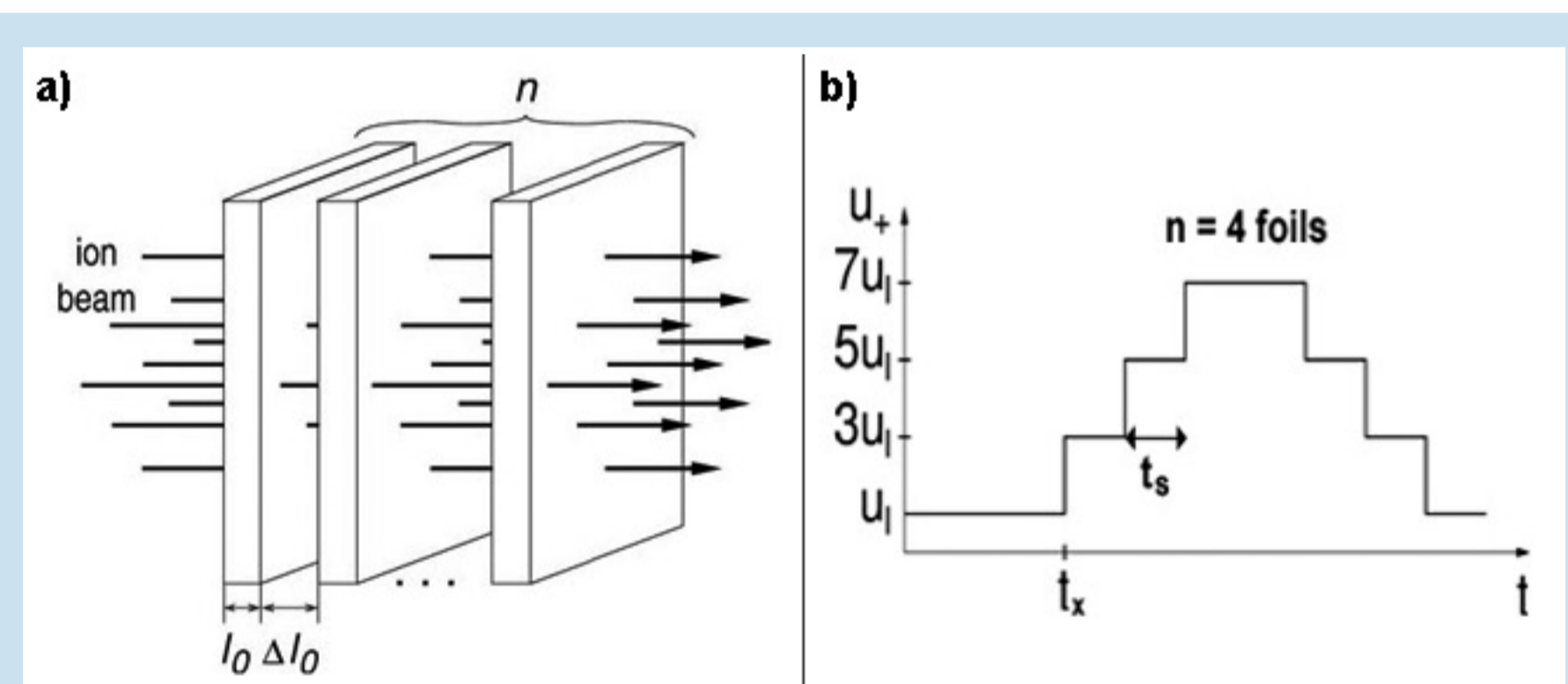


Figure 1: a) Schematic view of the stack target geometry; b) Evolution of the stack target surface velocity u_+

- The measured α_p / α_p^* can be used to improve CP data of a certain group of materials (W, Mo, Co, V, etc.) [2]. An important example is uranium (Fig. 2a).
- The subject of non-congruent phase transitions (NCPT) can also be addressed.
 - Non-congruence: coexistence of two (or more) phases with different chemical composition (stoichiometry)
 - Fig. 2b: non-congruent evaporation in UO_2 [3, 4]
 - First candidate for the stack target: fused silica (SiO_2)
 - Non-congruence is expected for SiO_2 .

