INSTITUTE FOR HIGH PRESSURE PHYSICS

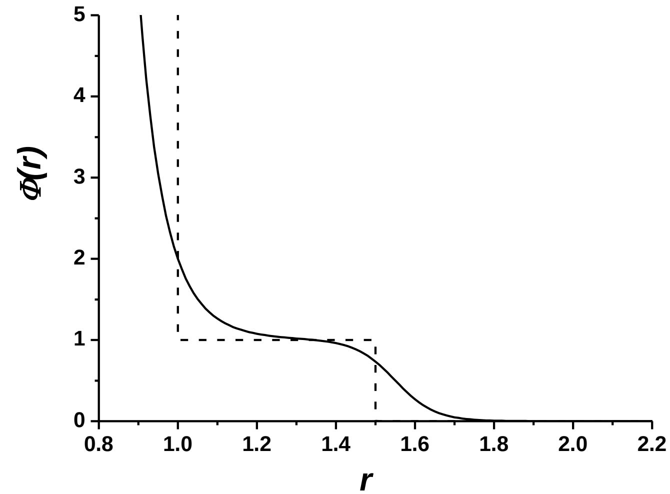
Влияние размерности (от 3D к 2D) на аномальные свойства системы сглаженных коллапсирующих сфер

Д.Е. Дудалов, Ю.Д Фомин, Е.Н. Циок, В.Н. Рыжов

Институт физики высоких давлений
им. Л.Ф. Верещагина РАН

Буревестник - 2014

Smooth Repulsive Shoulder Potentials (Yu. D. Fomin, N.V. Gribova, V.N.Ryzhov, S.M. Stishov, and Daan Frenkel, J. Chem. Phys. **129**, 064512 (2008); Yu.D. Fomin, V.N. Ryzhov, and E.N. Tsiok, J. Chem. Phys. **134**, 044523 (2011)).



Smooth Repulsive Shoulder System

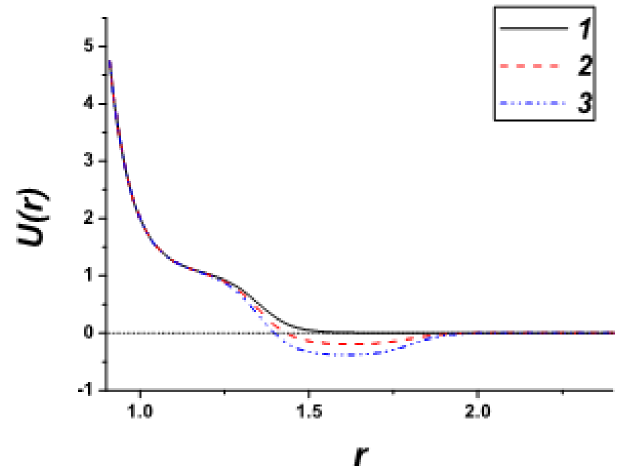
$$U(r) = \varepsilon\left(\frac{\sigma}{r}\right)^{14} + \frac{1}{2}\varepsilon(1 - \tanh(k_0[r - \sigma_1]))$$

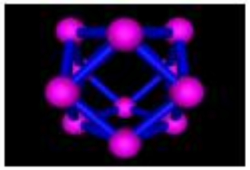
σ=1.15, 1.35,1.45, 1.55, 1.8

Smooth Repulsive Shoulder System With Attractive Well (SRSS-AW)

$$U(r) = \varepsilon\left(\frac{\sigma}{r}\right)^{14} + \varepsilon\left(\lambda_0 - \lambda_1 \tanh(k_1\{r - \sigma_1\} + \lambda_2 \tanh(k_2\{r - \sigma_2\})\right).$$

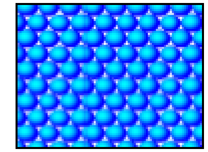
number	σ_1	σ_2	λ_0	λ_1	λ_2	well depth
1	1.35	0	0.5	0.5	0	0
2	1.35	1.80	0.5	0.60	0.10	0.20
3	1.35	1.80	0.5	0.7	0.20	0.4





