Termodinâmica das Transições de Fase

Aula 2

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Escola de Verão

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13 a 24/02/2006

Instituto de Física

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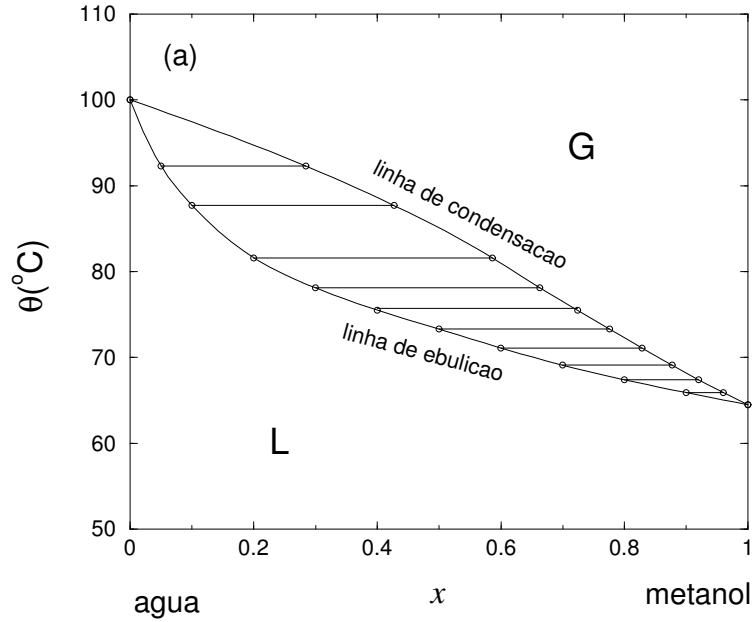
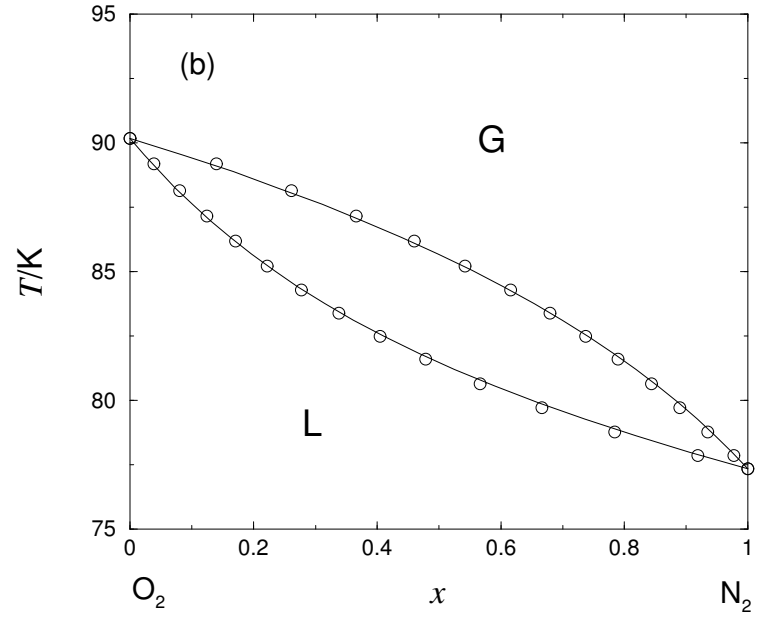
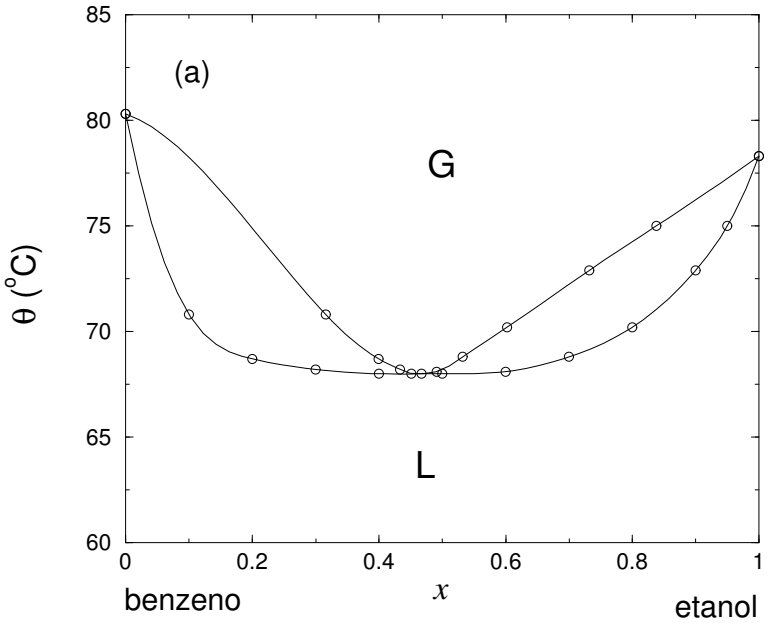
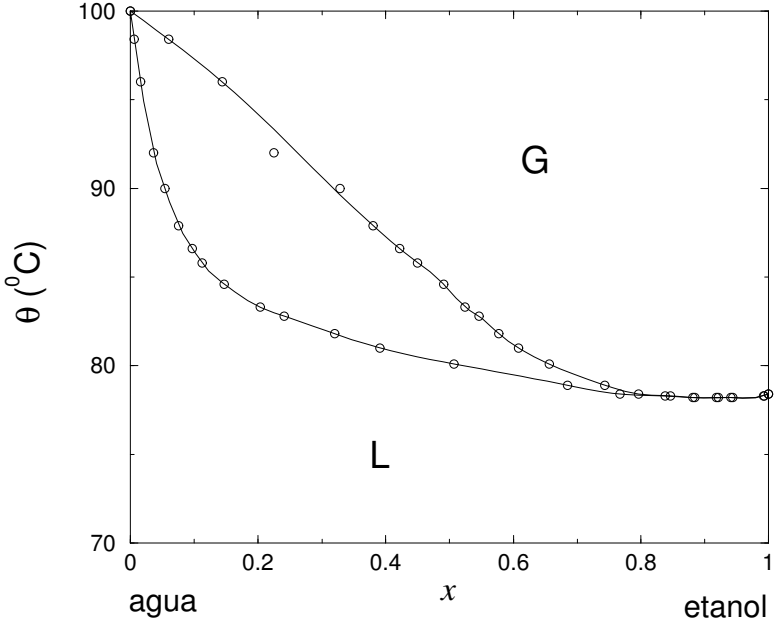
Misturas binárias

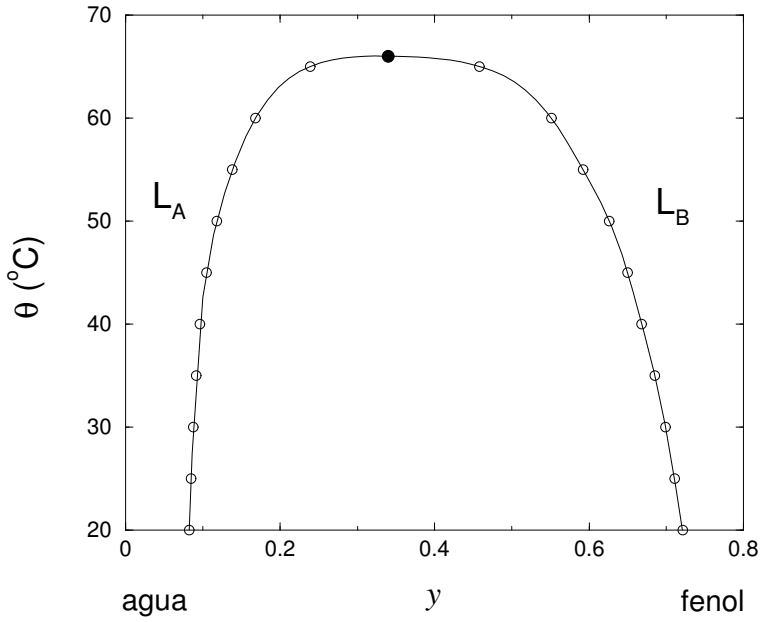


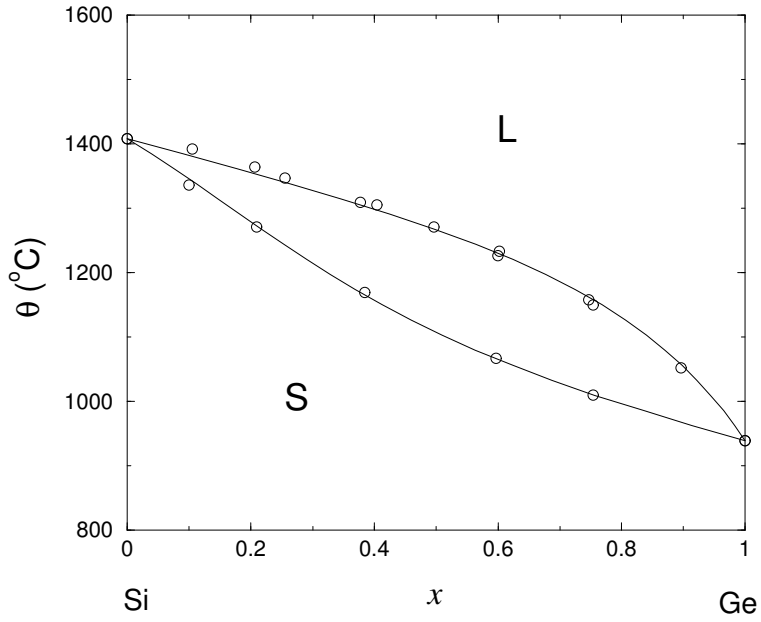


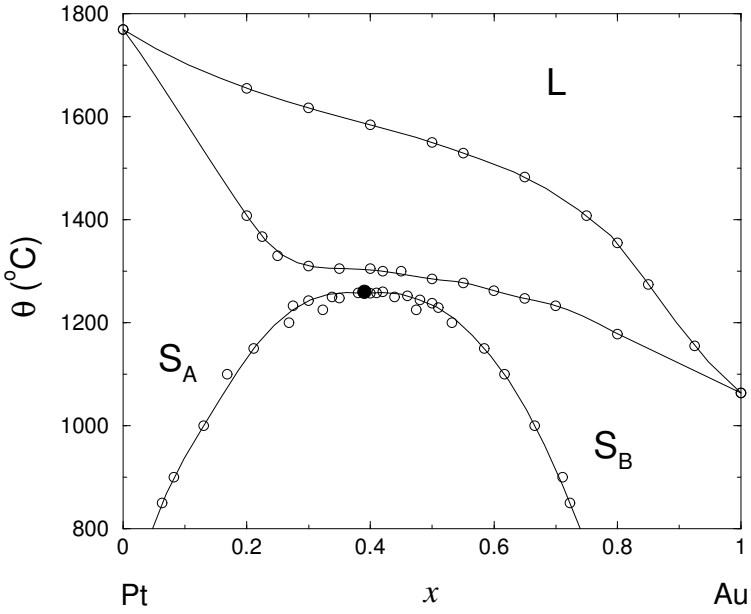


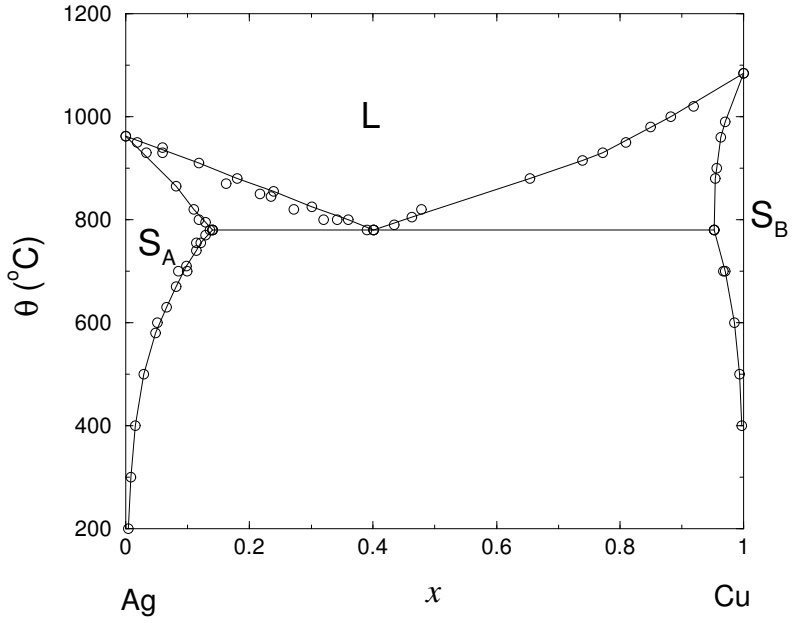


Misturas binárias









Expoentes críticos da transição líquido-líquido

sistema	α	β	γ	θ_c (°C)
ácido isobutírico + água	0,12	0,33	1,24	26,14
nitroetano + isooctano	0,11	0,32		30,03
polistireno + ciclo-hexano	0,14	0,33		30,50
nitroetano + 3-metilpentano	0,14	0,34		26,47
metanol + ciclo-hexano	0,10	0,33		49,1
fenol + água		0,33	1,32	65,87
trietilamina + água	0,11			18,5
tetracloreto de carbono				
+ perfluormetilciclo-hexano		0,33		28,64
anilina + ciclo-hexano		0,33		31
nitrobenzeno + heptano		0,33		18
dissulfeto de carbono + nitrometano		0,32		63,5
ciclo-hexano + anidrido acético		0,32		52,3
gálio + mercúrio		0,34		203,3
nitroetano + hexano			1,19	

