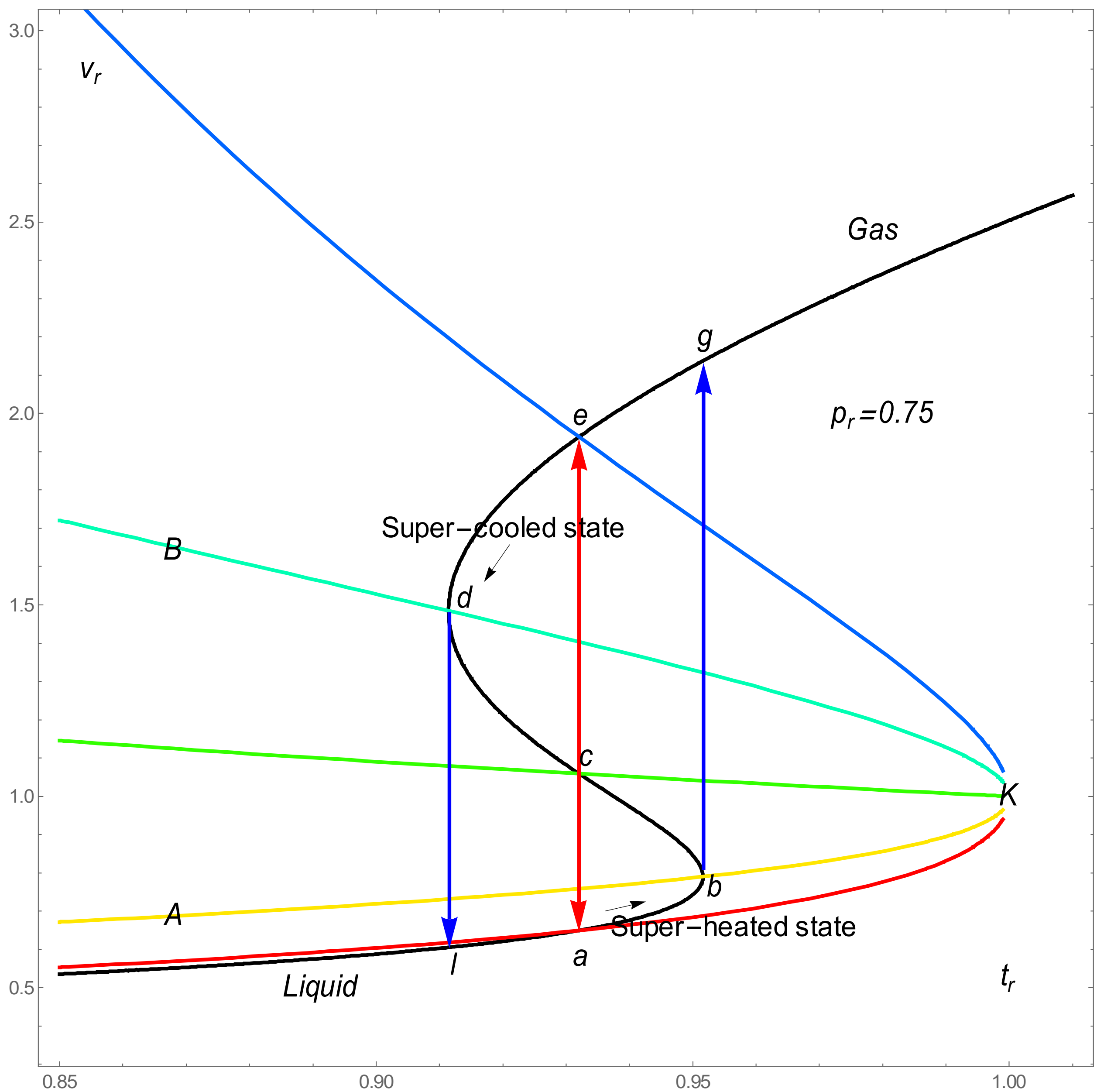
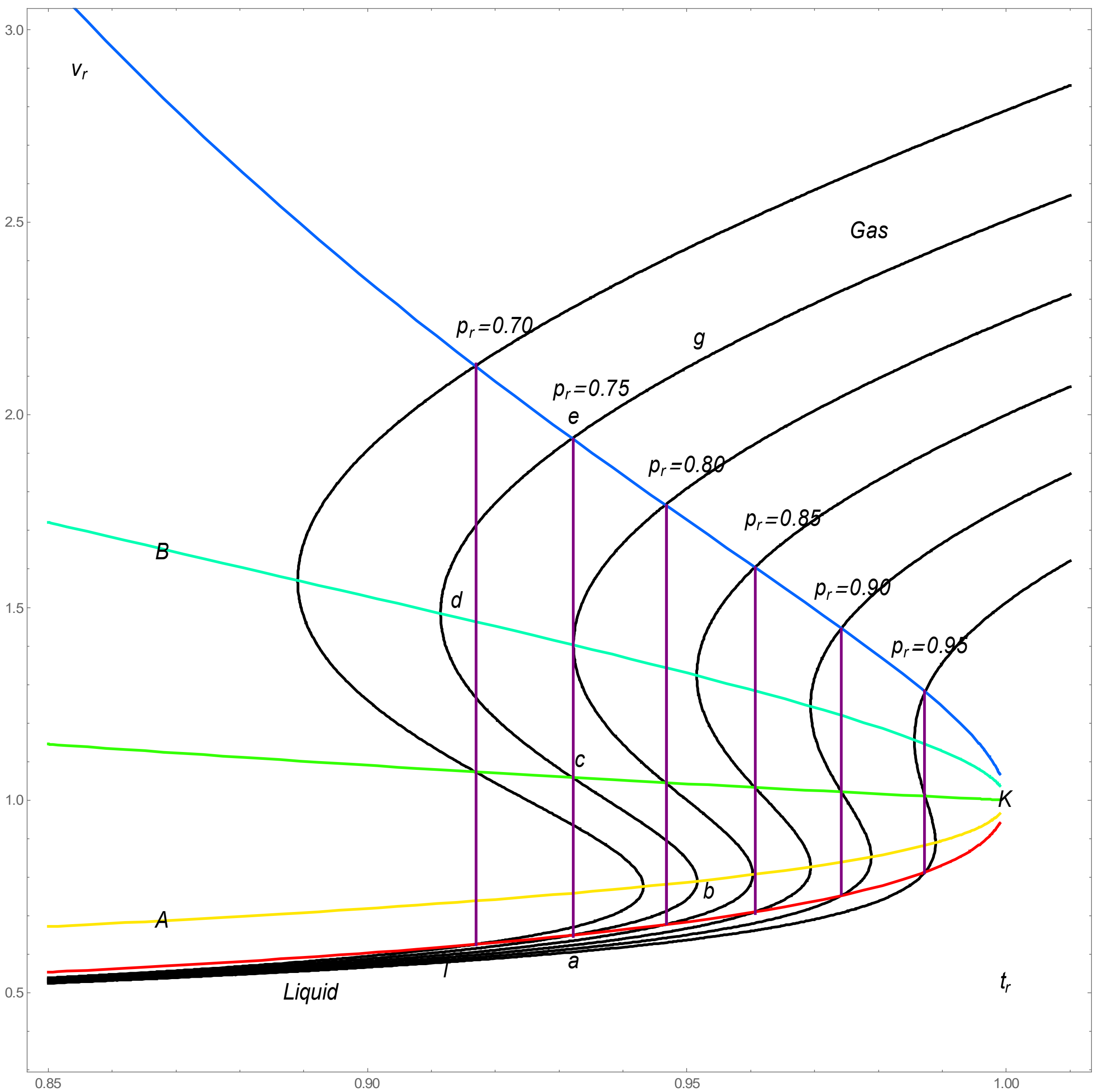
The metastable state:
Superheating and supercooling