3D

2D



$\sigma = 1.35$

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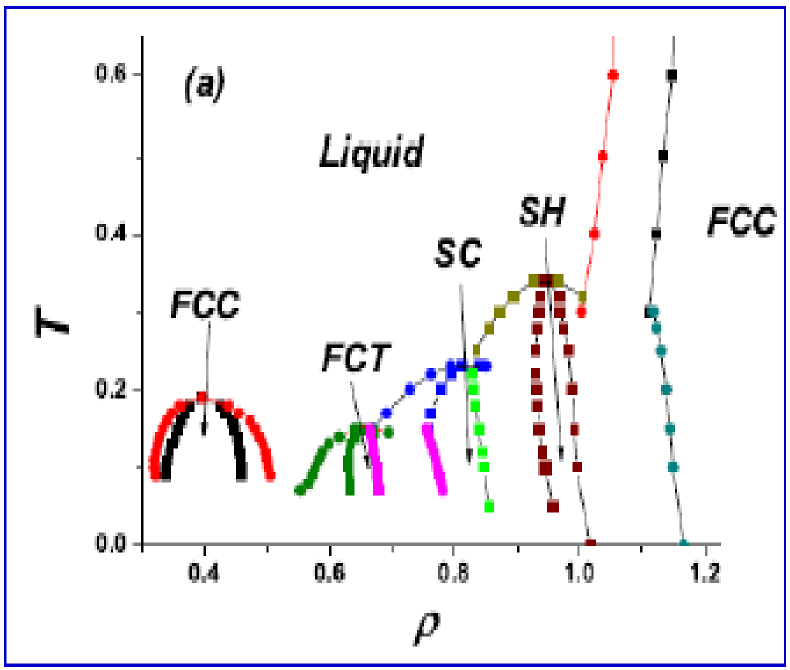
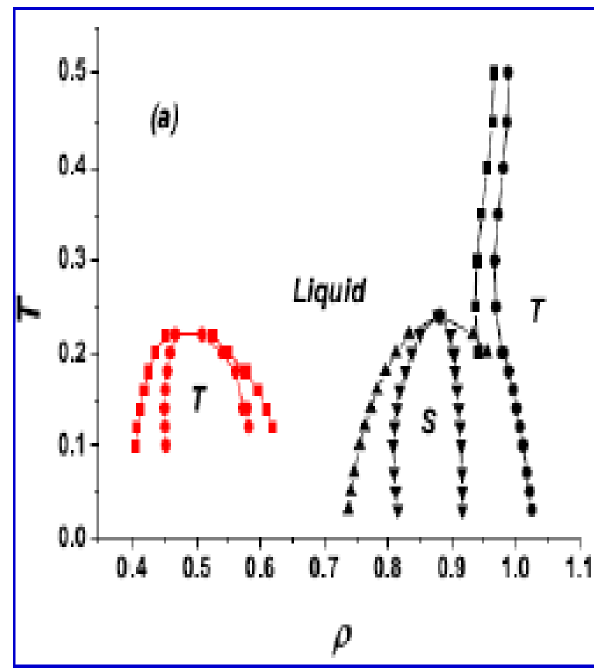
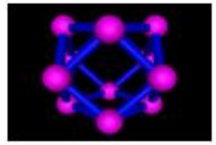
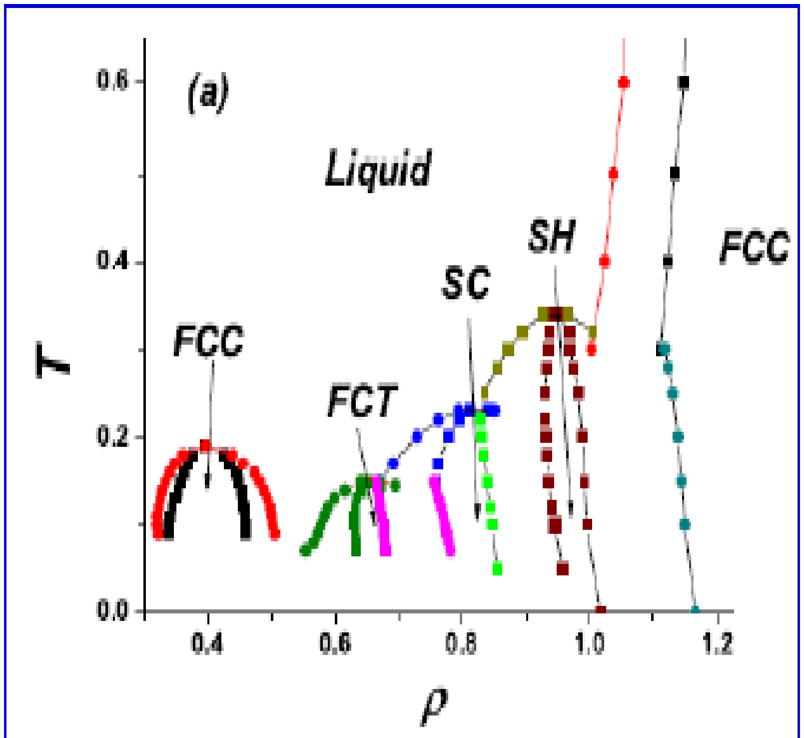