Teoria de Hildebrand-Heitler

$$g = wxy + g_1 y + g_2 x + RTy \ln y + RTx \ln x, \qquad y = 1 - x$$

$$\mu = \frac{\partial g}{\partial x} = w(1-2x) + g_2 - g_1 + RT \ln \frac{x}{1-x}$$

equilibrio $\rightarrow$ $\qquad \mu_A = \mu_B, \qquad g_A - \mu_a x_A = g_B - \mu_B x_B$

$$\Delta x - \frac{T}{2T_c} \ln \frac{1+\Delta x}{1-\Delta x} = 0, \qquad \Delta x = x_B - x_A$$

$$(1 - \frac{T}{T_c})\Delta x - \frac{1}{3}(\Delta x)^3 = 0$$

$$\Delta x \sim (T_c - T)^{1/2}$$

Regras das fases de Gibbs

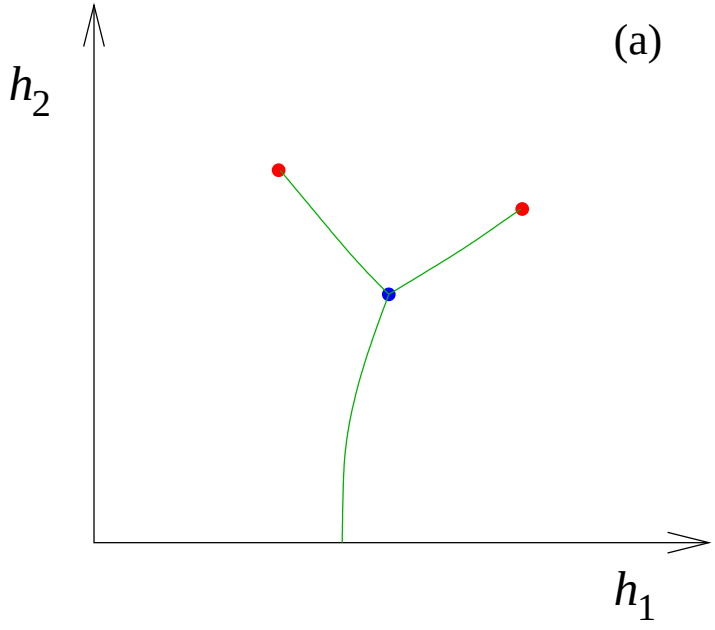
$$f = c + 2 - m$$

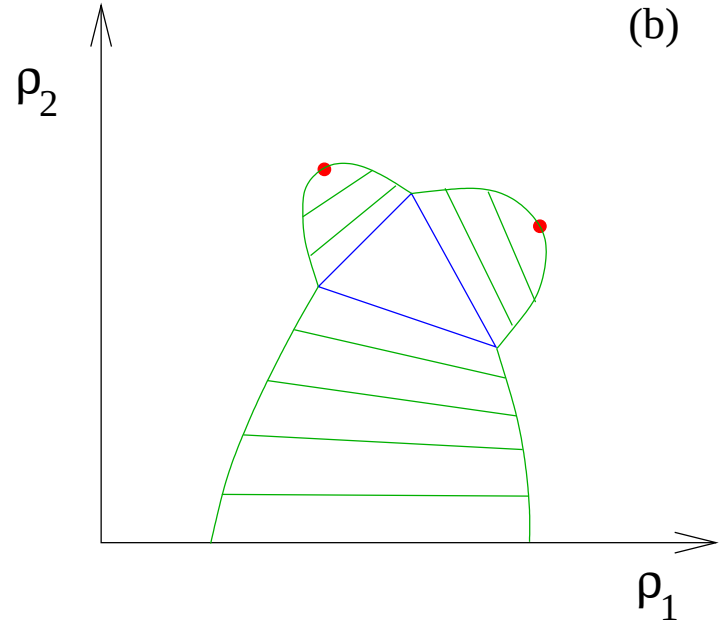
f, número de graus de liberdade (0, ponto; 1, linha; 2, superfície)

m, número de fases termodinâmicas

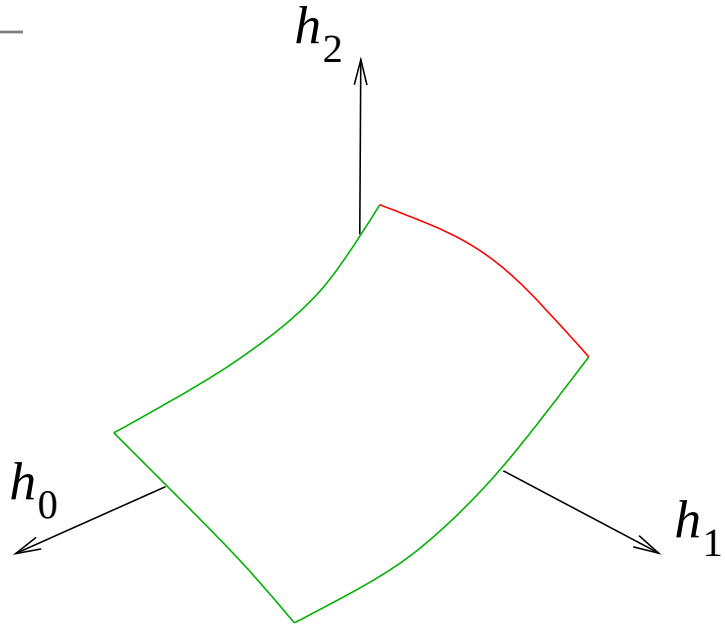
c, número de componentes do sistema ($c + 1$ variáveis independentes).