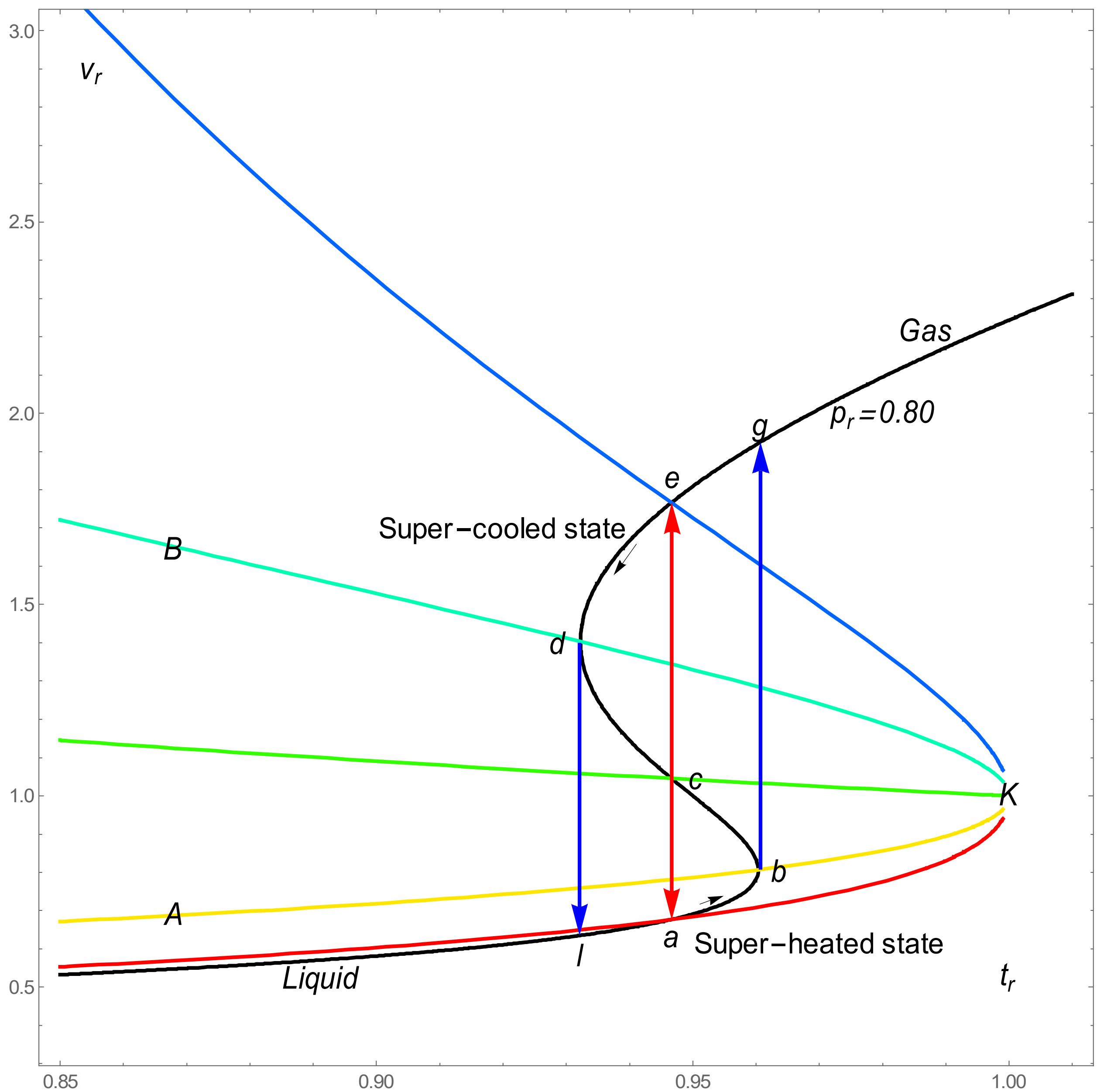
Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
(Date: November 10, 2019)