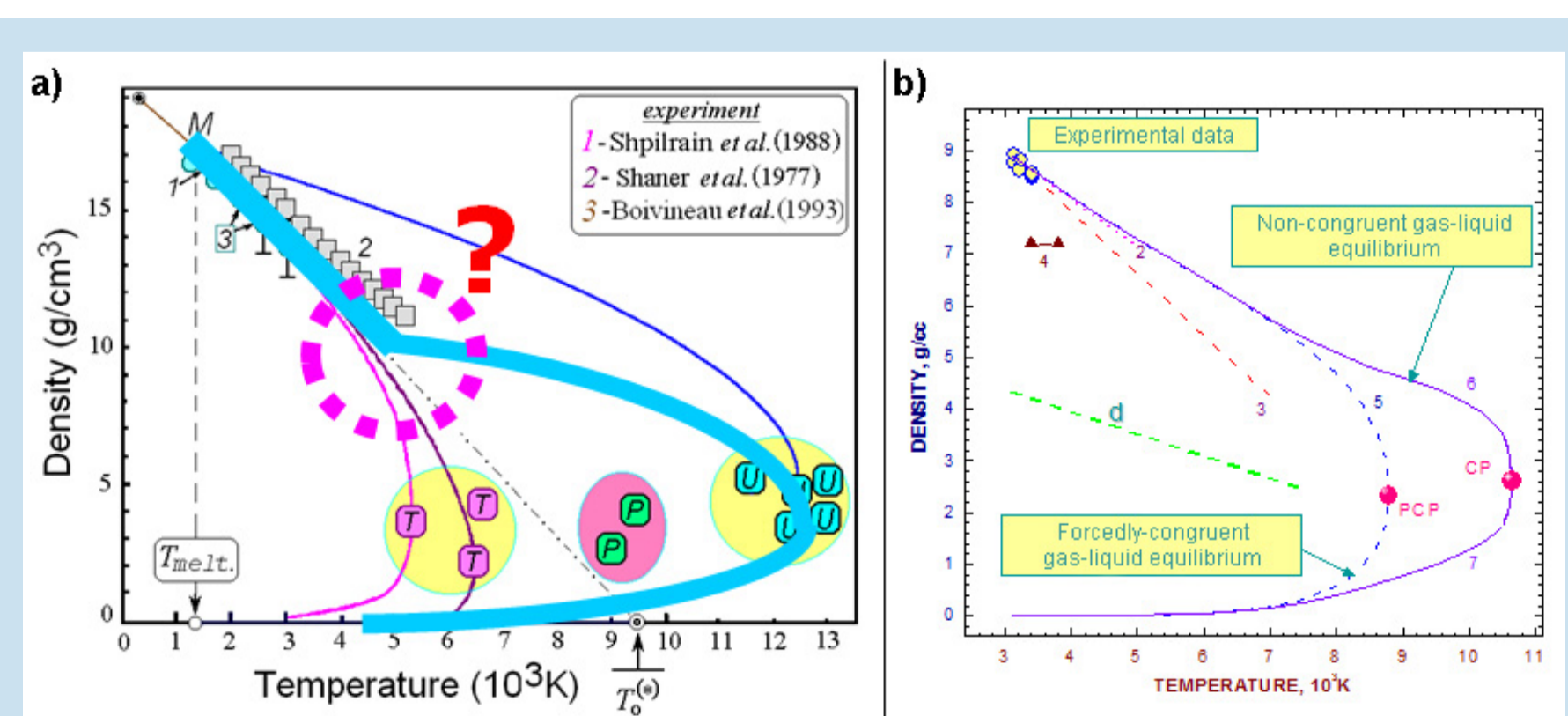


Figure 2: a) Uncertainty in theoretical estimations of the uranium CP [2]; estimations based on: U – caloric properties, T – thermal expansion experiments (1,2,3), P – the plasma nature of the CP; b) p - ρ phase diagram of the NCPT in UO_2 [3, 4]; CP: corresponding CP of NCPT; PCP: pseudo-CP of forcedly congruent phase coexistence; Magenta: corresponding unique boiling-saturation curve