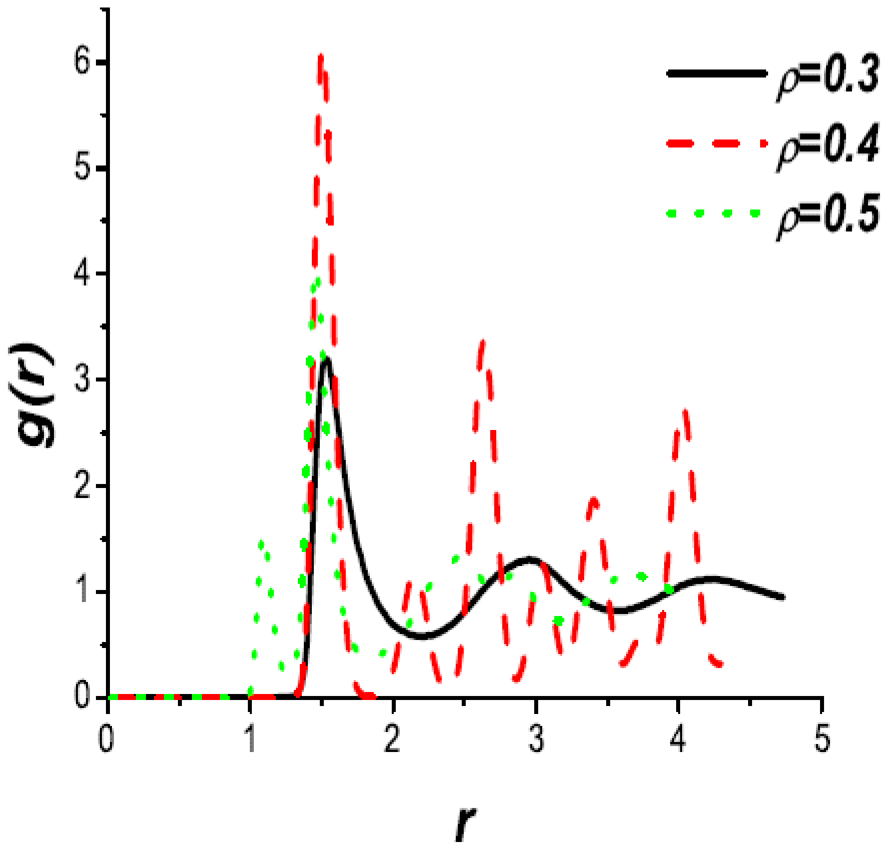


3D

$\sigma = 1.35$

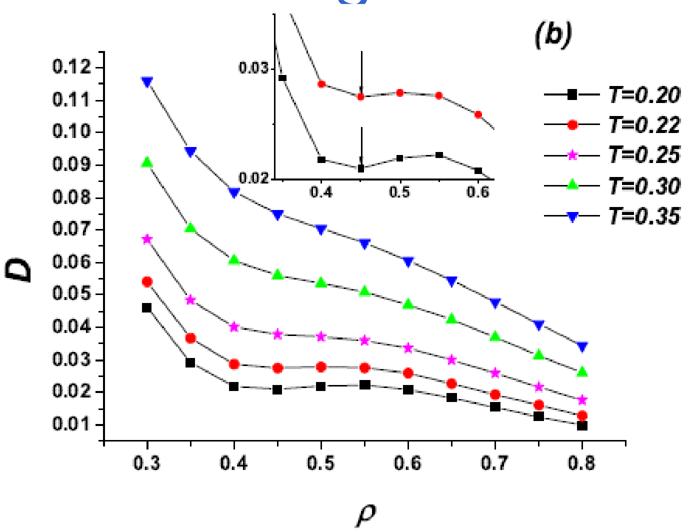


$T = 0.1$

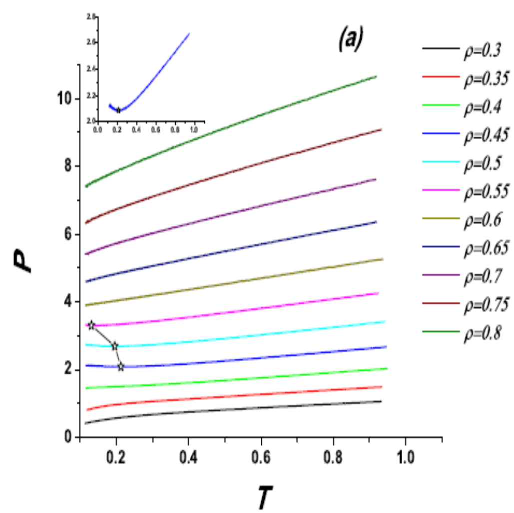


Liquid State Anomalies

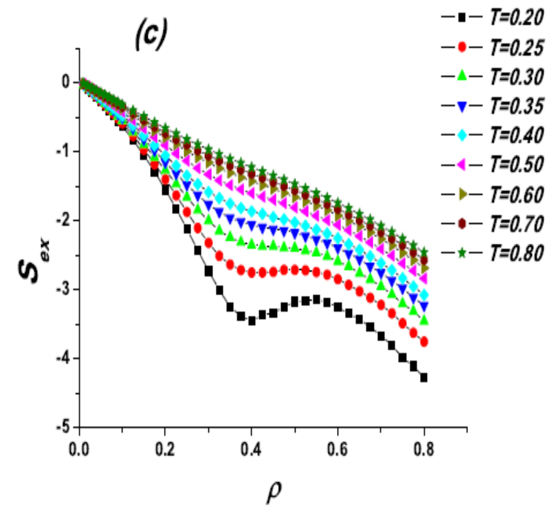
Diffusion anomaly



Density anomaly



Structural anomaly



Order of Anomalies

$$\left(\frac{\partial \rho}{\partial T}\right)_P = \rho^2 \left(\frac{\partial \rho}{\partial P}\right)_T \left(\frac{\partial s}{\partial \rho}\right)_T$$

$$s^{\mathrm{ex}} = s - s^{\mathrm{ig}}$$
$$s^{\mathrm{ig}} = -\ln \rho + c(T)$$

$$\left(\frac{\partial S_{ex}}{\partial \ln \rho}\right)_T > c$$ – condition for anomaly appearance