The binodal line is known as phase separation line, since it separates the homogeneous gas and liquid states. For parameters within the binodal line the equilibrium shows two-phase co-existence. In the region between the binodal line and the spinodal line, the homogeneous system is in a metastable state.



v_r
Gas
g
$p_r=0.70$
$p_r=0.75$
e
$p_r=0.80$
$p_r=0.85$
$p_r=0.90$
$p_r=0.95$
B
d
c
K
b
A
a
l
Liquid
t_r
3.0
2.5
2.0
1.5
1.0
0.5
0.85
0.90
0.95
1.00



e: the intersection of the ParametricPlot (denoted by black line) and the K-e line (binodal line)
d: the intersection of the ParametricPlot (denoted by black line) and the K-d line (spinodal line)
c: the intersection of the ParametricPlot (denoted by black line) and the K-c line
b: the intersection of the ParametricPlot (denoted by black line) and the K-b line (spinodal line)
a: the intersection of the ParametricPlot (denoted by black line) and the K-a line (binodal line)

Point a:	thermal equilibrium
Point e:	thermal equilibrium
Point c:	intermediate between the points a and b (temperature of point c is the same as that of points and e).

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{\partial(P,T)}{\partial(V,T)} = \frac{\dfrac{\partial(P,T)}{\partial(P,V)}}{\dfrac{\partial(V,T)}{\partial(P,V)}} = -\frac{\left(\dfrac{\partial T}{\partial V}\right)_P}{\left(\dfrac{\partial T}{\partial P}\right)_V}.$$

At the points *b* and *d*, we have $\left(\frac{\partial P}{\partial V}\right)_T = 0$ (isothermal process) and $\left(\frac{\partial T}{\partial V}\right)_P = 0$ (isobaric process).

In the thermal equilibrium, during the cooling process at fixed pressure p_r, we have the path (g-e-c-a-*l*).
Super-heated state:
Super-cooled state:

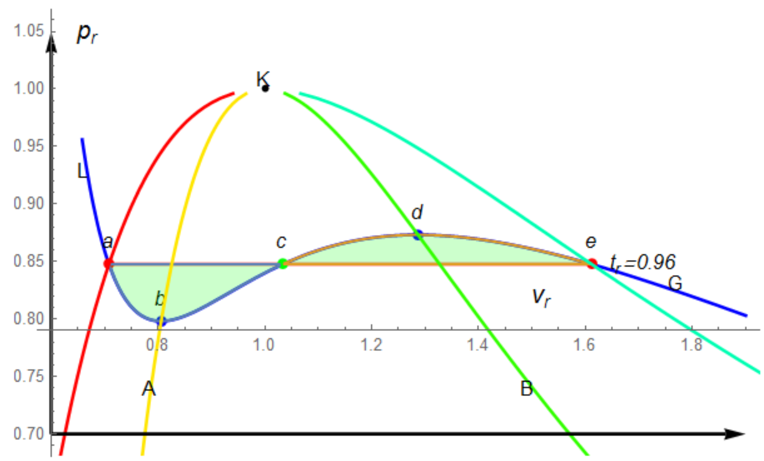


Fig. Isothermal curve. $t = t_r$. $p = p_r$.

Point *a*: $v = v_1(t)$, $p = p_r$

Point *b*: $v = v_{m1}(t)$, $p = p_{m1}(t)$

Point *c*: $v = v_2(t)$, $p = p_r$

Point *d*: $v = v_{m2}(t)$, $p = p_{m2}(t)$

Point *e*: $v = v_3(t)$, $p = p_r$

How to draw these graphs

(1) ContourPlot of $p_r = 0.70$, 75, 0.80, 0.85. 0.90, and 0.95 in the (t_r, v_r) plane.

$$p_r = \frac{8}{3} t_r \frac{1}{(v_r - \frac{1}{3})} - \frac{3}{v_r{}^2}$$

(2) Line (*K*-*e*): Plot of $v_3(t)$ (binodal line)

(3) Line (*K*-*d*): plot of $v_{m2}(t)$ (spinodal line)