MPQeos / QEOS

- MPQeos [5] is based on the EOS model QEOS [6].
- Input: standard conditions ρ_0 and T_0 ; bulk modulus K_0
- All quantities are derived from the Helmholtz free energy:

$$F(\rho, T) = F_c(\rho, T) + F_i(\rho, T) + F_b(\rho, T) \quad (1)$$
- Electron contribution: simple Thomas-Fermi model [7, 8]
 - Fermi gas in the self-consist. electrostatic atomic field
 - The TF equation is solved for spherical cells.
 - The TF quantities scale with the atomic number Z .
 - \Rightarrow The TF table must be calculated only once.
 - Disadvantages of the simple TF model:
 - * Critical pressure and temperature are overestimated.
 - * Pressures near standard conditions are overestimated.
- The bonding correction [9] tries to improve this. It adjusts the EOS to zero pressure and K_0 at (ρ_0, T_0) .
- The ion contribution is calculated by Cowan's model. It allows for limiting physical laws but not for melting.

MPQeos-JWGU (improved model)

1. Cold curve improvement

Despite the bonding correction, QEOS has two failures:

- Large overestimates in the location of the CP
- The value of the cohesive energy E_{coh} can be negative.

 Solution: replace TF cold curve and bonding correction for densities $\rho < \rho_0$ by a soft-sphere function [10]:

$$E_{cold}(\rho, T=0) = A\rho^n - B\rho^m + E_{coh} \quad (2)$$
 Zero total pressure and energy at $(\rho_0, T_0) \Rightarrow A, B, n, m$: adjustable parameters \Rightarrow Fit the known CP

2. Mixtures of elements

TF mixing of elements [6] was included in MPQeos.

- The ion and bonding contributions are handled as a single species of mean atomic number \bar{Z} and weight \bar{A} .
- Electrons: adjust the densities ρ_k in order to equilibrate all TF pressures and to fulfill an additive volume rule:

$$i) p_{e,k}(\rho_k, T) = p_e \quad \forall k; \quad ii) \frac{\bar{A}}{\rho} = \sum_k x_k \frac{A_k}{\rho_k} \quad (3)$$
- x_k : number fraction of species k
- All $F_{e,k}(\rho_k, T)$ are summed up, weighted by $x_k A_k / \bar{A}$.

3. Calculating phase coexistence data

Eliminating van der Waals loops by Maxwell's rule is computationally very intensive and imprecise.
 Solution: new routine which finds for each isotherm below T_c the densities with same Gibbs free energy and pressure

MPQeos-JWGU results for SiO_2

Input: $\rho_0 = 2.2 \text{ g/cm}^3$; $T_0 = 300 \text{ K}$; $K_0 = 37 \text{ GPa}$