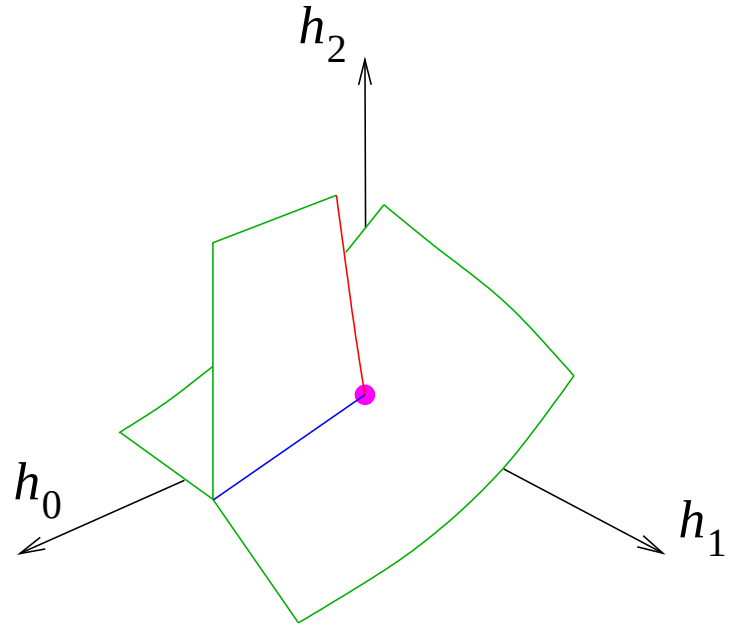
Ponto crítico

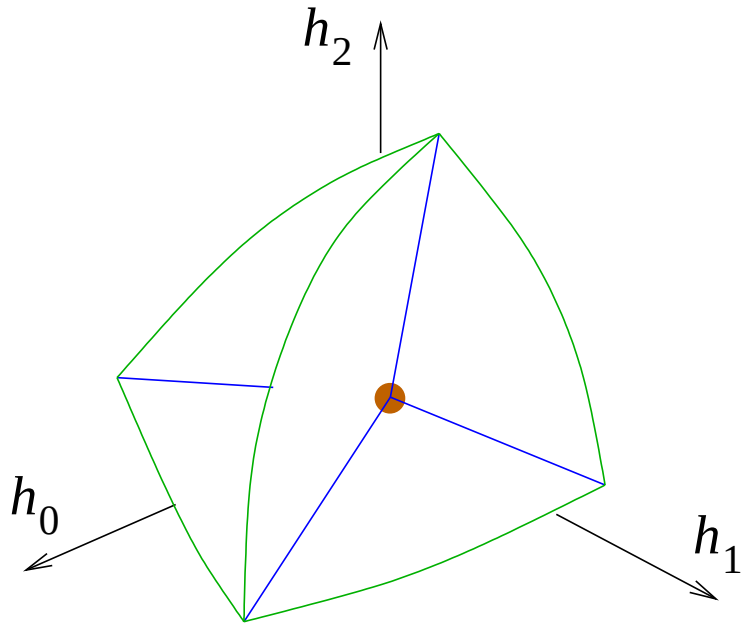




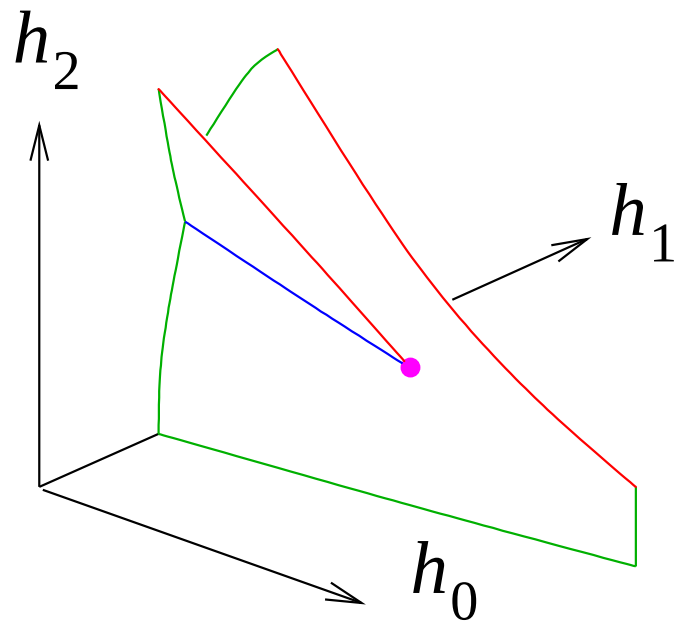
Ponto crítico terminal

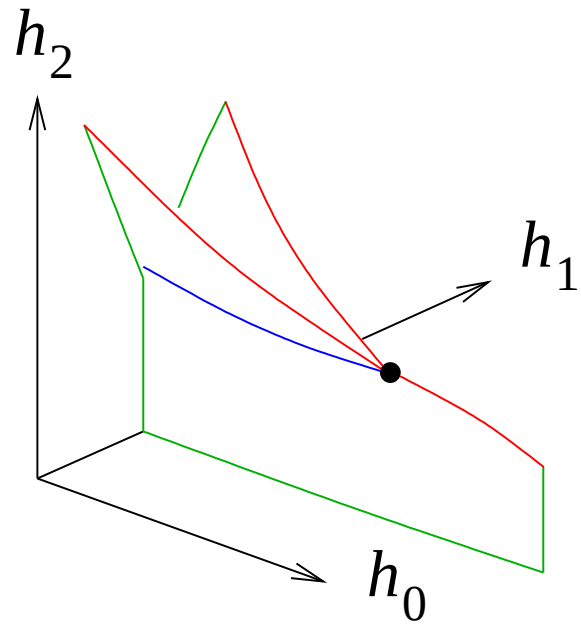


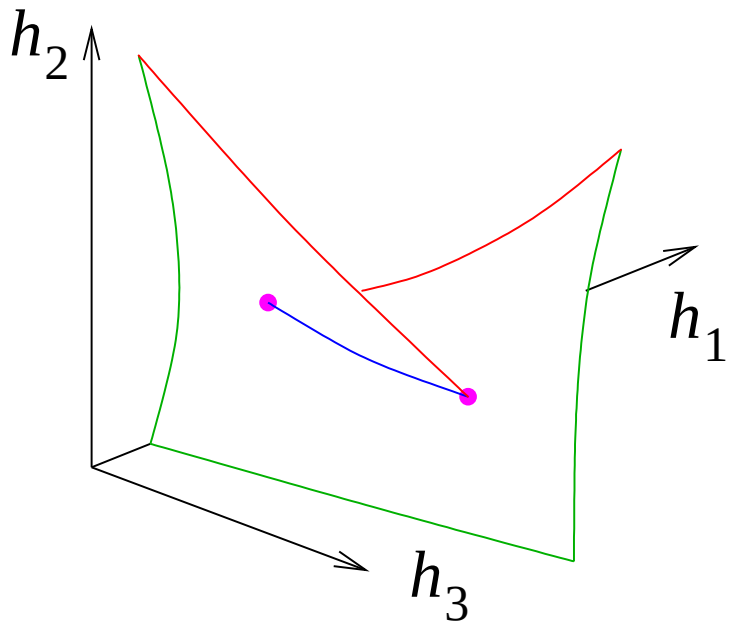


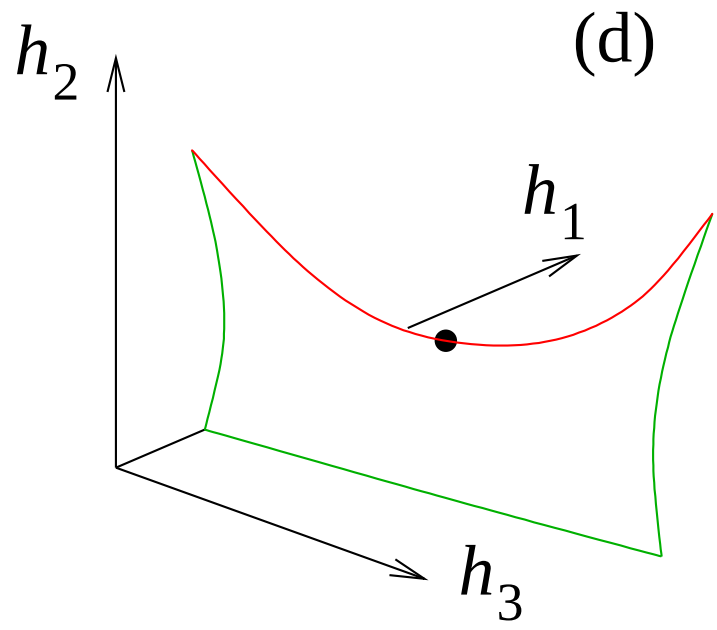


Ponto tricrítico

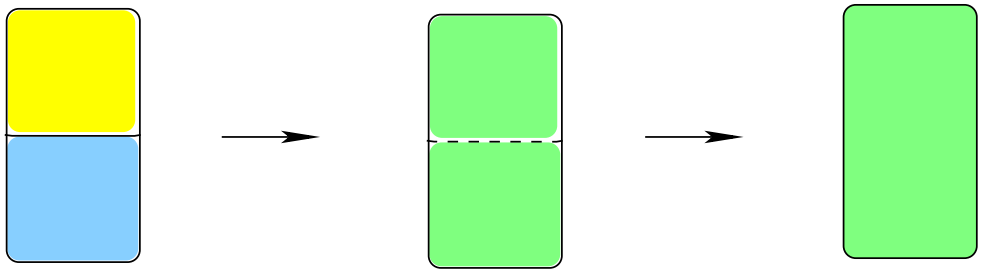




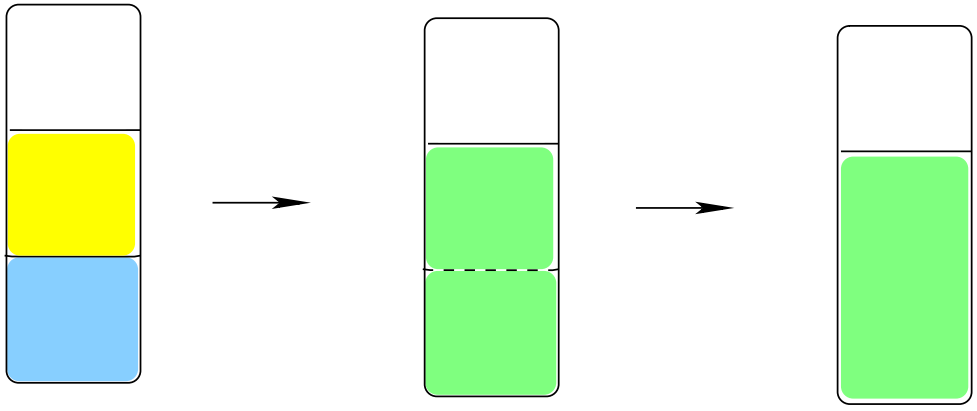




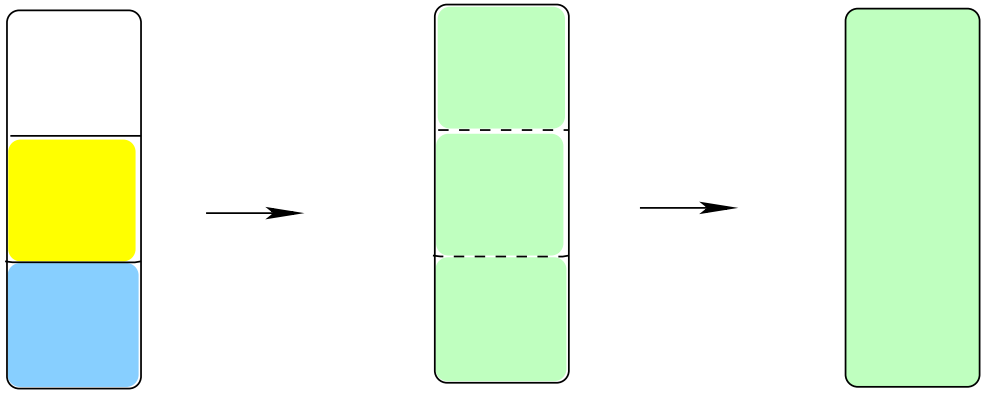
Pontos multicríticos



critico

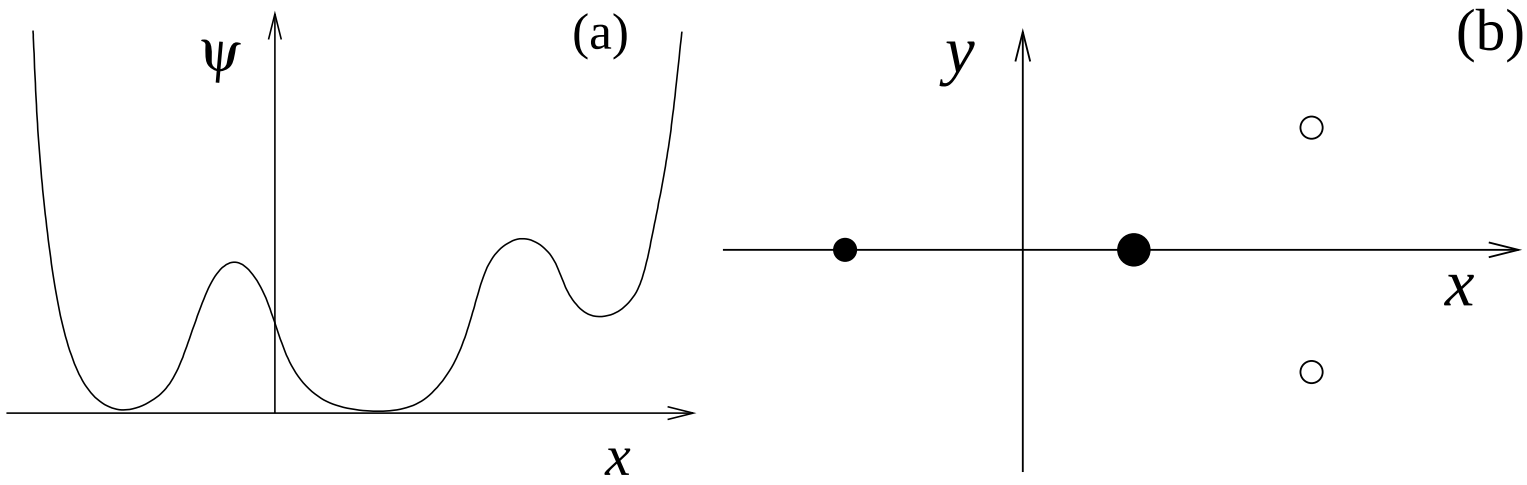


critico terminal



tricritico

Teoria de Griffiths-Landau



Polinômio de Landau

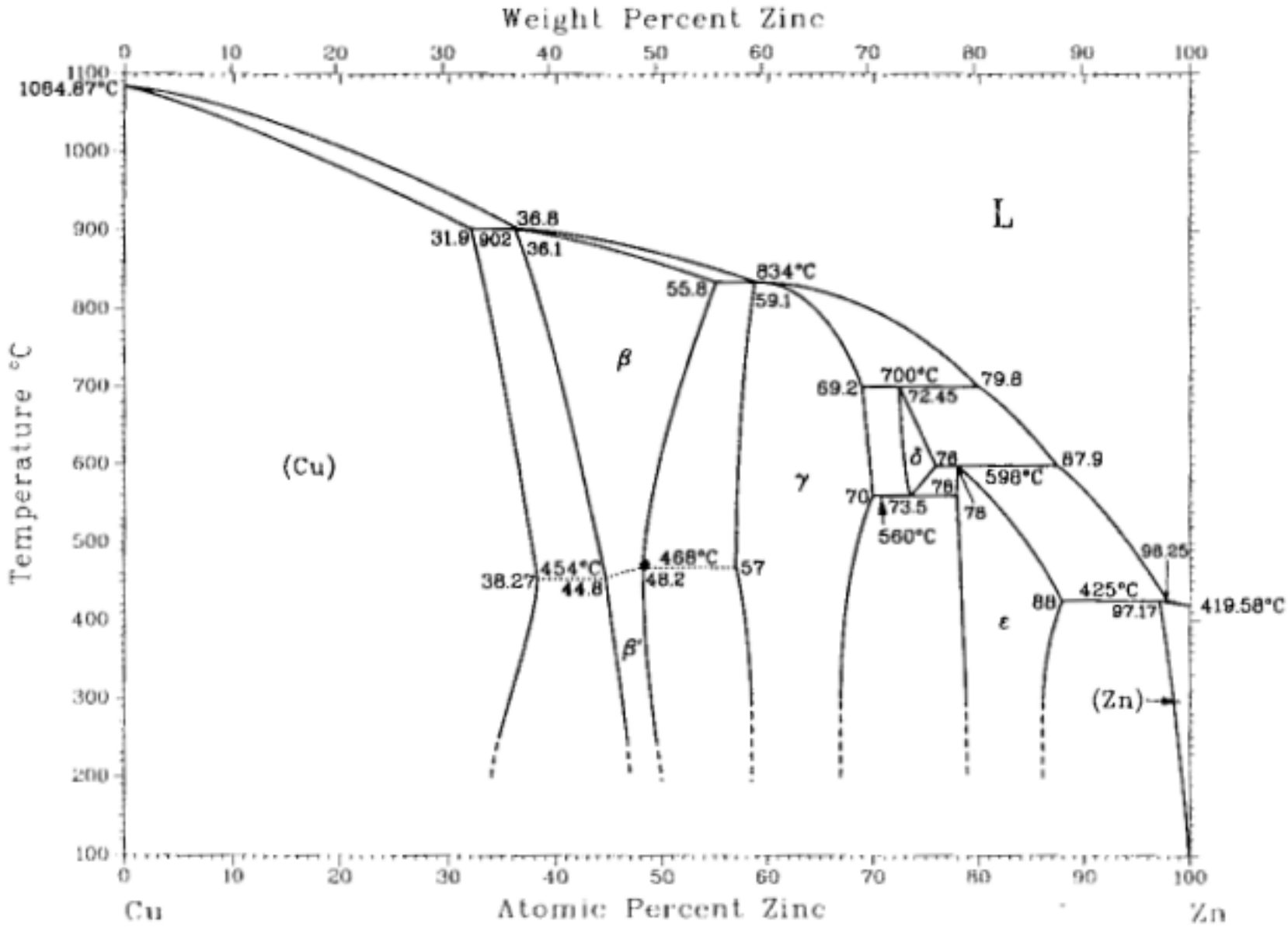
$$\psi(x) = a_0 + a_1 x + a_2 x^2 + \ldots + a_{n-2} x^{n-2} + a_n x^n$$

$$\psi(x) = \psi_{\min} + \tilde{\psi}(x)$$

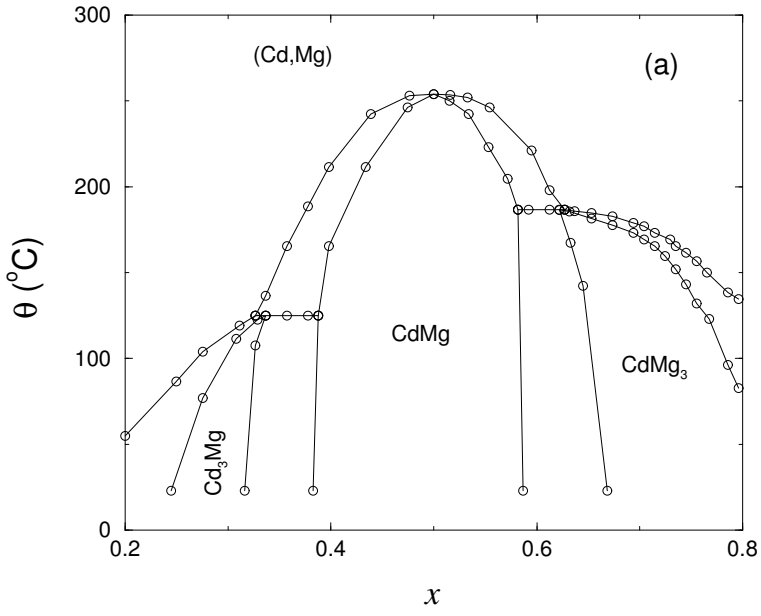
Representação fatorada

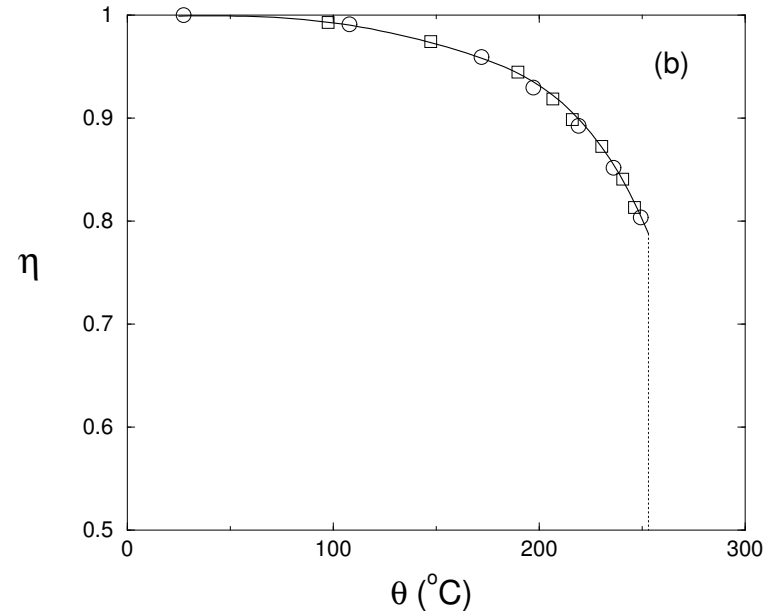
$$\tilde{\psi}(x) = (x - r_1)(x - r_2) \cdots (x - r_n)$$

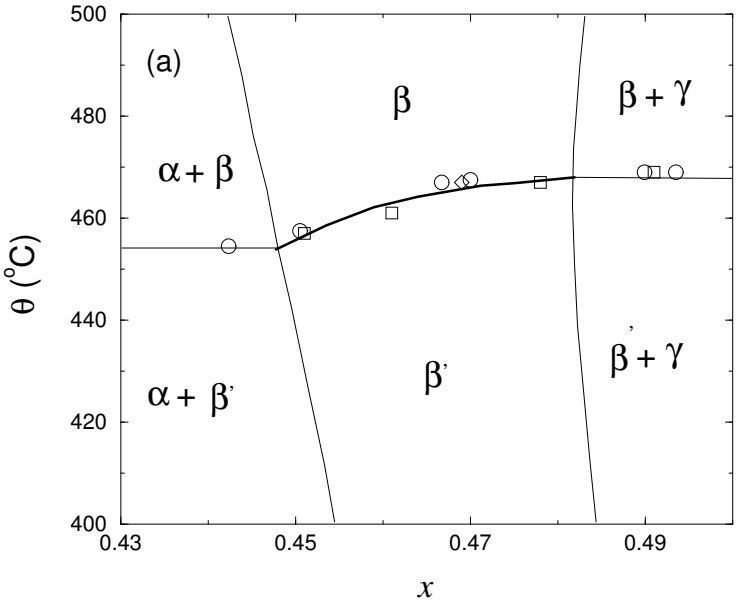
Latão (Cu-Zn)