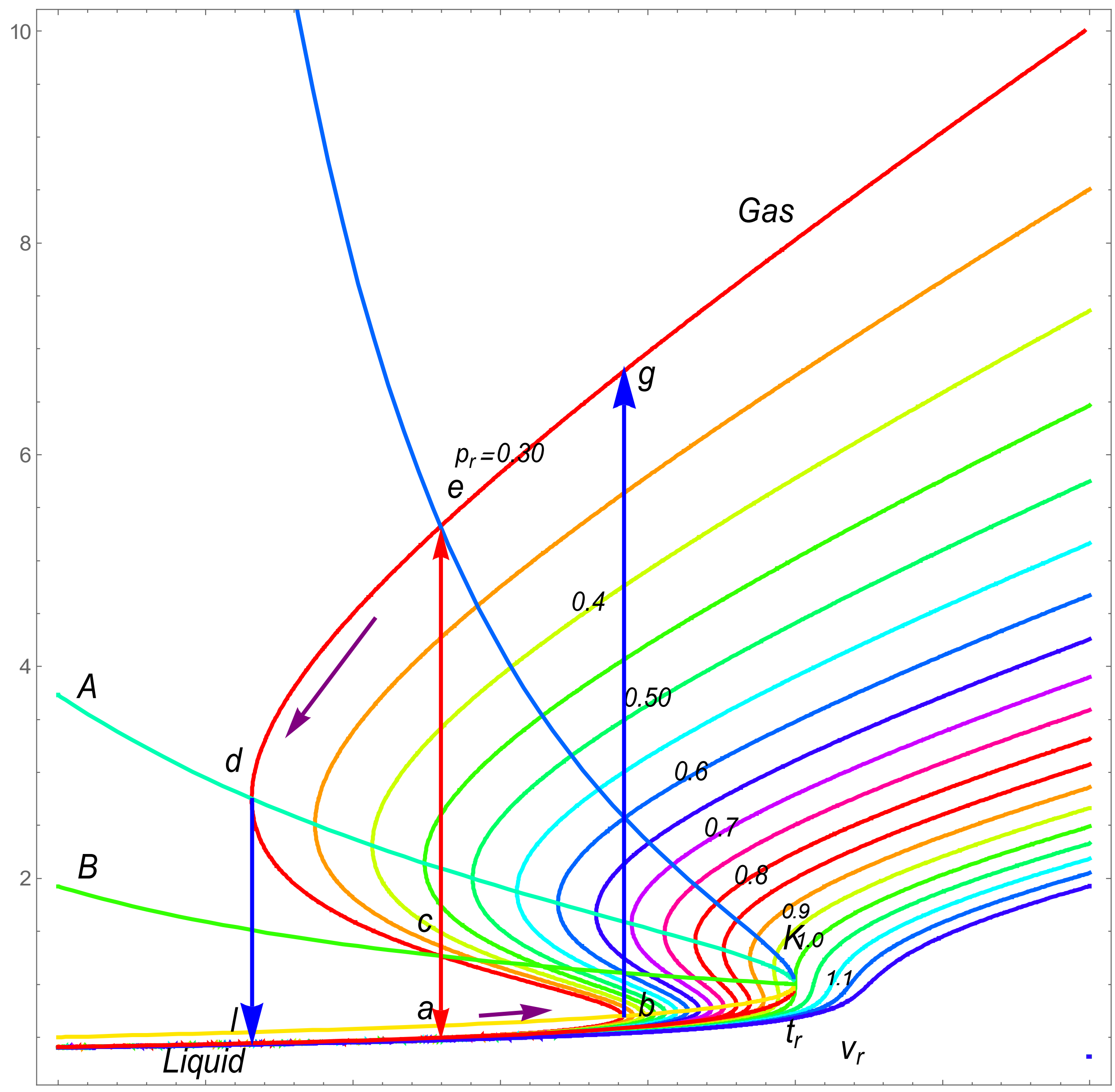
(4) Line (*K*-*c*): plot of $v_2(t)$

(5) Line (*K*-*b*): plot of $v_{m1}(t)$ (spinodal line)