Soft-sphere settings: $E_{coh} = 9.74 \text{ kJ/g}$; $m = 0.8$; $n = 2.8$

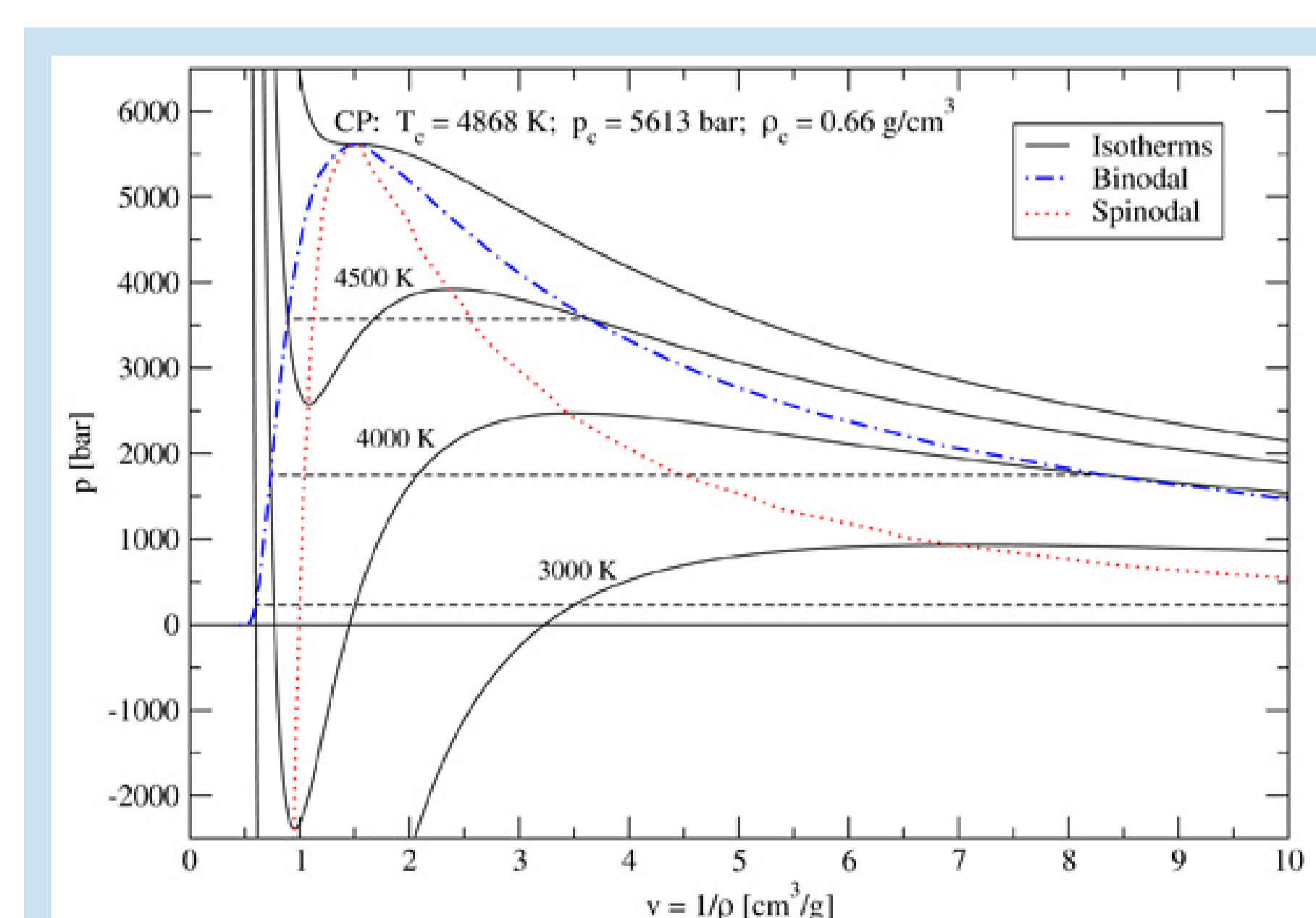


Figure 3: Coexistence data for SiO_2 : isotherms with / without Maxwell construction, binodal, and spinodal

Dynamics of the metastable state

- The lifetime θ of the superheated liquid metastable state was calculated for a foil made of SiO_2 .
- Fig. 4 adumbrates the quasi-static expansion of the foil.
 - The binodal and spinodal delimit the metastable regime.
 - States within the spinodal regime are unstable.
 - At time θ the transition to phase equilibrium occurs.