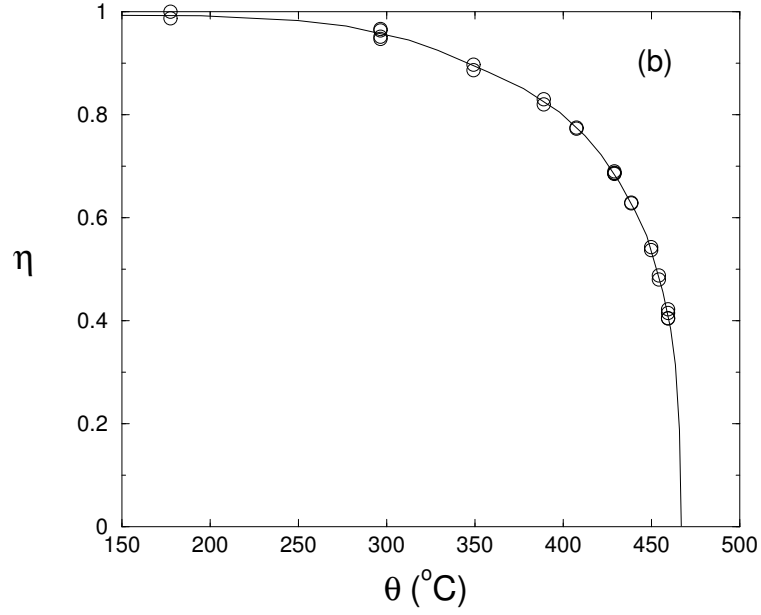

Weight Percent Zinc
0
10
20
30
40
50
60
70
80
90
100
1100
1084.87°C
1000
900
800
700
600
500
400
300
200
100
Temperature °C
L
(Cu)
β
γ
δ
ε
(Zn)
36.8
31.9
902
36.1
834°C
55.8
59.1
700°C
69.2
72.45
79.8
78
598°C
87.9
70
73.5
560°C
78
78
454°C
38.27
44.8
468°C
48.2
57
β'
98.25
425°C
88
97.17
419.58°C
Cu
Atomic Percent Zinc
Zn

Ligas: transição ordem-desordem

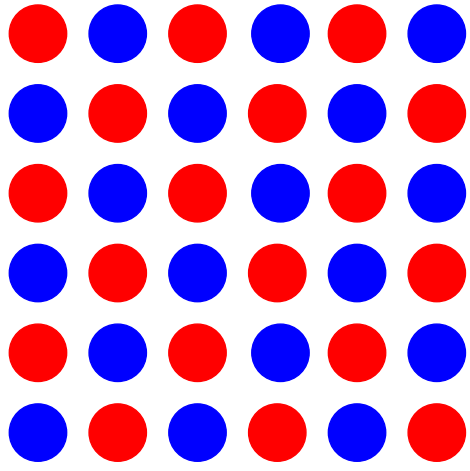


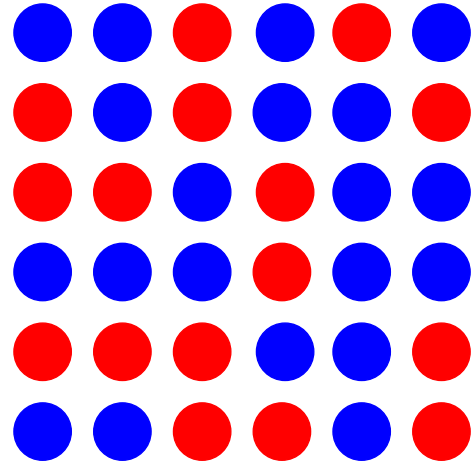


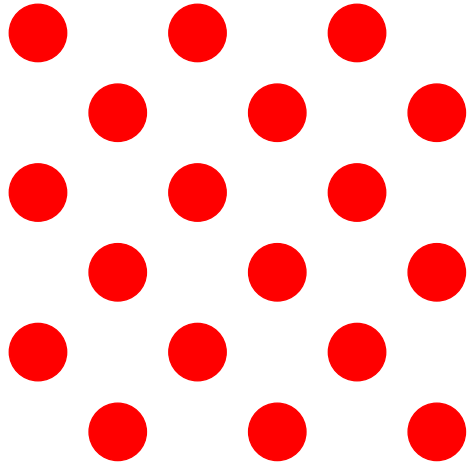


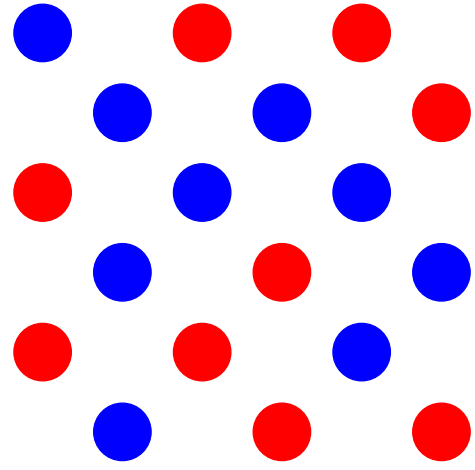


Duas subredes

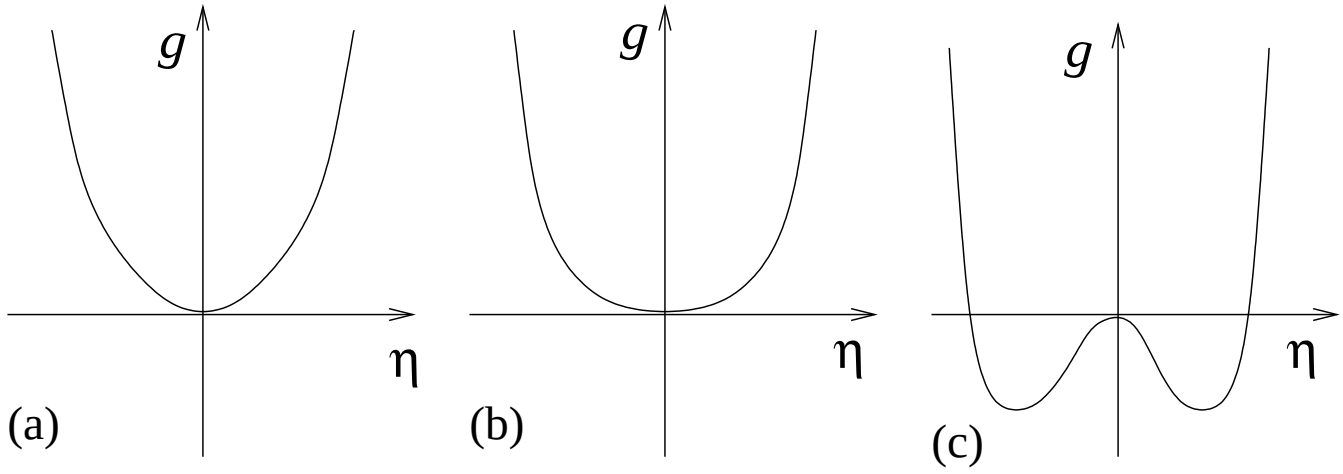








Teoria de Landau



$$g = a_0 + a_2\eta^2 + a_4\eta^4$$

$$a_2 = A(T - T_c) \qquad\qquad a_4 > 0$$

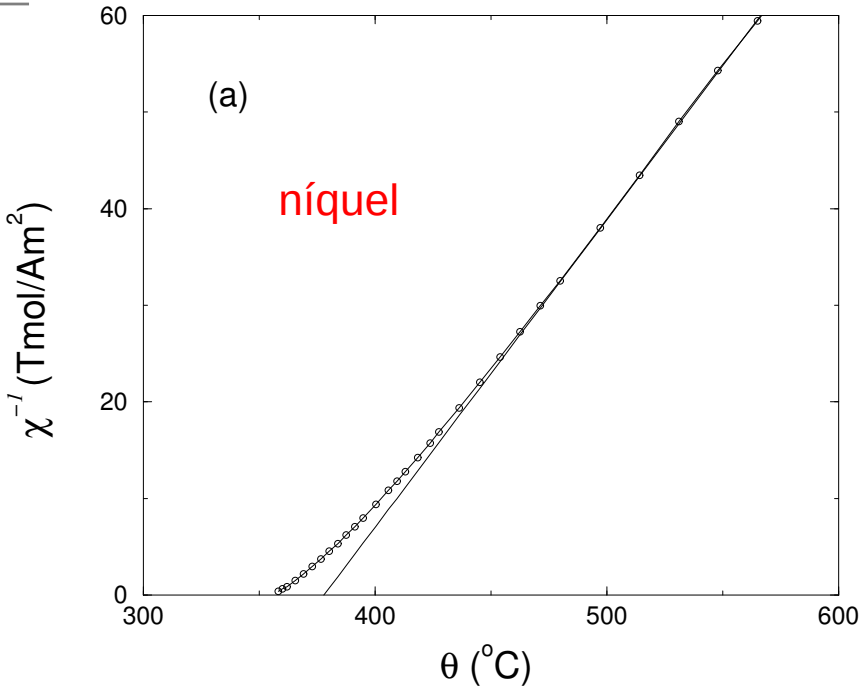
$$\frac{\partial g}{\partial \eta} = 2a_2\eta + 4a_4\eta^3 = 0$$

$$\eta = \pm\sqrt{\frac{|a_2|}{2a_4}} \qquad\qquad \eta \sim |T - T_c|^{1/2}$$

Expoentes críticos da transição ordem-desordem

liga	α	β	γ
CuZn, latão	0,11	0,31	1,25
Fe_3Al		0,31	
FeCo		0.30	

Ferromagnetismo

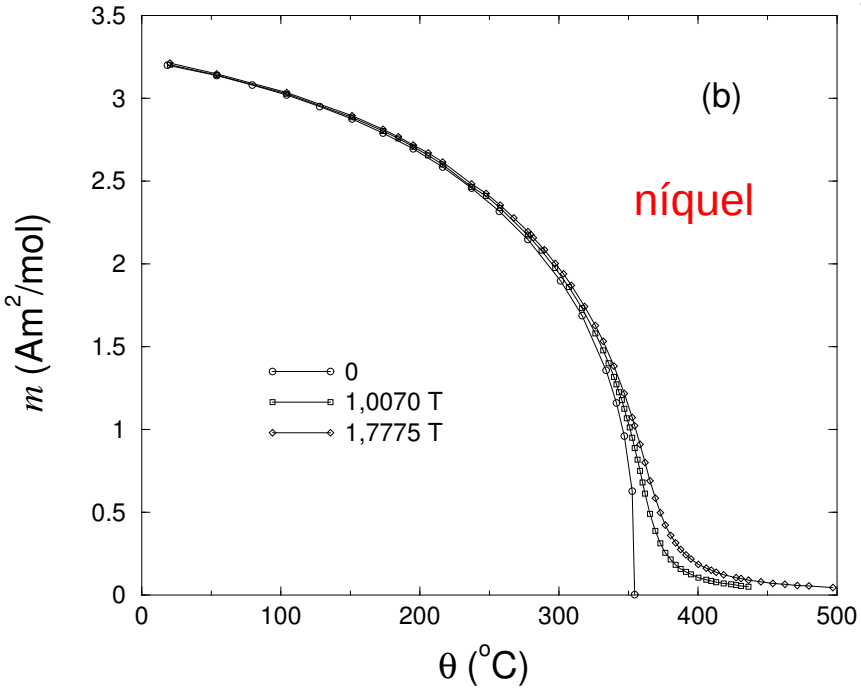


Susceptibilidade

$$\chi \sim (T - T_c)^{-\gamma}$$

Lei de Curie-Weiss

$$\chi = \frac{C}{T - \Theta}$$

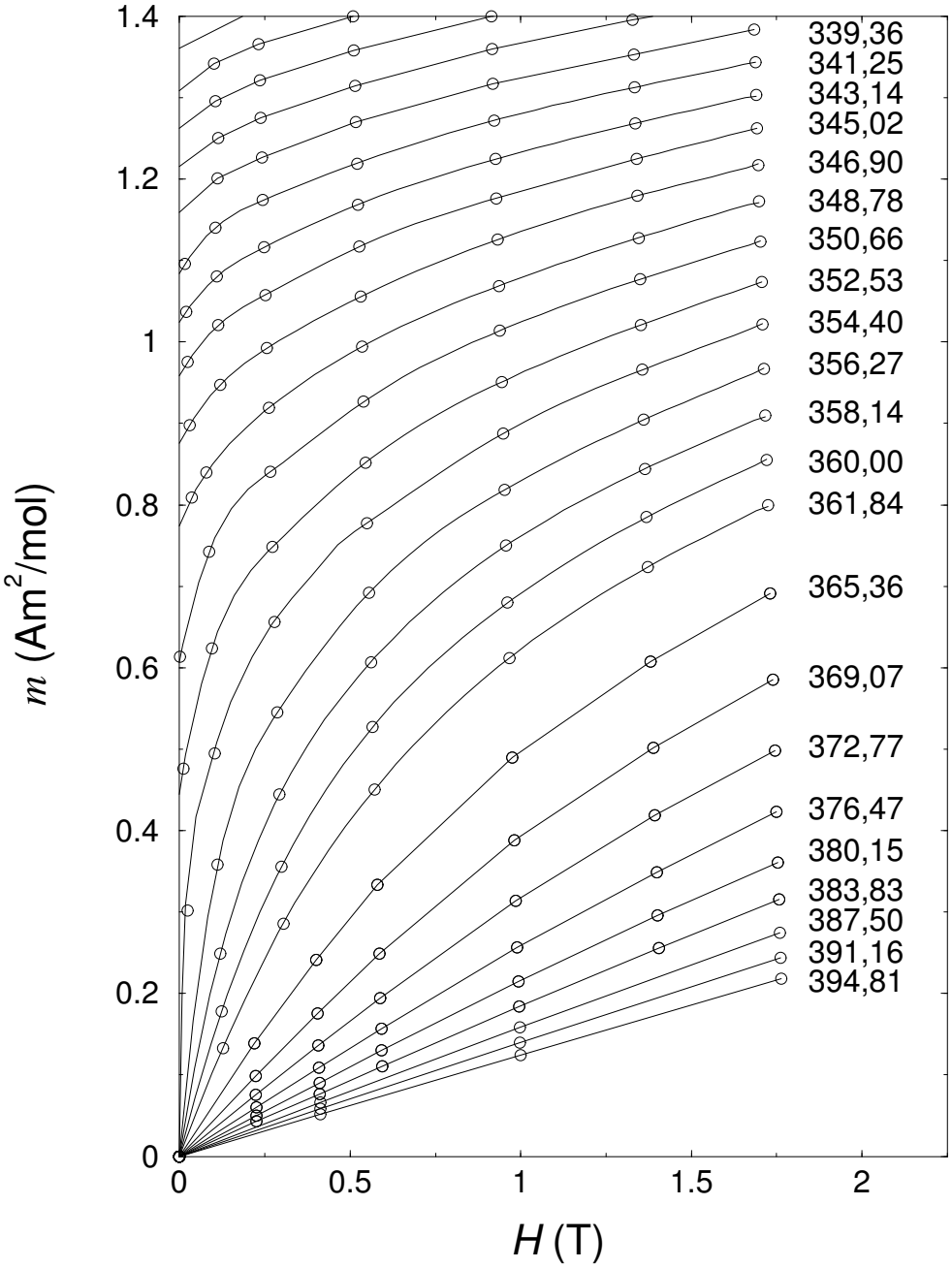


Magnetização

$$m \sim (T_c - T)^{\beta}$$

Weiss e Forrer (1926)