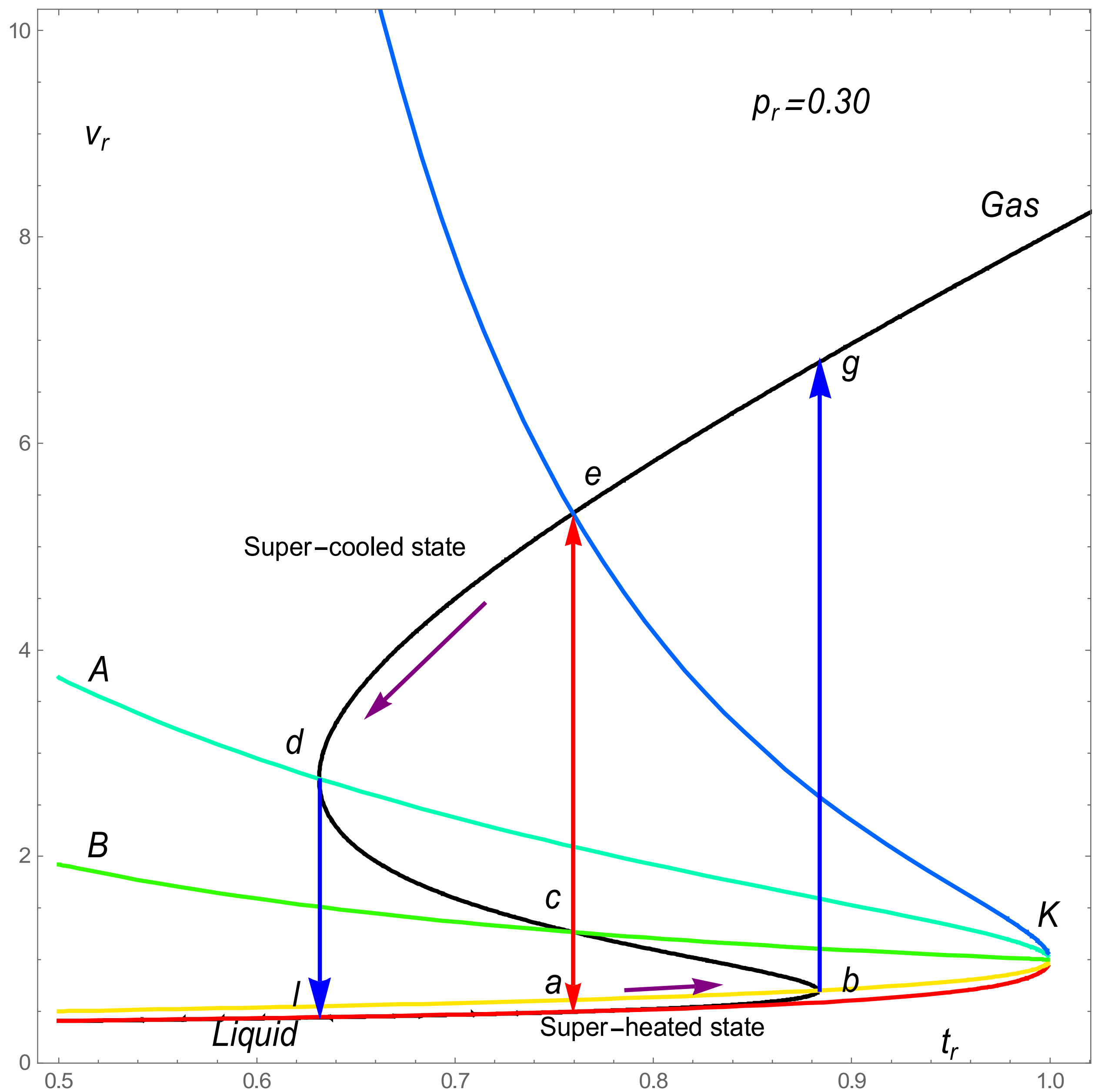
(6) Line (*K*-*a*): plot of $v_1(t)$ (binodal line)

Physical meaning of $v_1(t)$

We make ParametricPlots of $\{t, v_1(t)\}$, $\{t, v_2(t)\}$, $\{t, v_{m1}(t)\}$, $\{t, v_{m2}(t)\}$, as well as the ContourPlot of $p_r = 0.70$, 75, 0.80, 0.85. 0.90, and 0.95 in the (t_r, v_r) plane.