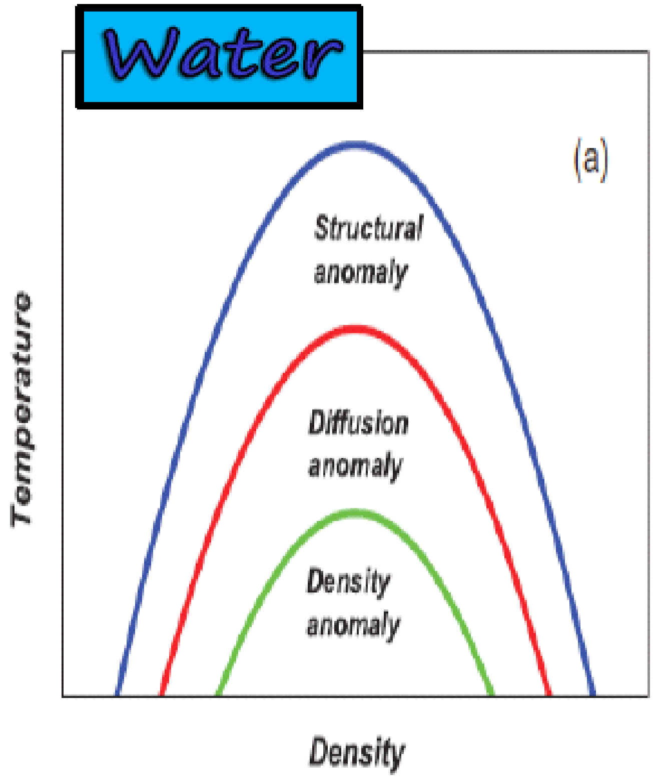
c=0 – structural anomaly

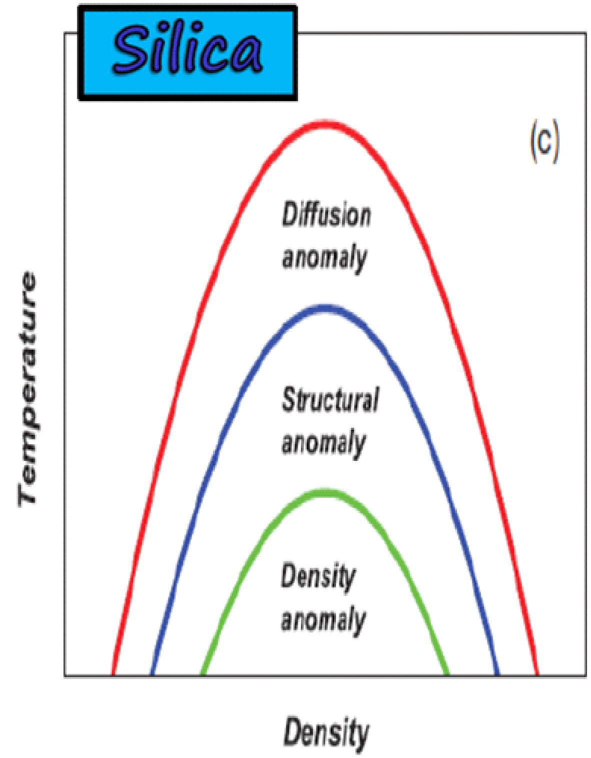
c=1 – density anomaly

Density anomaly region is always inside structural anomaly one. However, no thermodynamic restriction for the location of diffusion anomaly.

J.R. Errington, Th.M Trusket and J. Mittal, JCP 125, 244502 (2006)
Yu.D. Fomin, E.N. Tsiok and V.N. Ryzhov, JCP 135, 234502 (2011)

Order of Anomalies

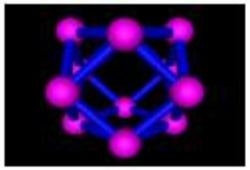


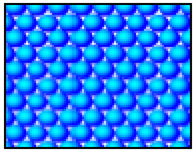


Other sequences of anomalies are also possible:

Yu. D. Fomin, E.N. Tsiok, V.N. Ryzhov, J. Chem. Phys., 135, 234502, (2011)

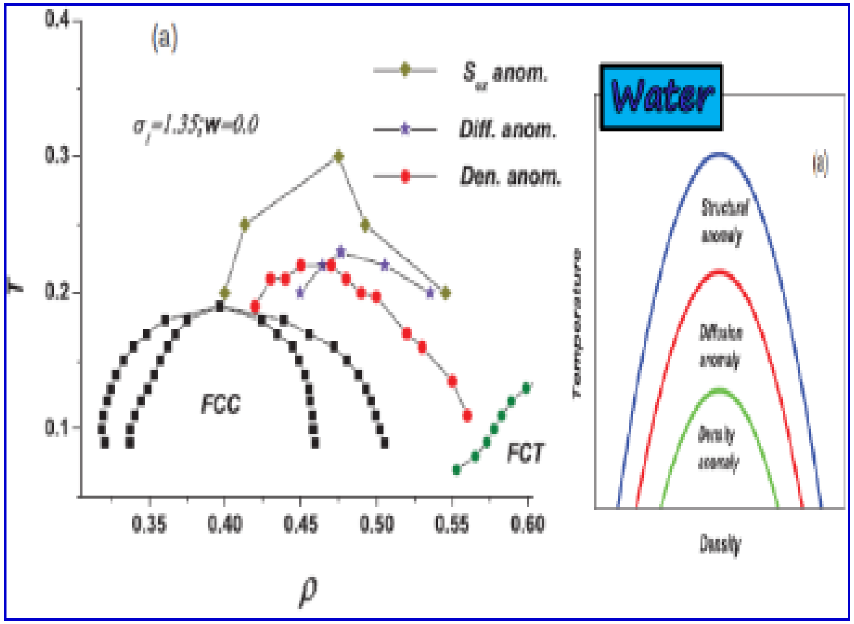
and Eur. Phys. J. Special Topics 216, 165-173 (2013)