Magnetização versus campo

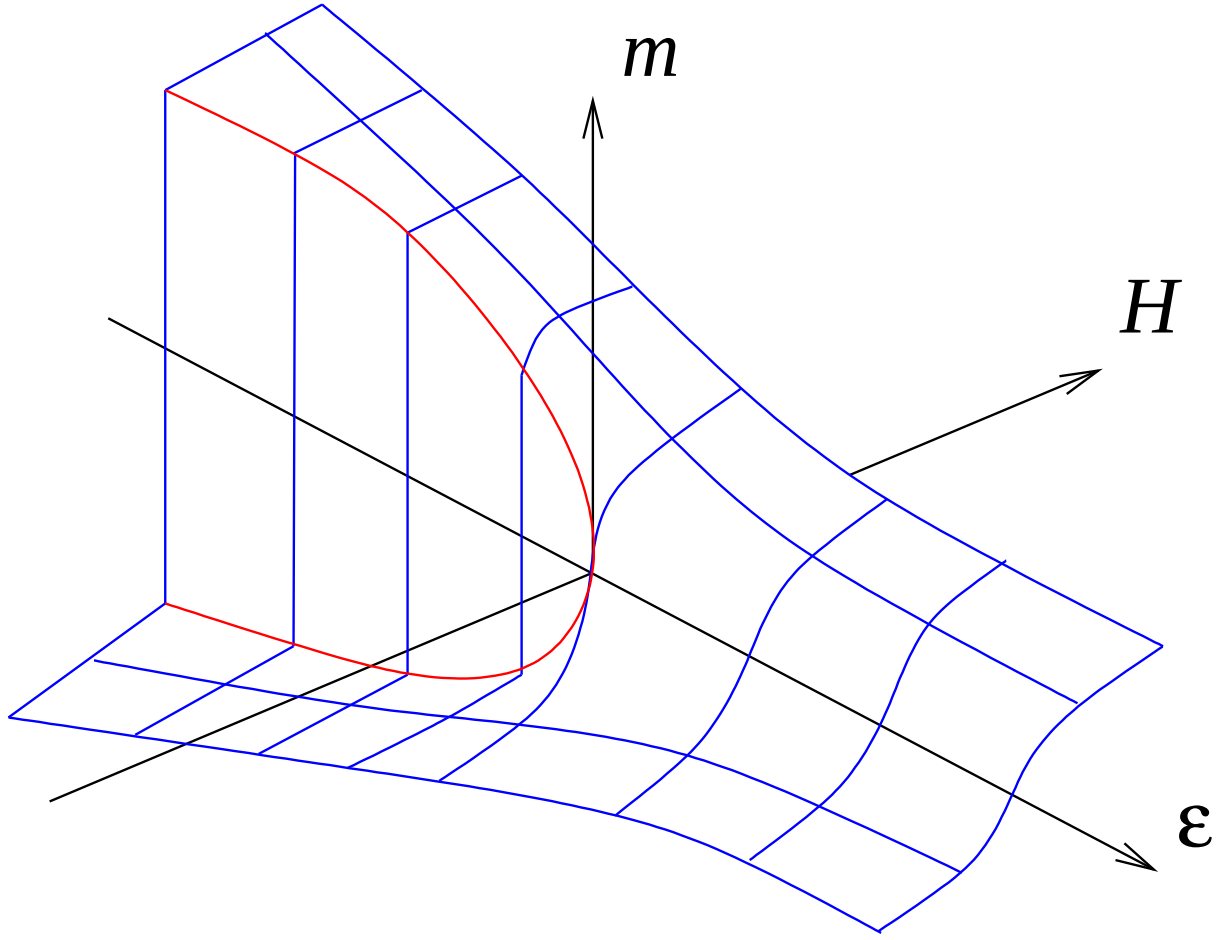


Níquel

Isotermas obtidas experimentalmente por

Weiss e Forrer (1926)

Vizinhança do ponto crítico



$$\varepsilon = T - T_c$$

Teoria de Weiss-Landau

$$f = f_0 + \frac{a}{2}\varepsilon m^2 + \frac{b}{4}m^4$$

$$a > 0, \qquad b > 0, \qquad \varepsilon = T - T_c$$

$$H = \frac{\partial f}{\partial m} = a\varepsilon m + bm^3$$

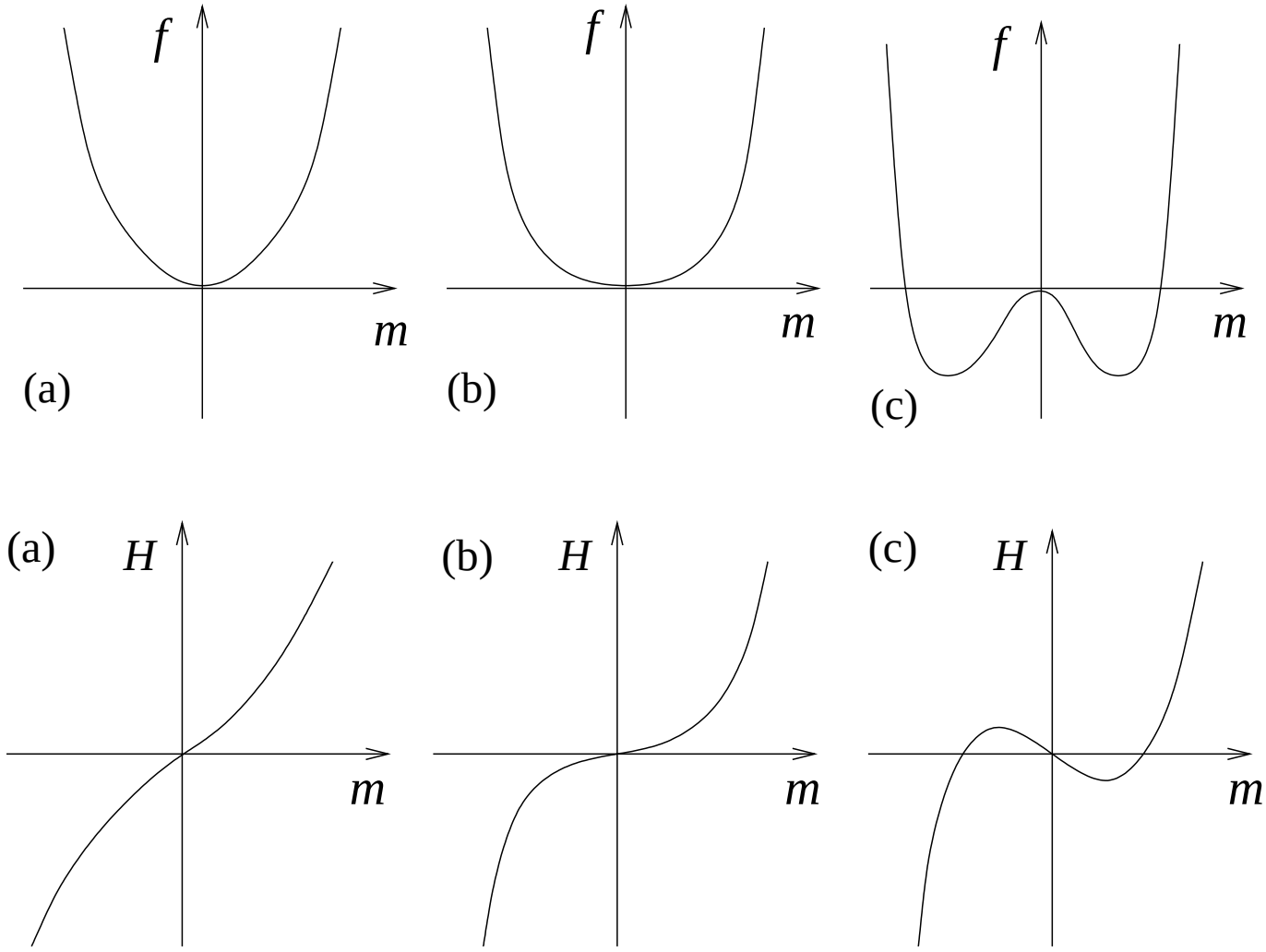
Quando $H = 0$

$$m = 0, \qquad \varepsilon \geq 0 \qquad\qquad m = \pm m^*, \qquad \varepsilon < 0$$

$$m^* = (\frac{a|\varepsilon|}{b})^{1/2} \sim |T - T_c|^{1/2}$$

$$\chi = \frac{\partial m}{\partial H} \sim |T - T_c|^{-1}$$

Teoria de Weiss-Landau

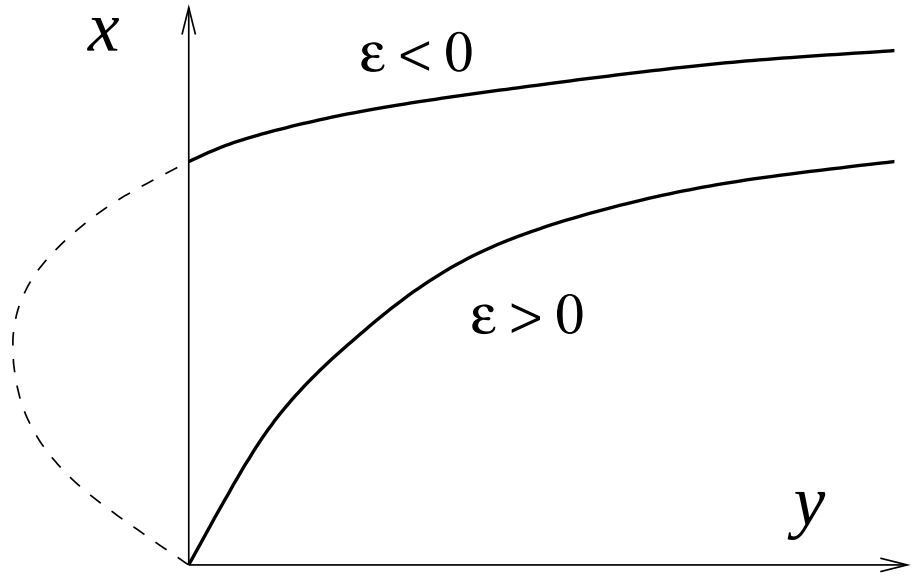


Teoria de escala

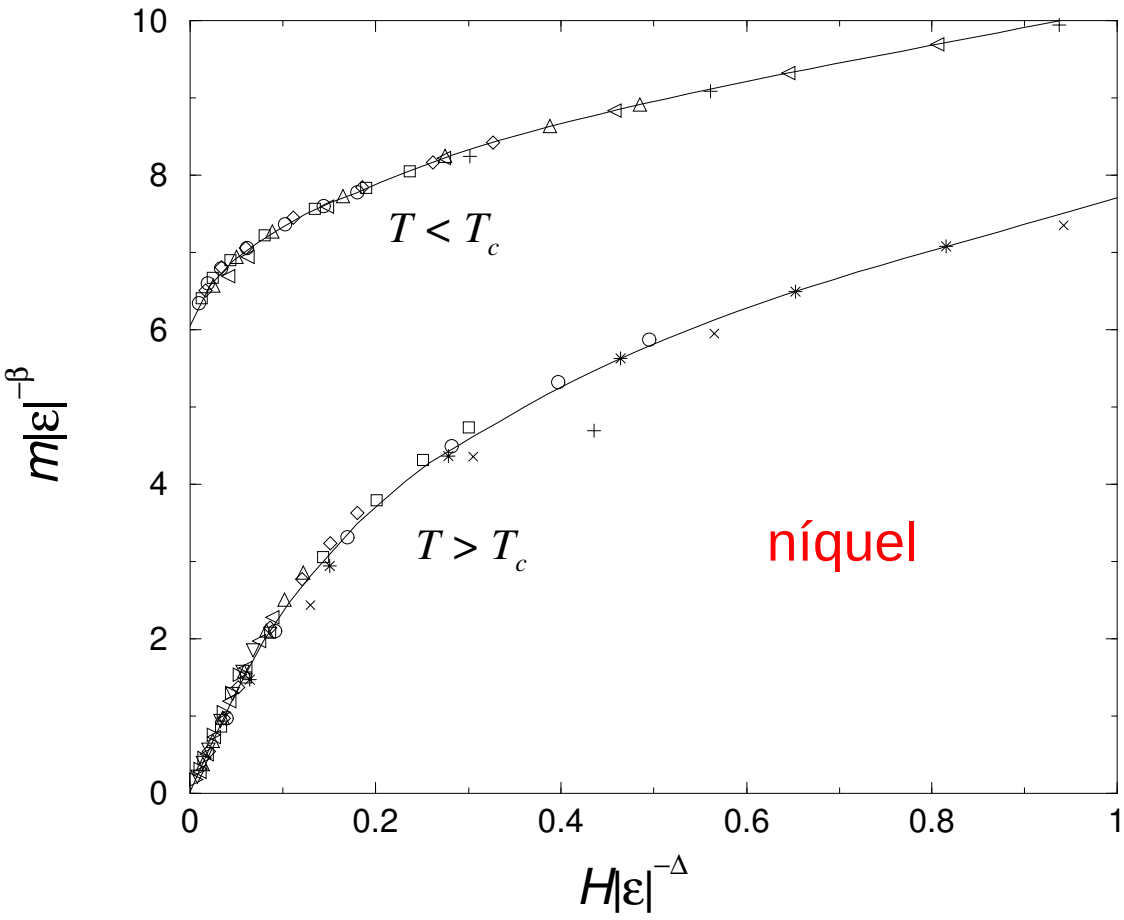
$$H = a\varepsilon m + bm^3$$

$$y = H|\varepsilon|^{-3/2} \qquad x = m|\varepsilon|^{-1/2}$$

$$y = -ax + \frac{b}{3}x^3 \qquad \varepsilon \geq 0 \qquad\qquad y = +ax + \frac{b}{3}x^3 \qquad \varepsilon < 0$$