Gas
g
p_r=0.30
e
0.4
0.50
0.6
0.7
0.8
0.9
K
1.0
1.1
A
B
d
c
a
b
l
Liquid
t_r
v_r



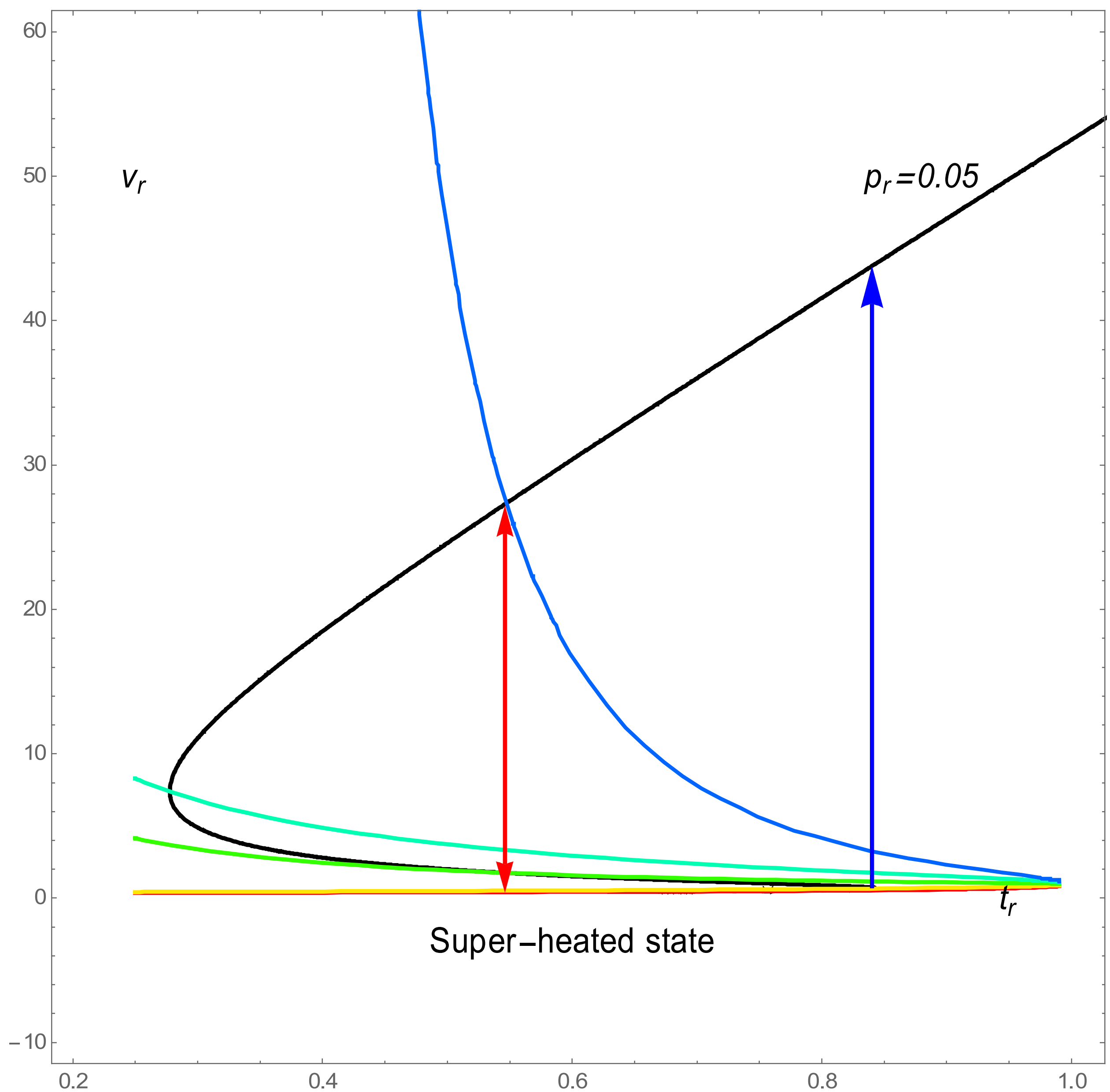
It is well known that systems exhibiting first-order phase transitions can exhibit hysteresis in the transition temperature and therefore in other physical properties upon cooling and warming, where the transition temperature is lower on cooling (supercooling) and higher on warming (superheating) than the equilibrium transition temperature.