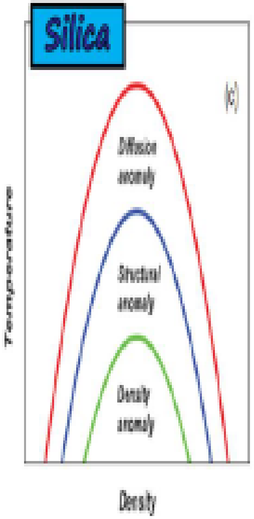


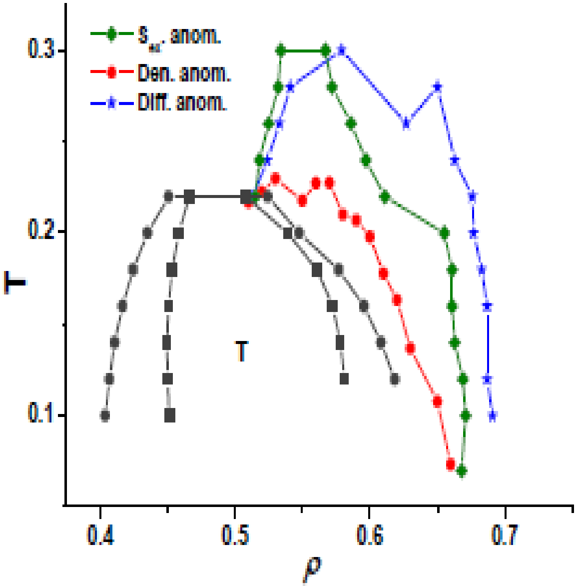
$\sigma = 1.35$

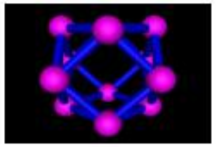
$\sigma = 1.35$



Inversion!!!

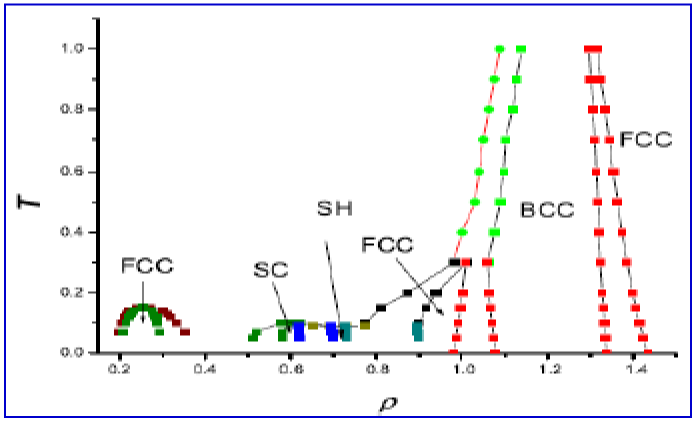


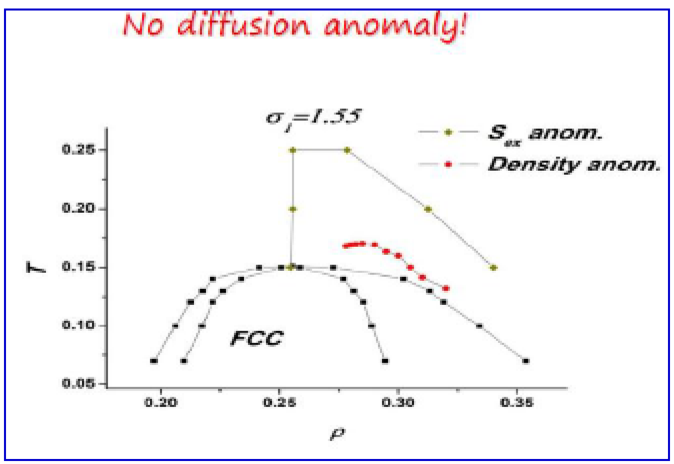




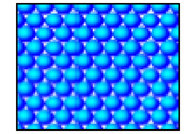
3D

$\sigma = 1.55$

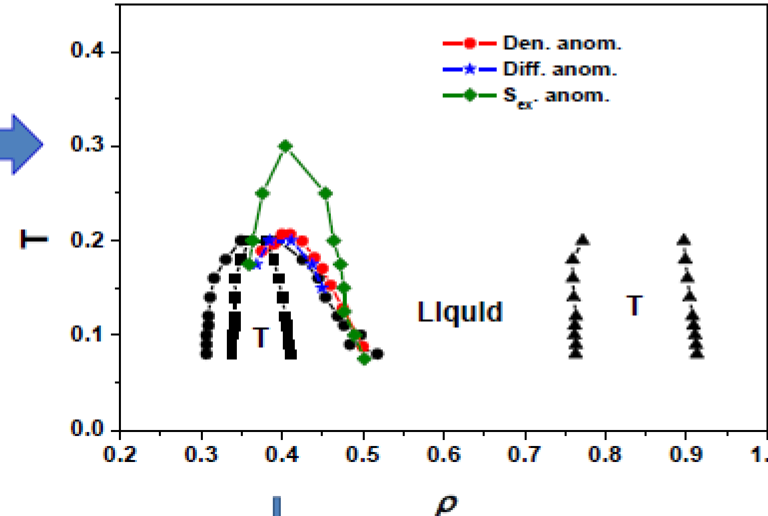


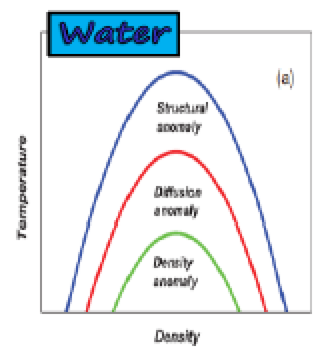


2D



$\sigma = 1.55$





Conclusions

•We investigate the relation of the anomalous behavior with the phase diagram of the system. All three anomalies take place in the system and their regions appear after the maximum on the low-density FCC- or T-crystal part.