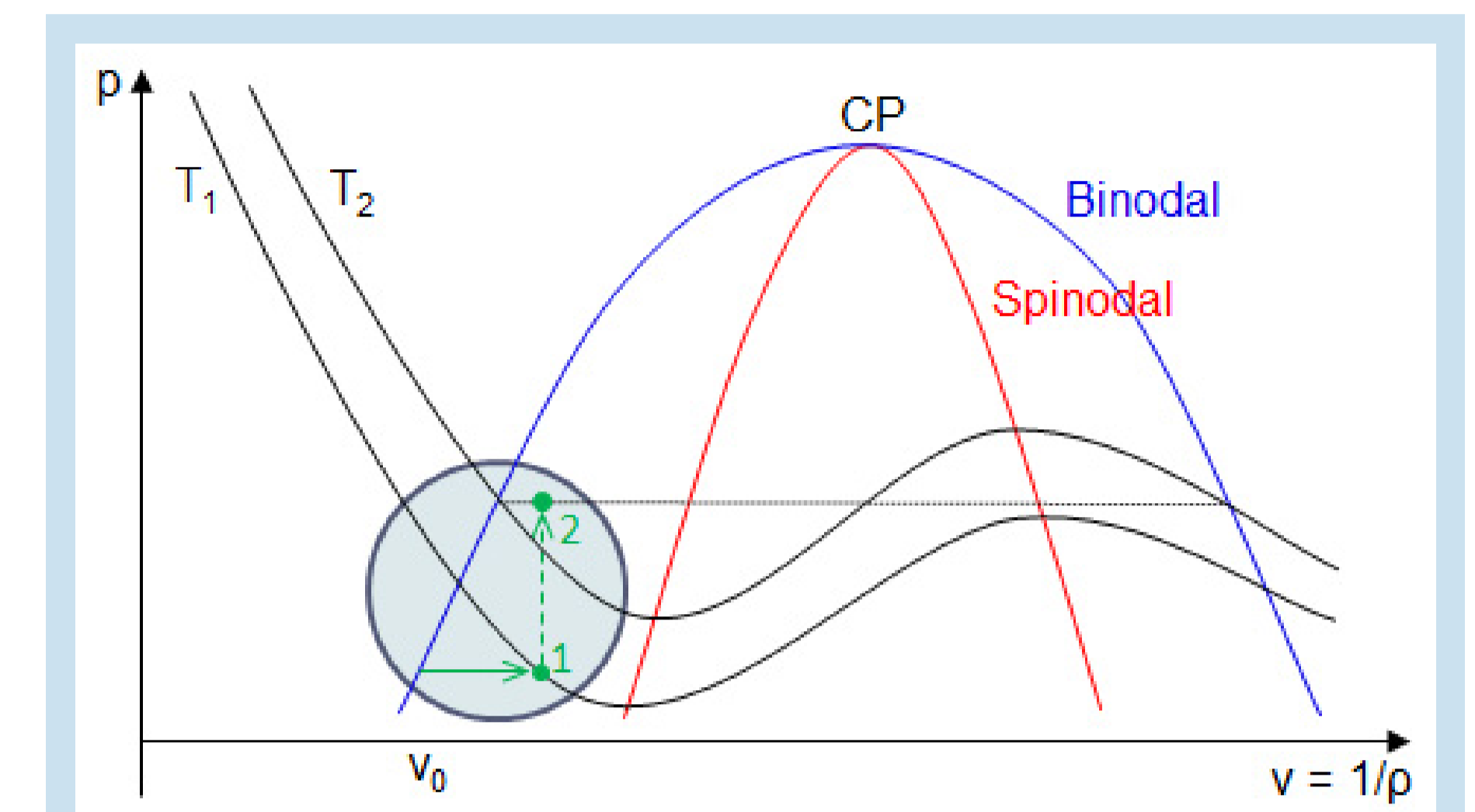


Figure 4: Quasi-static expansion of a foil within metastable region; 1 \rightarrow 2: transition to phase equilibrium

- Vapor bubbles are formed. Bubble equilibrium conditions:

$$p_{vap} = p_{liq} + \frac{2\sigma}{r}; \quad \mu_{vap}(p_{vap}, T) = \mu_{liq}(p_{liq}, T) \quad (4)$$

$$\sigma$$
: surface tension; r : bubble radius; μ : chem. potential
- Bubbles of critical size continue to grow / do not collapse.
- The mean critical bubble waiting time τ [11] is:

$$\tau = (VNB \cdot e^{-W_{cr}/kT})^{-1}; \quad B \approx 10^{10} \text{ s}^{-1} \quad (5)$$

$$V$$
: volume; N : concentration; B : kinetic coefficient
- W_{cr} is the work for the formation of a critical bubble:

$$W_{cr} \approx \frac{16\pi\sigma^3}{3(p_{sat} - p)^2} \quad (6)$$

$$p_{sat}$$
: saturated vapor pressure
- The surface tension was calculated with the Guggenheim-Katayama law [12] and an extended Eötvös law [13]:

$$\sigma(T) = \sigma_0 \left(1 - \frac{T}{T_c}\right)^n \quad (7)$$

$$\sigma(T, \rho) = \sigma_0 \left(\frac{T_c - T}{T_c - T_m}\right) \left(\frac{\rho_{bn}^l(T) - \rho_{bn}^v(T)}{\rho_{bn}^l(T_m) - \rho_{bn}^v(T_m)}\right)^{2/3} \cdot \left(\frac{\rho - \rho_{sp}^l(T)}{\rho_{bn}^l(T) - \rho_{sp}^l(T)}\right)^{1/2} \quad (8)$$

$$\sigma_m = 307 \text{ dyne/cm}$$
 [14] and the thermal expansion coefficient $\alpha_m = 1.0694 \cdot 10^{-4} \text{ K}^{-1}$ (MPQeos-JWGU) at melting temperature $T_m = 2073 \text{ K}$ determine σ_0 and n .
- Fig. 5a shows τ for $l_0 = 10 \mu\text{m}$ (beam spot of 10^{-2} cm^2). The strong decrease of τ with T causes an instantaneous transition with constant ρ . \Rightarrow Bubble dynamics plays no role.