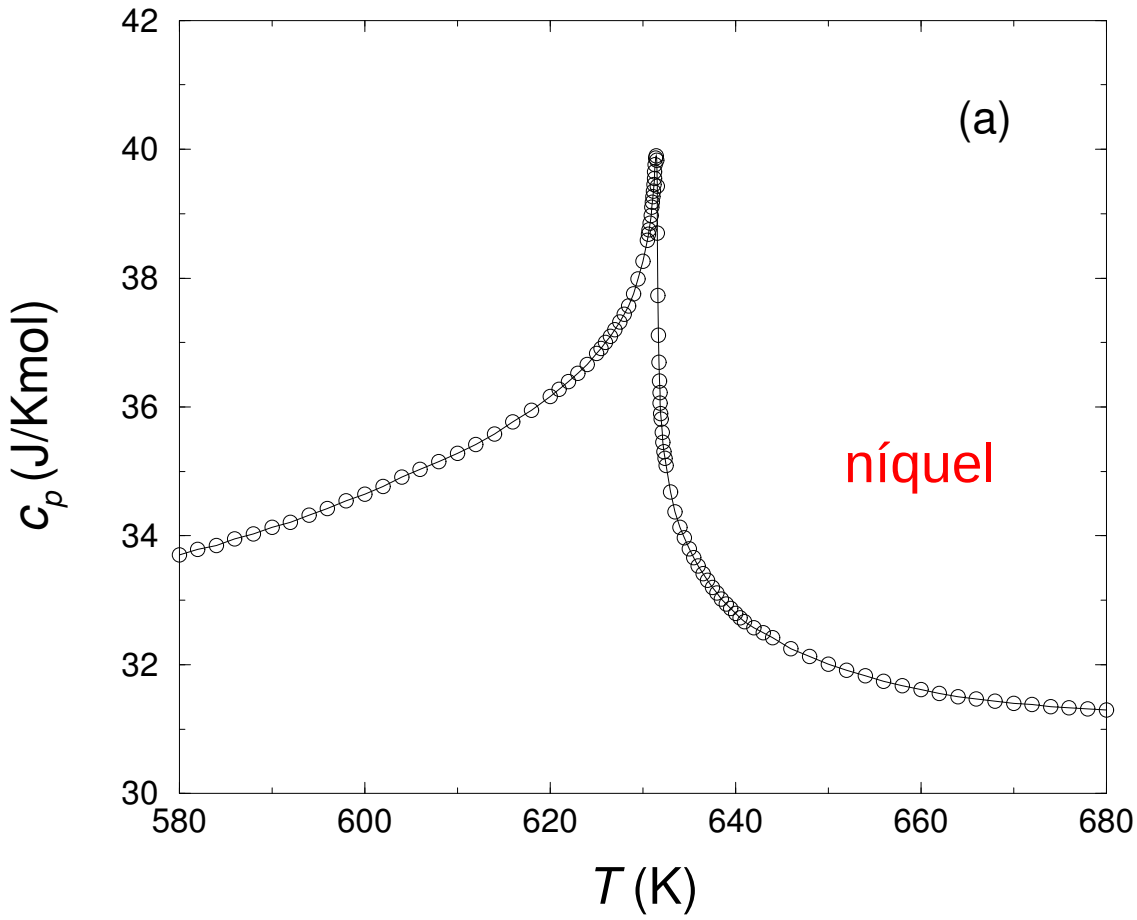


Teoria de escala



$$m = \varepsilon^{\beta}\phi(H\varepsilon^{-\Delta})$$

Calor específico



$$c_0 - c_p \sim \varepsilon^{-\alpha} \qquad \alpha = -0,1 \qquad \text{cuspide}$$

Dados experimentais de Connely et al. (1971).

Expoentes críticos da transição ferro-paramagnética

ferromagnetos	α	β	γ	δ	T_c (K)
Fe	-0,12	0,39	1,34	4,2	1043
Ni	-0,10	0,38	1,34	4,6	631
Co		0,42	1,23		1395
$CrBr_3$		0,37	1,22	4,3	32,7
EuO	-0,04	0,37	1,40	4,5	69,4
EuS	-0,13	0,36	1,39		16,4
$Cu(NH_4)_2Cl_4{\cdot}2H_2O$			1,37		0,701
$CuK_2Cl_4{\cdot}2H_2O$			1,36		0,877
$Cu(NH_4)_2Br_4{\cdot}2H_2O$		0,38	1,33	4,3	1,83
$CuRb_2Br_4{\cdot}2H_2O$		0,37			1,87
$CuCs_2Cl_4{\cdot}2H_2O$			1,33		

$$|c_H - c_0| \sim |\Delta T|^{-\alpha} \qquad \Delta m \sim |\Delta T|^{\beta} \qquad \chi_T \sim |\Delta T|^{-\gamma} \qquad H \sim m^{\delta}$$

Antiferromagnetismo

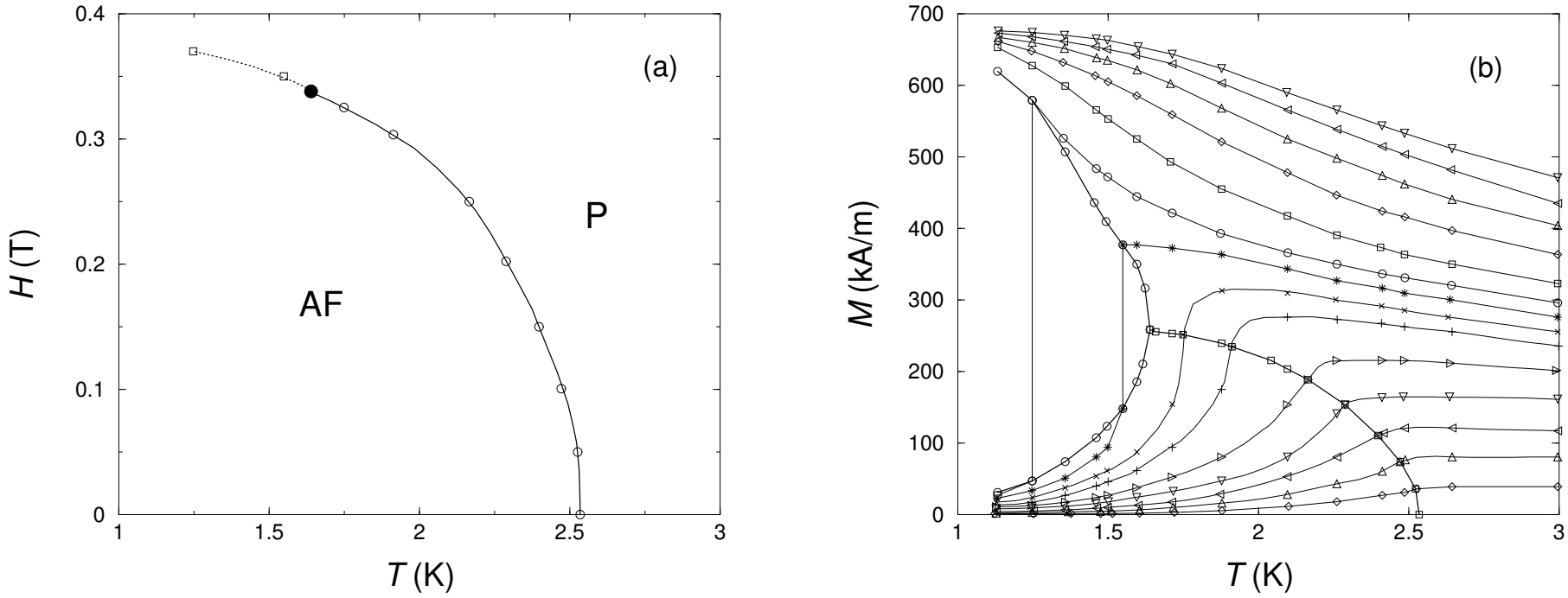


Diagrama de fase do composto metamagnético $Dy_3Al_5O_{12}$.
Dados experimentais de Landau, Keen, Schneider e Wolf (1970).
(a) Campo versus temperatura. (b) Magnetização volumétrica versus temperatura.

$$g = a_0 + a_2\eta^2 + a_4\eta^4 + a_6\eta^6$$

Ponto bicrítico

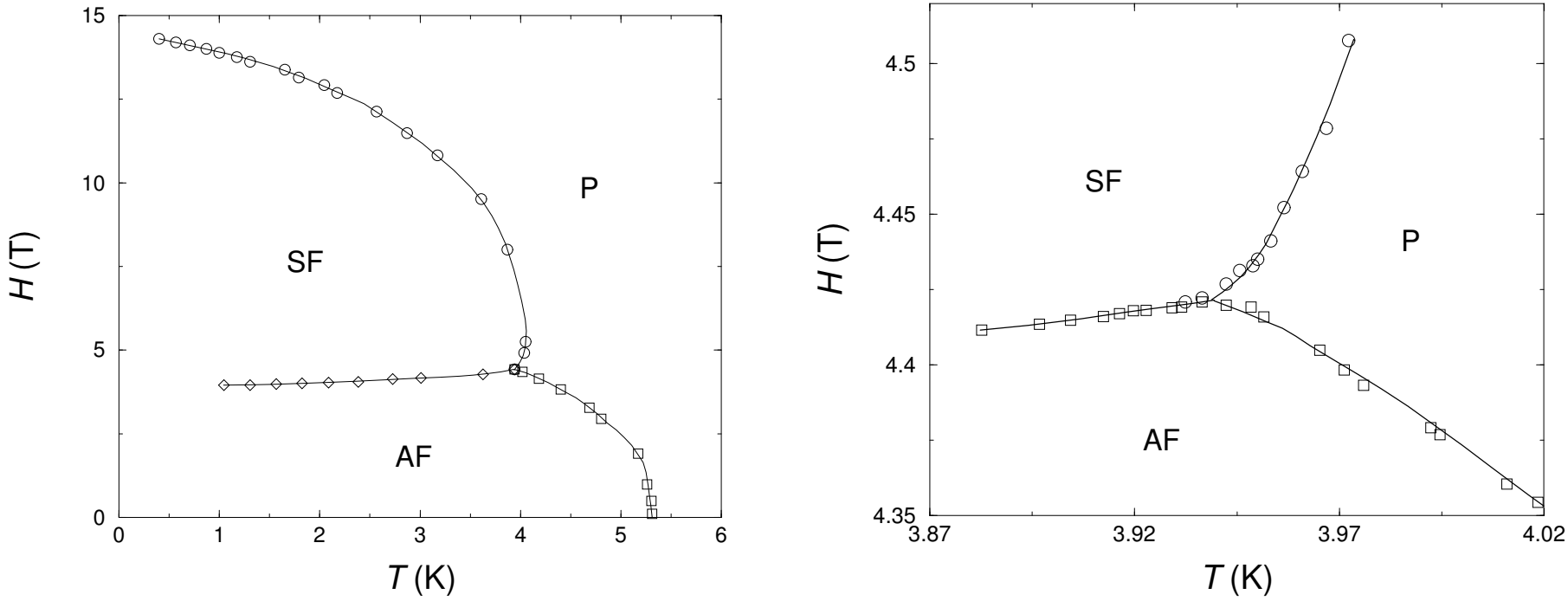
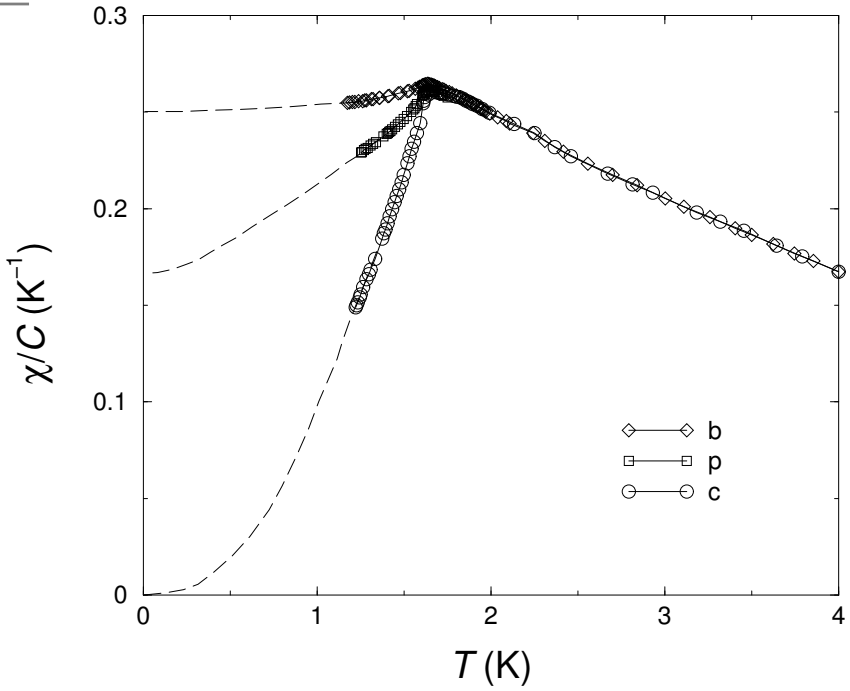