•Recently we have shown that in ***3D*** system the order of the region of anomalous diffusion and the regions of density and structural anomalies may be inverted depending on the parameters of the potential and may have a waterlike, a silicalike or some other sequences.
However, in ***2D*** system with the same purely repulsive core-softening potential (σ **= *1.35***) the order of the region of anomalous diffusion and the region of structural anomaly is inverted in comparison with the ***3D*** case, where there exists the waterlike sequence of anomalies, and has the silicalike sequence.

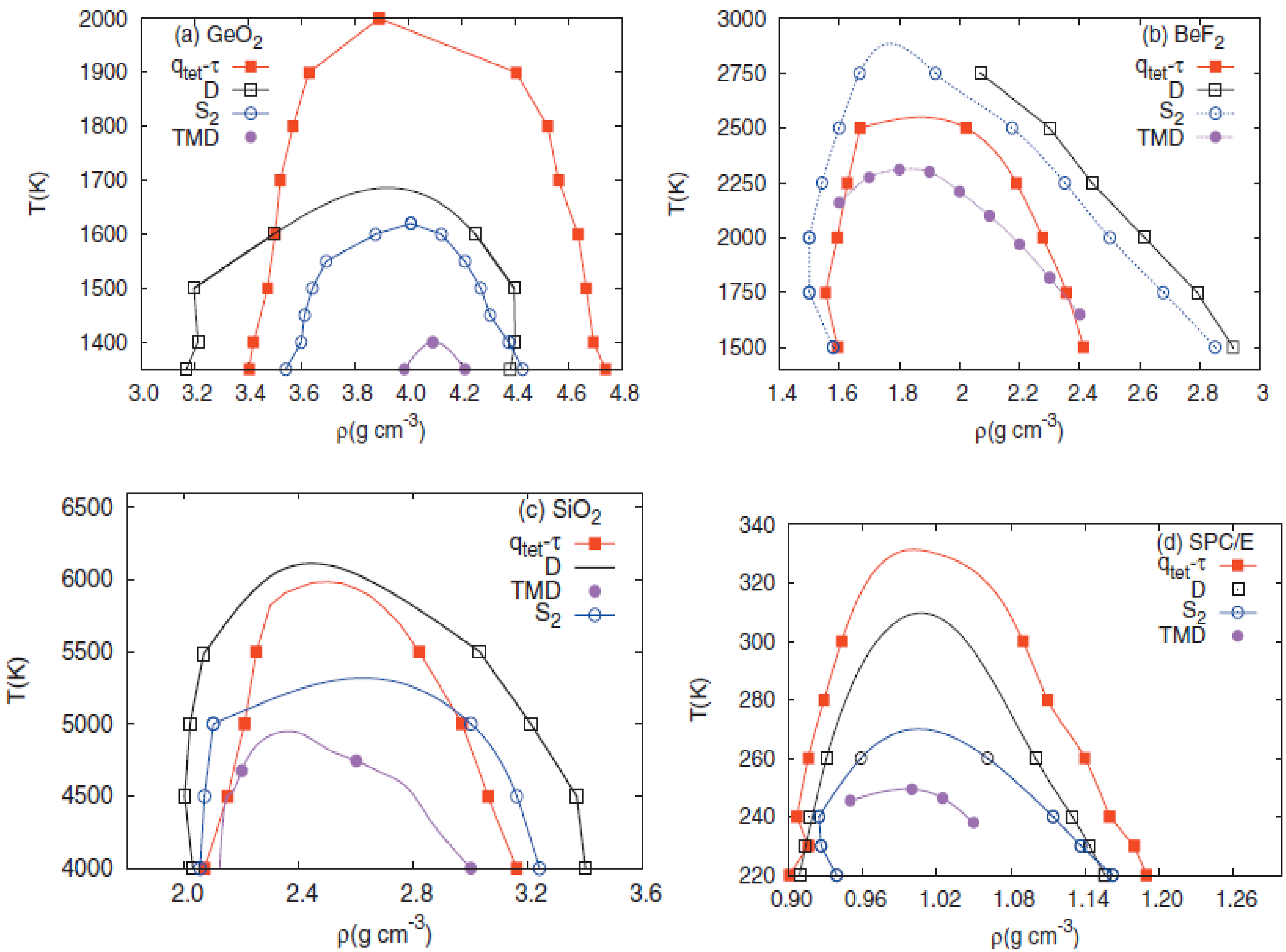
•In the ***3D*** case for σ **= *1.55*** we do not find diffusion anomaly.

•In ***2D***, with increasing the step width from ***1.35*** to ***1.55*** the order of the region of anomalous diffusion and the region of structural anomaly is inverted in comparison with the ***3D*** case and has the waterlike sequence. This fact shows that the dynamics of ***2D*** liquids is really different from the dynamics of the corresponding ***3D*** system.

•In ***3D*** and ***2D***, we show that both low density crystal phase and all anomalous regions move to lower densities and lower temperatures and shrink with increasing the step width. However, the rate of the decrease is different.

