Leibniz-Institut für Polymerforschung Dresden e.V.
Hohe Str. 6, D-01069 Dresden
Tel. +49 351 46580
http://www.ipfdd.de

TU Dresden, D-01062 Dresden
Tel. +49 351 463 43178
http://www.dresden-concept.de

ABOUT THE TIME DEPENDENCY OF THE VAN DER WAALS EQUATION OF STATE

Peter Friedel

Leibniz-Institut für Polymerforschung Dresden e.V., Germany
Institut Theorie der Polymere

Wissenschaftsgemeinschaft
Gottfried Wilhelm Leibniz
Postfach 120169, D-53043 Bonn
Tel. +49 228 308150
http://www.wgl.de

PROBLEM: Infinite susceptibility coefficients (α , κ) obstruct the simulation of phase transitions under natural (isobar/isotherm) conditions, until now.
SOLUTION: The combination of the Time Dependency with the Van der Waals Equation of State (as a blue print for other EoS) allows corresponding simulations of **CROSSING PHASE TRANSITION POINTS** by the new **DIFFERENTIAL SIMULATED ANNEALING/COMPRESSING** methods.

Van der Waals Equation of State

(J.D. van der Waals, Ph.D. thesis (1873))

$$(p_0 + \frac{a}{V_{m,0}^2})(V_{m,0} - b) = N_A k_B T_0 \quad (1)$$

$$a = \frac{27 R^2 T_{cr}^2}{64 p_{cr}} \quad b = \frac{1 R T_{cr}}{8 p_{cr}} \quad (2)$$

$$p_r = \frac{p_0}{p_{cr}} \quad V_{m,r} = \frac{V_{m,0}}{V_{m,cr}} \quad T_r = \frac{T_0}{T_{cr}} \quad (3)$$

$$(p_r + \frac{3}{V_{m,r}^2})(3 \cdot V_{m,r} - 1) = 8 \cdot T_r \quad (4)$$

Time dependency

(H. Berendsen, J.Chem.Phys. (1984))

$$\lambda = \left[1 + \frac{\Delta t}{\tau_T} \left\{ \frac{T_0}{T(t - 0.5\Delta t)} - 1 \right\} \right]^{\frac{1}{2}} \quad (5)$$

$$p(t) = \frac{2}{3V} (E_{kin}(t) - \Xi(t)) \quad (6)$$

$$\mu(t) = 1 - \frac{\Delta t}{\tau} (p_0 - p(t)) \quad (7)$$

$$V(t + \Delta t) = \mu V(t)$$

Total Time Differentials

(Bronstein, Verlag Harri Deutsch, (2013))

$$\frac{\delta F}{\delta p_r} \frac{dp_r(t)}{dt} + \frac{\delta F}{\delta V_{m,r}} \frac{dV_{m,r}(t)}{dt} + \frac{\delta F}{\delta T_r} \frac{dT_r(t)}{dt} = 0 \quad (9)$$

$$0 = (3V_{m,r}^3 - V_{m,r}^2) \frac{dp_r(t)}{dt} + (9p_r V_{m,r}^2 - 2(p_r + 8T_r)V_{m,r} + 9) \frac{dV_{m,r}(t)}{dt} + (-8V_{m,r}^2) \frac{dT_r(t)}{dt} \quad (10)$$

Rearrangement gives explicit fracture expressions for $\frac{dp_r(t)}{dt}$, $\frac{dV_{m,r}(t)}{dt}$ and $\frac{dT_r(t)}{dt}$.

Some additional mathematical considerations

Some common definitions

$$\frac{dx}{dt} = - \left(\frac{\frac{\delta F}{\delta y}}{\frac{\delta F}{\delta x}} \right)_{z=const} \frac{dy}{dt} \quad (11)$$

$$\frac{dx(t)}{dy(t)} = \frac{1}{\frac{dy(t)}{dx(t)}} \quad (12)$$

$$\phi(t) = \frac{1}{x(y(t))} \frac{dx(t)}{dy(t)} = \frac{d \ln x(y(t))}{dy(t)} = - \frac{1}{x(y(t))} \left(\frac{\frac{\delta F}{\delta y}}{\frac{\delta F}{\delta x}} \right)_{z=const} \quad (13)$$

$$x_{i+1} \approx x_i - \left(\frac{\frac{\delta F}{\delta y}}{\frac{\delta F}{\delta x}} \right)_{z=const, t_i} \left(\frac{dy}{dt} = const. = k_{dy} \right) \Delta t \quad (14)$$

Functions and their inverse functions

$$x(y, z = const) \quad \text{and} \quad y(x, z = const) \quad (15)$$

Different function characters:

1. monotonic increasing: $p_r(T_r, V_{m,r} = const)$ and $T_r(p_r, V_{m,r} = const)$;
2. unambiguous with extrema: $T_r(V_{m,r}, p_r = const)$ and $p_r(V_{m,r}, T_r = const)$;
3. ambiguous: $V_{m,r}(T_r, p_r = const)$ and $V_{m,r}(p_r, T_r = const)$;

Important (Bronstein at page 52): Cite: "If there is a function with non-monotonic behavior separable into monotonic pieces then the corresponding inverse function exists for every of that monotonic piece."