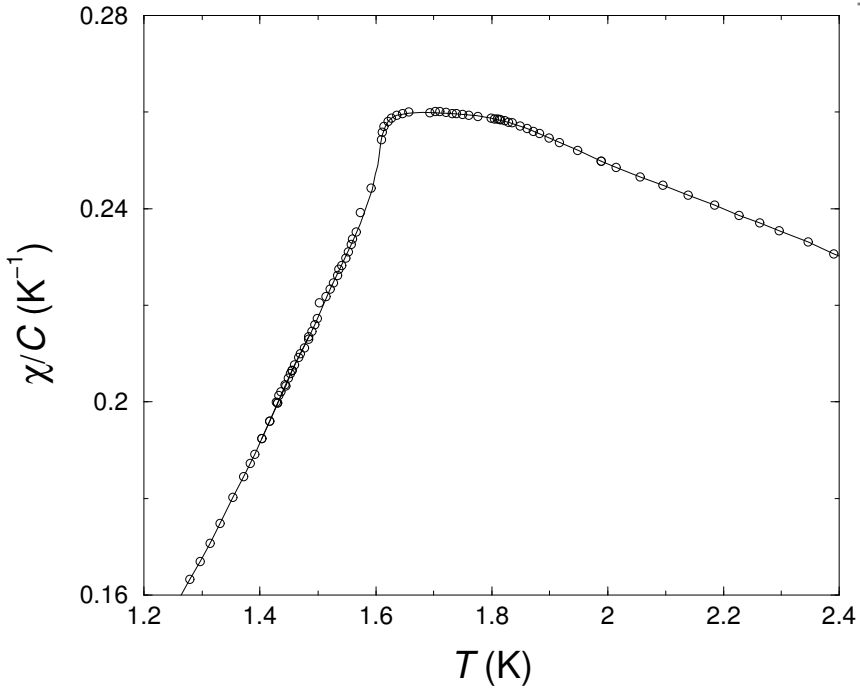
Diagrama de fase do sal antiferromagnético $NiCl_2 \cdot 6H_2O$.

Dados experimentais de Oliveira, Paduan e Salinas (1975).

$$g = a_{00} + a_{20}\eta^2 + a_{20}\omega^2 + a_{40}\eta^4 + a_{22}\eta^2\omega^2 + a_{04}\omega^4$$

Susceptibilidade





Susceptibilidade do composto antiferromagnético $MnCl_2 \cdot 4H_2O$.

Dados experimentais de Lasher, van den Broek e Gorter (1958).

c: paralela ao eixo preferencial,

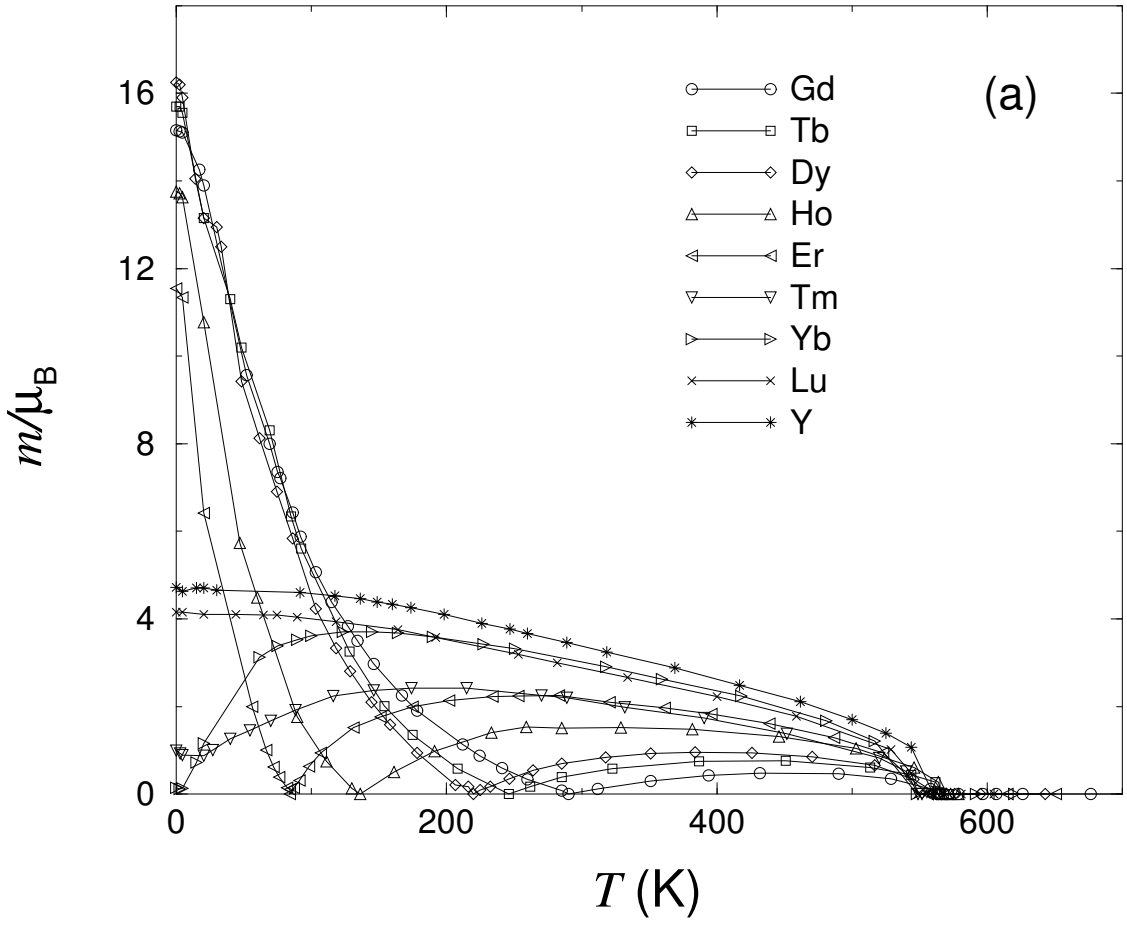
b: perpendicular ao eixo preferencial,

p: susceptibilidade do pó.

Expoentes críticos da transição antiferro-paramagnética

composto	α	β	γ	T_N
$RbMnF_3$	$-0{,}14$	0,32	1,37	83,1
MnF_2		0,34	1,27	67,3
FeF_2	+0,14	0,33	1,25	78,3
$DyPO_4$		0,31		3,39
$DyAlO_3$		0,31		3,52

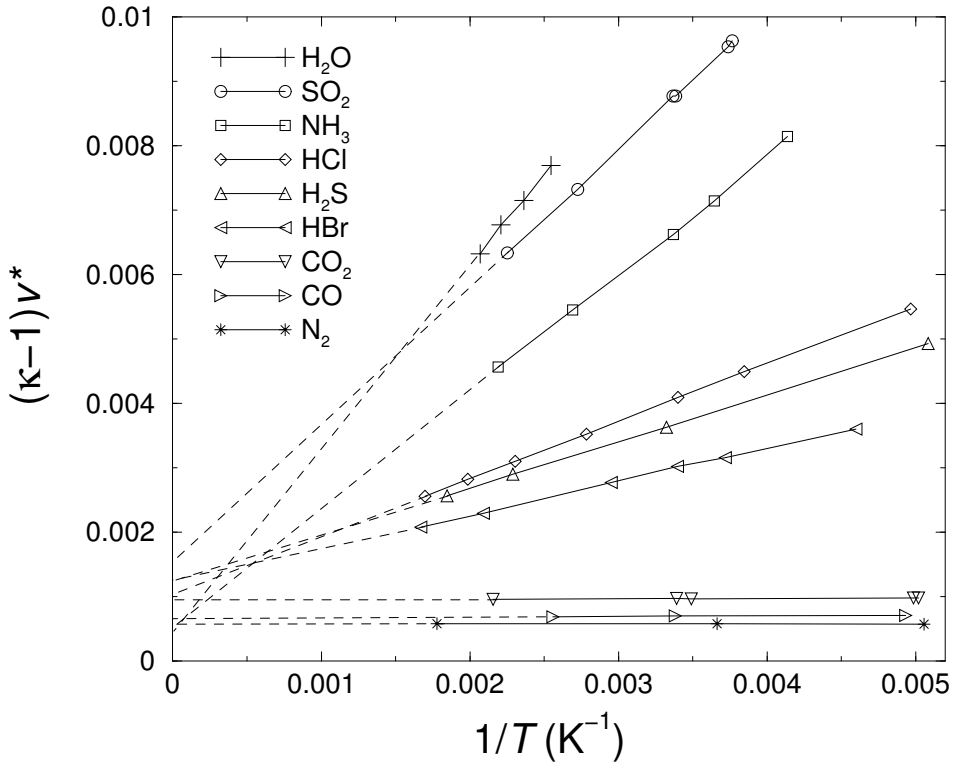
Ferrimagnetismo



Magnetização espontânea molar das granadas de ferro $M_3Fe_5O_{12}$, em que M é um metal das terras-raras ou o Ítrio.

Dados experimentais de Pauthenet (1958).

Dielétricos



Lei de Debye

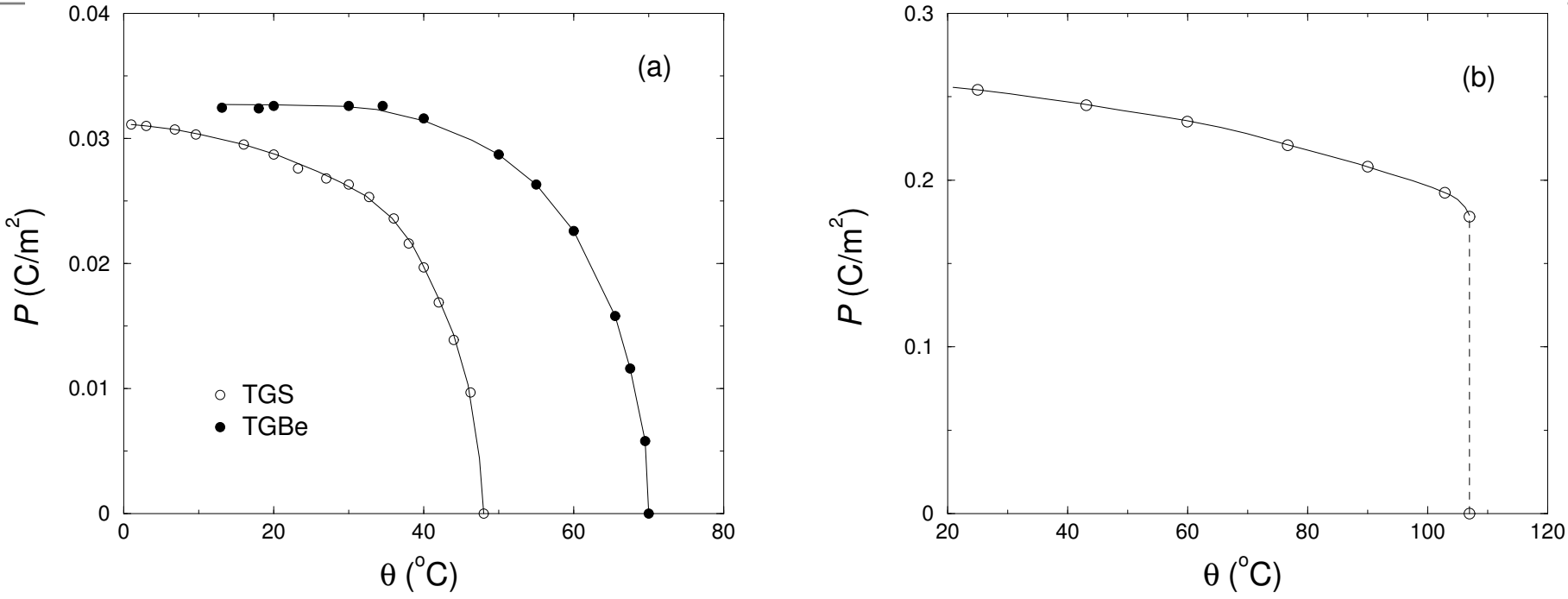
$$\chi = \alpha + \frac{p_0^2}{3RT}$$

Susceptibilidade elétrica

$$\chi = (\kappa - 1)v\epsilon_0$$

Constante dielétrica κ de gases obtidos experimentalmente por Zahn (1924), Zahn (1926) e Zahn e Miles (1928)
e do vapor d´água obtida experimentalmente por Sangers et al. (1932).
$v^* = v/v_0$ onde v é o volume molar do gas e v_0 é o volume molar de um gás ideal à pressão de 1 atm e 0 °C.