•In ***3D*** and ***2D***, the structural anomaly is much more stable than the diffusion and the density ones and the relative height of the structural anomaly even increased from σ **= *1.35*** to ***1.55***.
On the basis of our study we propose that the most reliable definition of structural anomaly is the one based on excess entropy

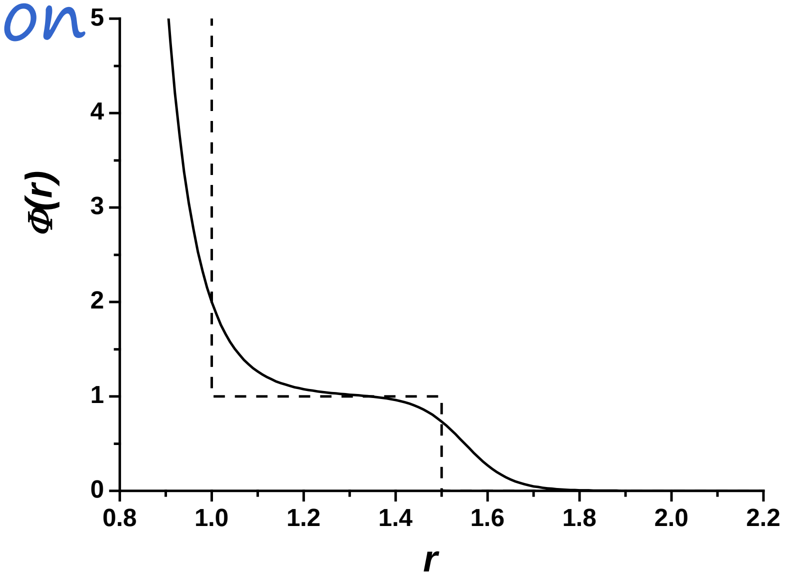
Are all definitions equivalent?



J. Chem. Phys. 132, 234507 (2010)

Methods

Molecular Dymanics Simulation
400 particles in a cubic box
Densities from 0.15 up to 0.75 with step 0.05
Temperatures from 0.1 up to 0.7

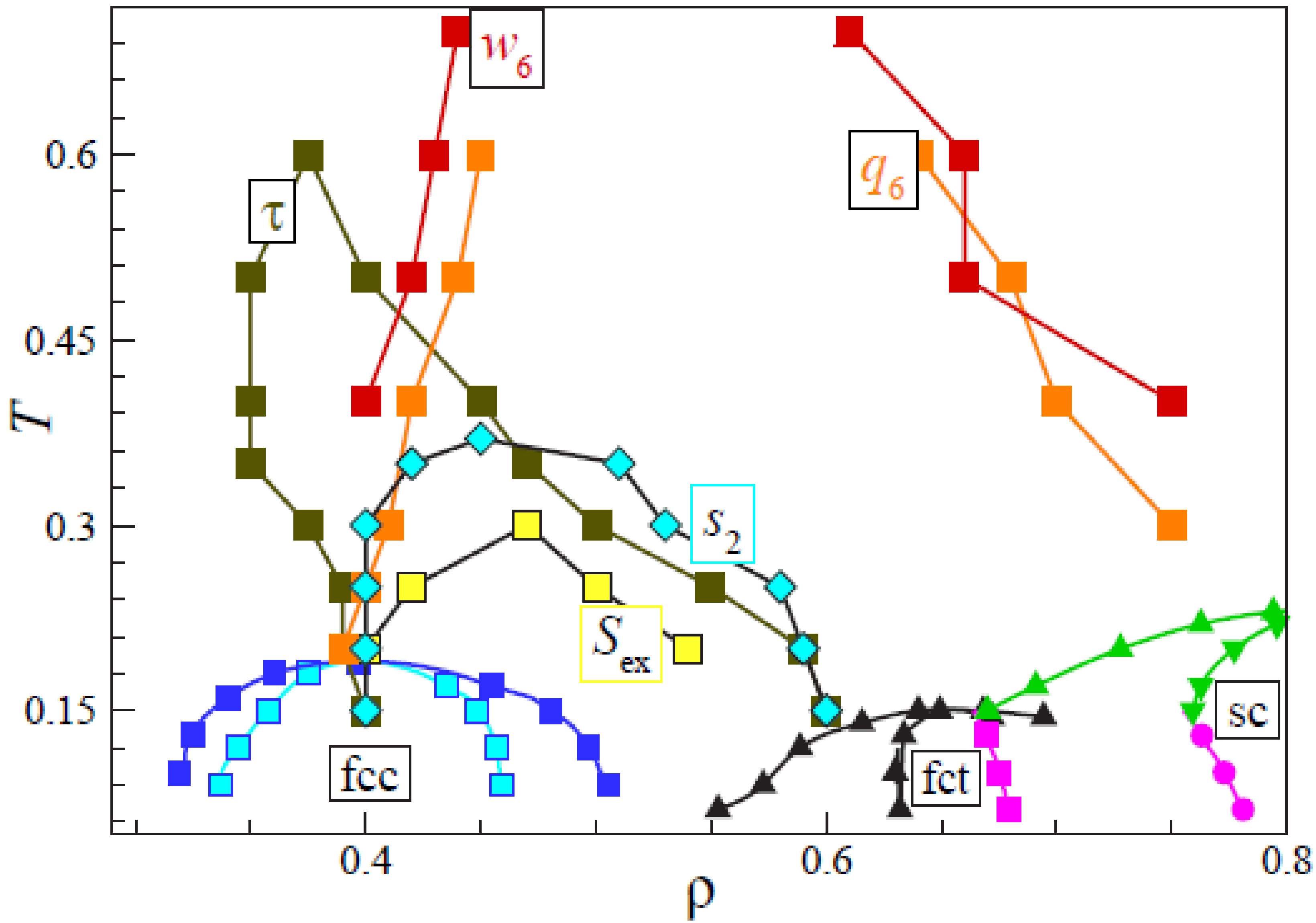


Simulation with Lammps package

$$\Phi(r) = \left(\frac{d}{r}\right)^n + \frac{1}{2}\varepsilon\left(1 - \tanh\left(k_0\left(r - \sigma_s\right)\right)\right)$$