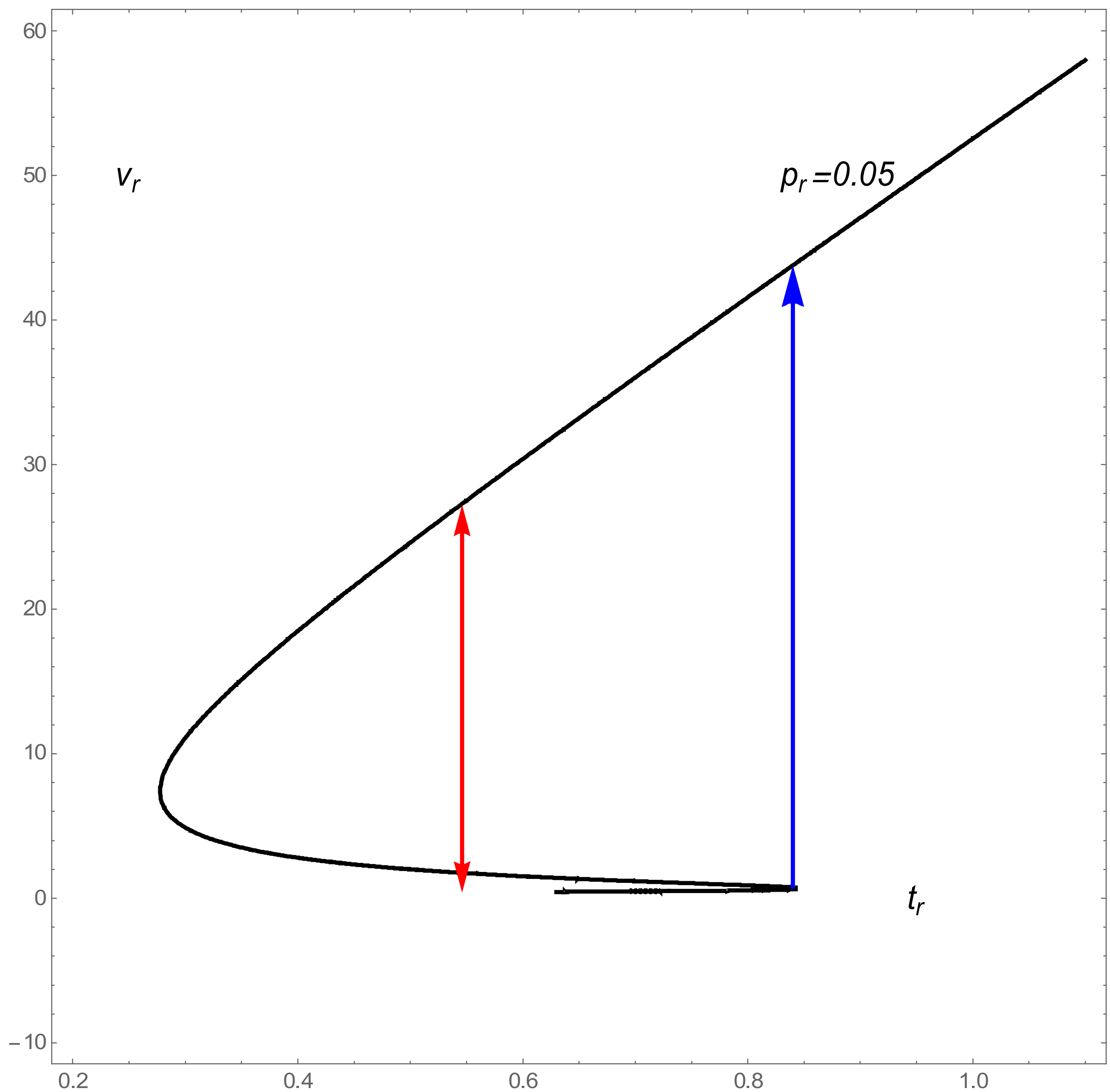
Water:

Critical point: $T_c = 647$ K. $P_c = 22.064$ MPa $= 217.7$ atm

Boiling point:
$P = 101.325$ kPa = 1 atm. $T = 373$ K.

$$p_r = \frac{P}{P_c} = 4.592 \times 10^{-3}$$





v_r
$p_r = 0.05$
t_r