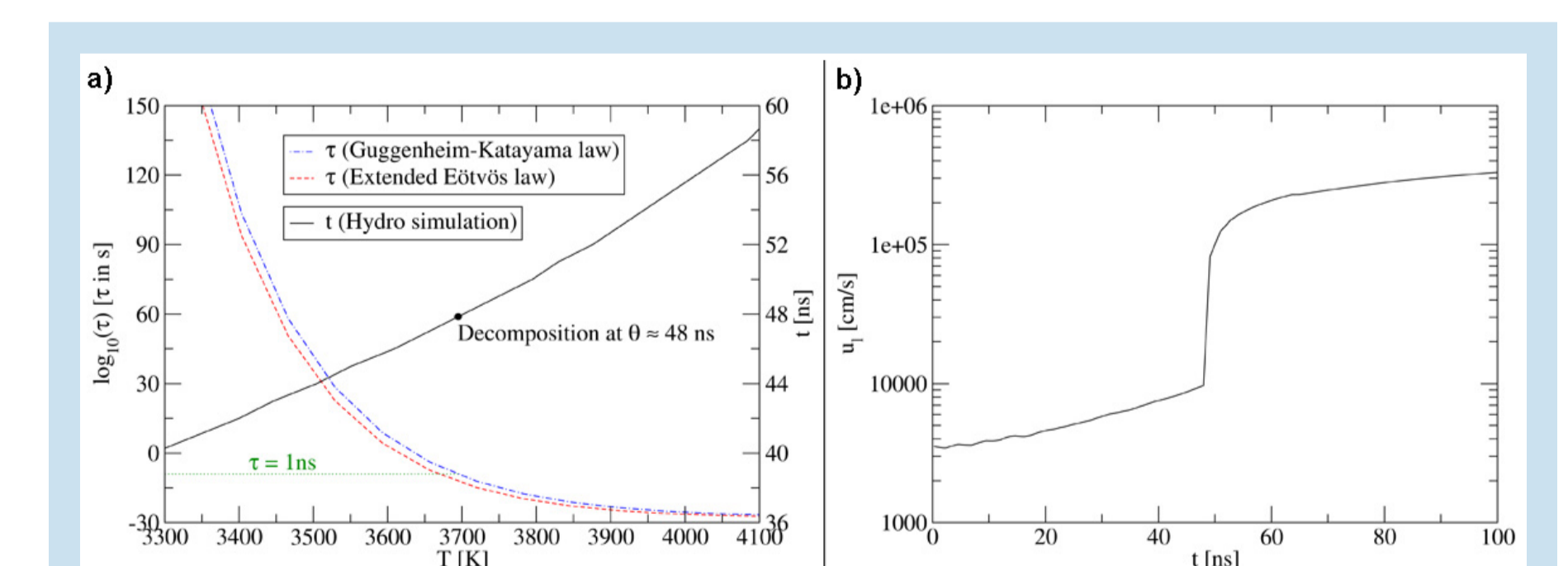


Figure 5: a) Mean critical bubble waiting time τ and hydro simulation for the time evolution of the foils temperature $t(T)$ calculated with the metastable SiO_2 EOS ($q = 10^{11} \text{ J/(g s)}$); b) Hydro simulation for the surface velocity u_l including the transition to the equilibrium EOS ($u_{l0} = 3545 \text{ cm/s}$)

- The transition happens when $\tau \approx 1 \text{ ns}$ at $T \approx 3700 \text{ K}$.
- Hydro simulation (Fig. 5a): $T \approx 3700 \text{ K} \Rightarrow \theta \approx 48 \text{ ns}$
- Not entropy [15], but internal energy must be constant during the transition (first law of thermodynamics).
- Fig. 5b: The correct treatment of the metastable state influences significantly the description of the heated foil.

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