Ferroeletricidade

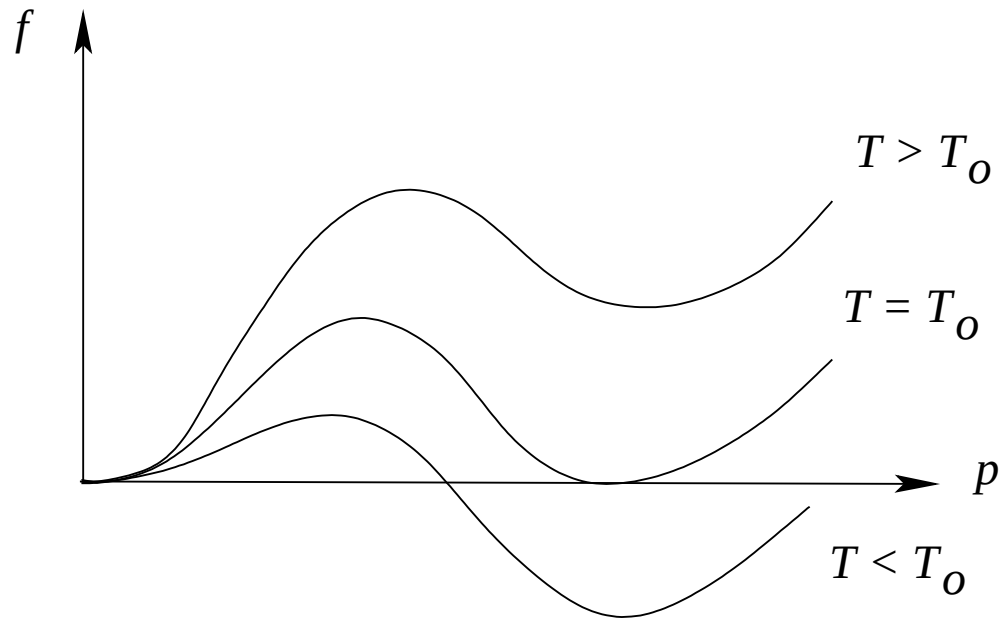


(a) Polarização espontânea do sulfato de triglicina (TGS) e do flúor-berilato de triglicina (TGBe).
Dados experimentais de Hoshino et al. (1957).
(b) Polarização espontânea do titanato de bario.
Dados experimentais de Merz (1953).

Teoria de Devonshire

$$f = f_0 + b(T - T_1)p^2 - cp^4 + dp^6$$

As constantes b, c e d são positivas. O coeficiente negativo de p^2 garante que a transição seja descontínua.



Cristais líquidos

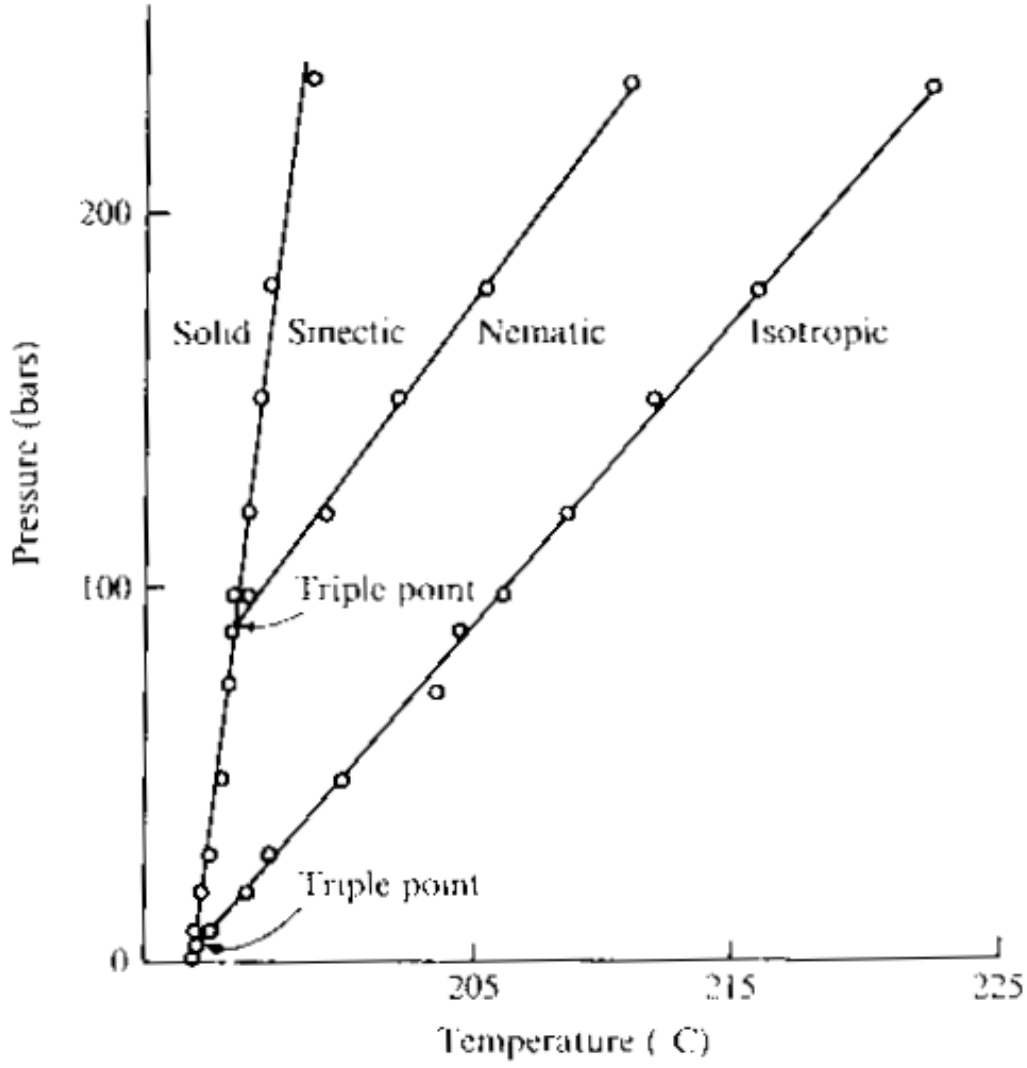


Diagrama de fase para o ácido p-etoxibenzóico,

S. Chandrasekhar, Liquid Crystals, 1977.

Teoria de Landau - de Gennes

$$Q = \begin{pmatrix} Q_1 & 0 & 0 \\ 0 & Q_2 & 0 \\ 0 & 0 & Q_3 \end{pmatrix} \qquad \mathrm{Tr}\, Q = Q_1 + Q_2 + Q_3 = 0$$

$$Q_1 = -\frac{1}{2}(q + \eta) \qquad Q_2 = -\frac{1}{2}(q - \eta) \qquad Q_3 = q$$

$$f = f_0 + a_2\,\delta + a_3\,\Delta + a_4\,\delta^2 + a_5\,\delta\Delta + a_6\,\Delta^2 + a_6'\,\delta^3$$

$$\delta = \mathrm{Tr}\, Q^2 = \frac{1}{2}(3q^2 + \eta^2)$$

$$\Delta = \mathrm{Tr}\, Q^3 = \frac{3}{4}q(q^2 - \eta^2)$$

Cristais líquidos nemáticos

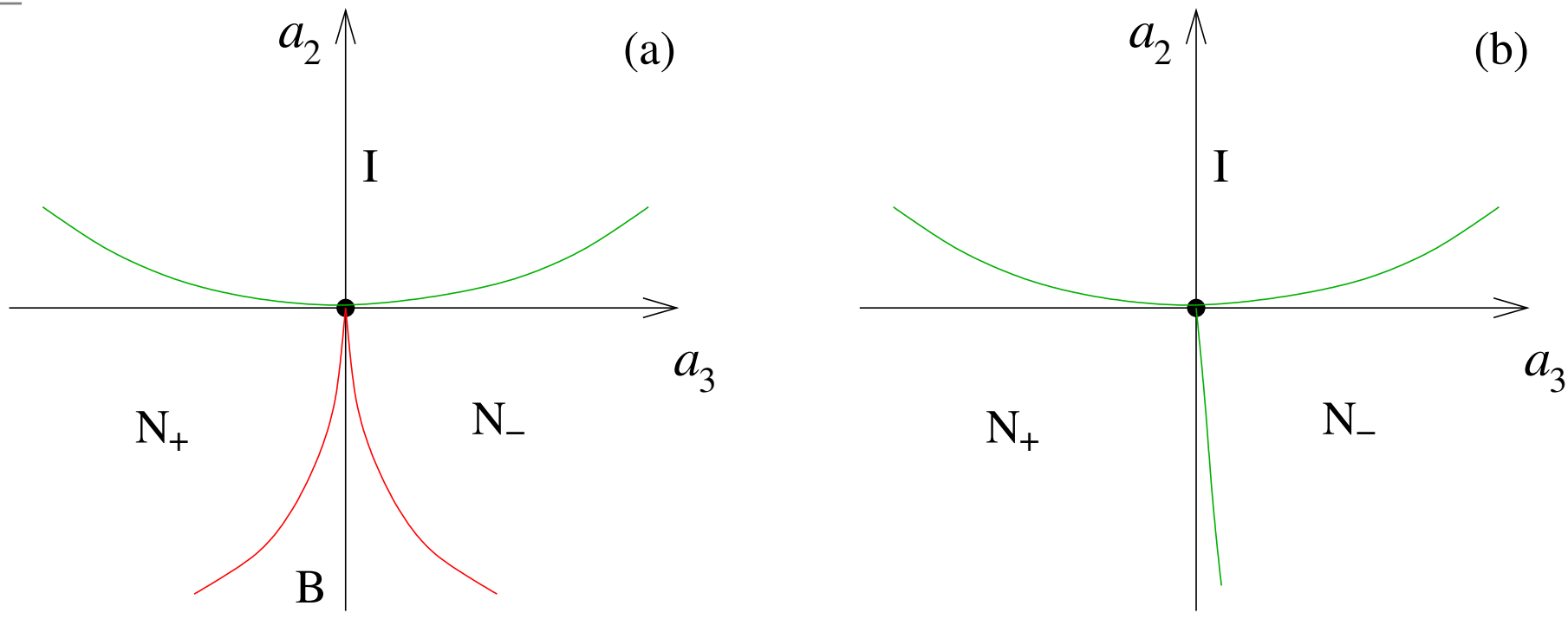


Diagrama de fase de acordo com a teoria de Landau-de Gennes.

I: fase isotrópica

N_+ e N_-: fases nemáticas uniaxiais

B: fase nemática biaxial.

Cristais líquidos esméticos

$$\psi = \sigma e^{i\varphi}$$

$$\rho = \rho_0 + \sigma \cos(\frac{2\pi}{L} z + \varphi) = \rho_0 + \sigma \cos(\frac{2\pi}{L} z + \varphi)$$

$$f = f_0 + a_2 q^2 + a_3 q^3 + a_4 q^4 + b_2 \sigma^2 + b_4 \sigma^4 - c_4 q^2 \sigma^2$$

Cristais líquidos esméticos

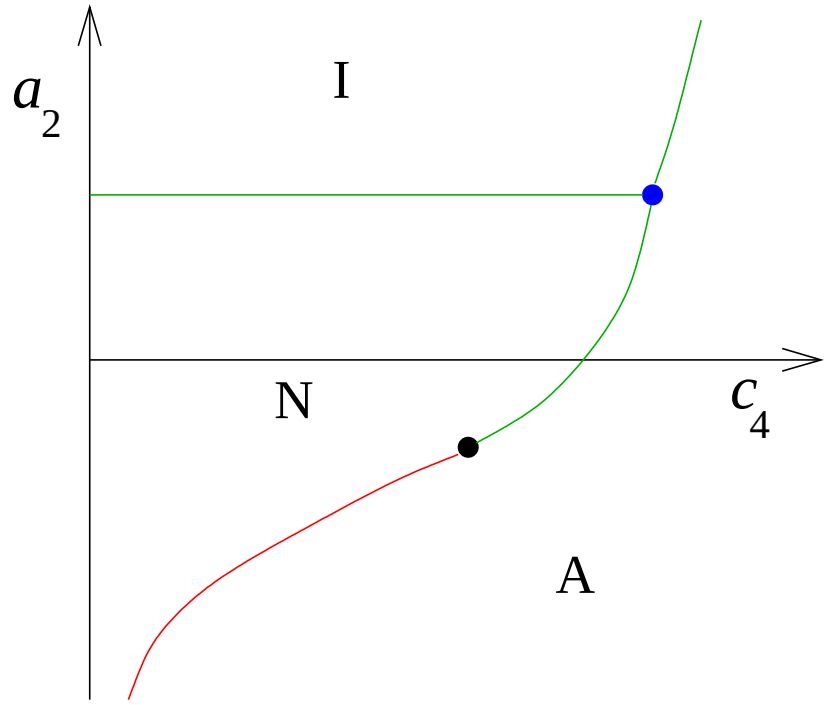
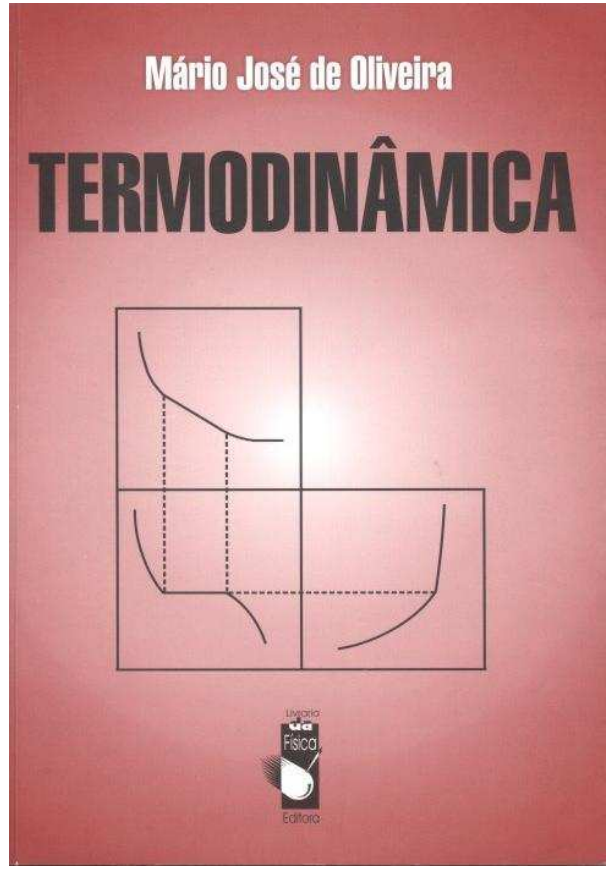


Diagrama de fase de acordo com a teoria de Landau-de Gennes.

I: fase isotrópica

N: fase nemática

A: fase esmética.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