$$f(x) = y \quad <==> \quad f(y) = x \quad (16)$$

Three special cases

Isochor - $\frac{dV_{m,r}}{dt} = 0$

$$\frac{dp_r}{dt} = - \left(\frac{\frac{\delta F}{\delta p_r}}{\frac{\delta F}{\delta V_{m,r}}} \right)_{V_{m,r}} \frac{dT_r}{dt} \quad (17)$$

$$\beta_r = \frac{1}{p_r} \frac{dp_r}{dT_r} = \frac{1}{p_r} \frac{8}{(3V_{m,r} - 1)} \quad (19)$$

$$T_{r,i+1} = T_{r,i} + k_{dT} \Delta t \quad (21)$$

SIMULATED ANNEALING

Isobar - $\frac{dp_r}{dt} = 0$

$$\frac{dV_{m,r}}{dt} = - \left(\frac{\frac{\delta F}{\delta V_{m,r}}}{\frac{\delta F}{\delta p_r}} \right)_{p_r=const} \frac{dT_r}{dt} \quad (23)$$

$$\alpha_r = \frac{1}{V_{m,r}} \frac{dV_{m,r}}{dT_r} = \frac{8V_{m,r}}{(9p_r V_{m,r}^2 - 2(p_r + 8T_r)V_{m,r} + 9)} \quad (25)$$

$$T_{r,i+1} = T_{r,i} + k_{dT} \Delta t \quad (27)$$

INFINITE HIGH
VOLUME FLUCTUATIONS
!!! CRASH !!!

$$\frac{dT_r}{dt} = - \left(\frac{\frac{\delta F}{\delta T_r}}{\frac{\delta F}{\delta V_{m,r}}} \right)_{p_r=const} \frac{dV_{m,r}}{dt} \quad (24)$$

$$\alpha_{r,p} = \frac{1}{T_r} \frac{dT_r}{dV_{m,r}} = \frac{1}{T_r} \frac{(9p_r V_{m,r}^2 - 2(p_r + 8T_r)V_{m,r} + 9)}{8V_{m,r}^2} \quad (26)$$

$$V_{m,r,i+1} = V_{m,r,i} + k_{dV} \Delta t \quad (28)$$

$$T_{r,i+1} \approx T_{r,i} + \left(\frac{9p_r}{8} - \frac{(p_r + 8T_{r,i})}{4V_{m,r,i}} + \frac{9}{8V_{m,r,i}^2} \right)_{p_r=const, t_i} k_{dT} \Delta t \quad (29)$$

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Isotherm - $\frac{dT_r}{dt} = 0$

$$\frac{dV_{m,r}}{dt} = - \left(\frac{\frac{\delta F}{\delta p_r}}{\frac{\delta F}{\delta V_{m,r}}} \right)_{T_r=const} \frac{dp_r}{dt} \quad (30)$$

$$\kappa_r = - \frac{1}{V_{m,r}} \frac{dV_{m,r}}{dp_r} = - \frac{1}{V_{m,r}} \frac{(3V_{m,r}^3 - V_{m,r}^2)}{(9p_r V_{m,r}^2 - 2(p_r + 8T_r)V_{m,r} + 9)} \quad (32)$$

$$p_{r,i+1} = p_{r,i} + k_{dp} \Delta t \quad (34)$$

INFINITE HIGH
VOLUME FLUCTUATIONS
!!! CRASH !!!

$$\frac{dp_r}{dt} = - \left(\frac{\frac{\delta F}{\delta p_r}}{\frac{\delta F}{\delta V_{m,r}}} \right)_{T_r=const} \frac{dV_{m,r}}{dt} \quad (31)$$

$$\kappa_{r,p} = - \frac{1}{p_r} \frac{dp_r}{dV_{m,r}} = - \frac{1}{p_r} \frac{(9p_r V_{m,r}^2 - 2(p_r + 8T_r)V_{m,r} + 9)}{(3V_{m,r}^3 - V_{m,r}^2)} \quad (33)$$

$$V_{m,r,i+1} = V_{m,r,i} + k_{dV} \Delta t \quad (35)$$

$$p_{r,i+1} \approx p_{r,i} + \left(\frac{(9p_{r,i} V_{m,r,i}^2 - 2(p_{r,i} + 8T_r)V_{m,r,i} + 9)}{(3V_{m,r,i}^3 - V_{m,r,i}^2)} \right)_{T_r=const, t_i} k_{dV} \Delta t \quad (36)$$

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1 (a) p_r over T_r (acc. Equ.(4))

1 (b) T_r over p_r (acc. Equ.(4))

2 (a) $V_{m,r}$ over T_r (acc. rez. Equ.(29))

2 (b) T_r over $V_{m,r}$ (acc. Equ.(29))

3 (a) $V_{m,r}$ over p_r (acc. rez. Equ.(36))

3 (b) p_r over $V_{m,r}$ (acc. Equ.(36))

1 (c) β_r over T_r (acc. Equ.(19))

1 (d) $\beta_{r,p}$ over p_r (acc. Equ.(20))

2 (c) α_r over T_r (acc. Equ.(25))

2 (d) $\alpha_{r,p}$ over $V_{m,r}$ (acc. Equ.(26))

3 (c) κ_r over p_r (acc. Equ.(32))

3 (d) $\kappa_{r,p}$ over $V_{m,r}$ (acc. Equ.(33))

Known: SIMULATED ANNEAL./COMPRESS.

New: DIFFERENTIAL SIMULATED ANNEALING

New: DIFFERENTIAL SIMULATED COMPRESSING