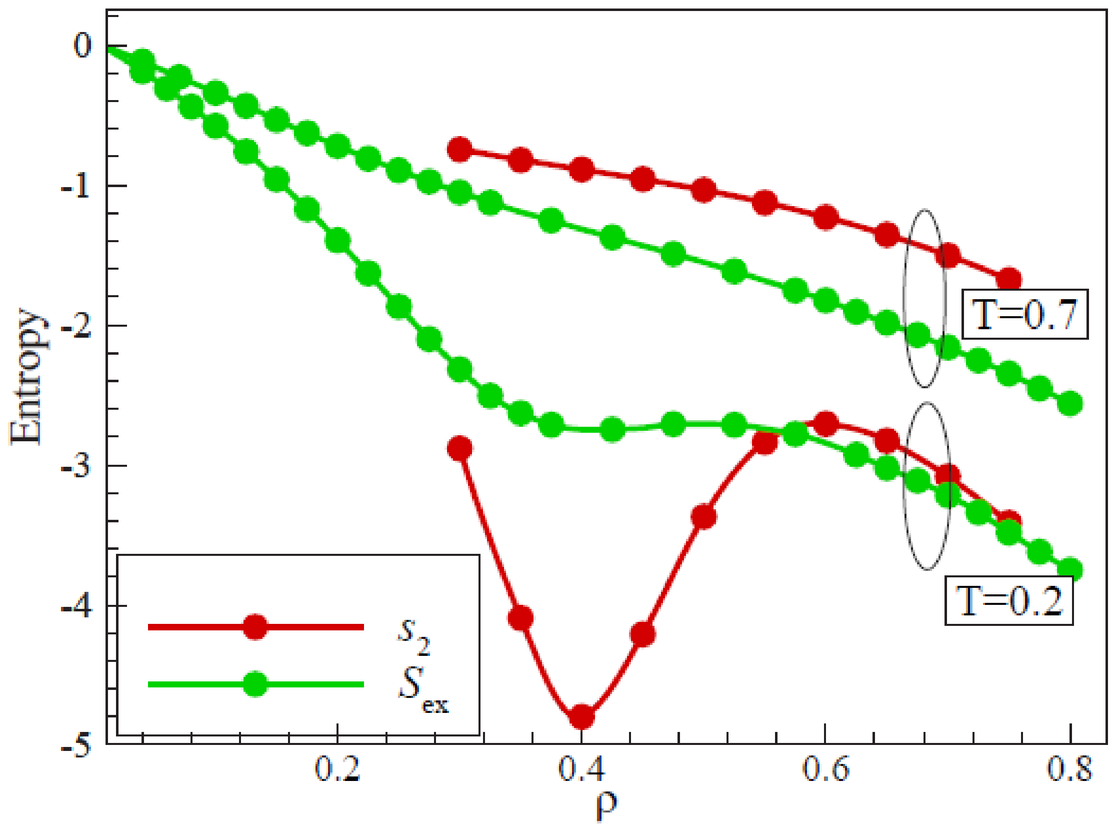
J. Chem. Phys. 129, 064512 (2008)

Results: regions of structural anomaly



Results: excess and pair entropy

$$S_{\text{ex}} = S - S_{\text{id}} \qquad s_2 = -2\pi\rho \int \left(g(r)\cdot \ln(g(r)) - g(r) + 1\right)\cdot r^2 dr,$$

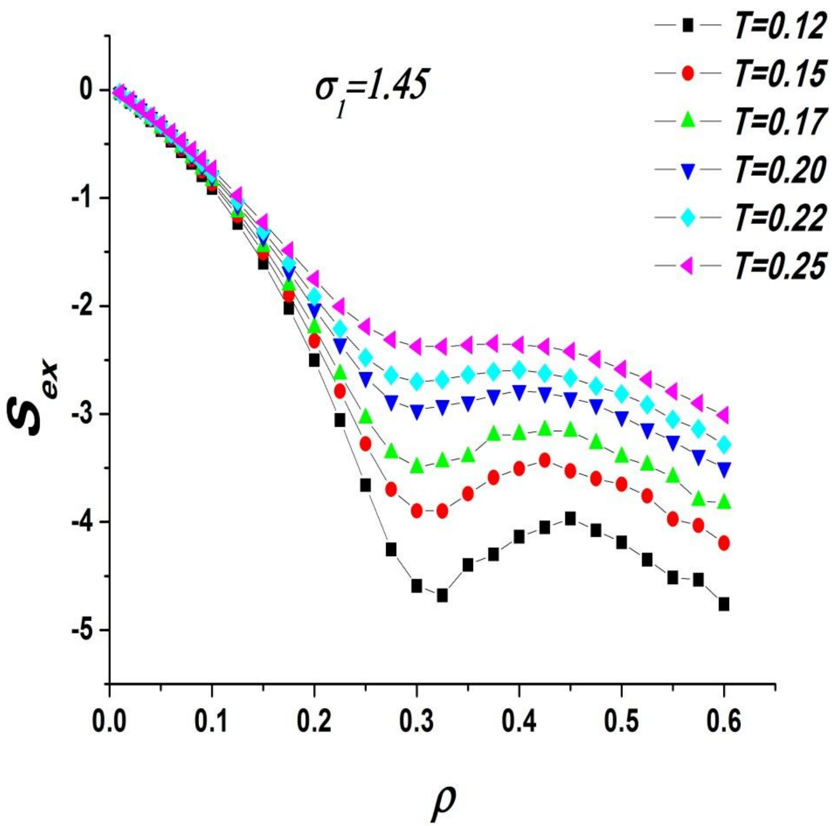


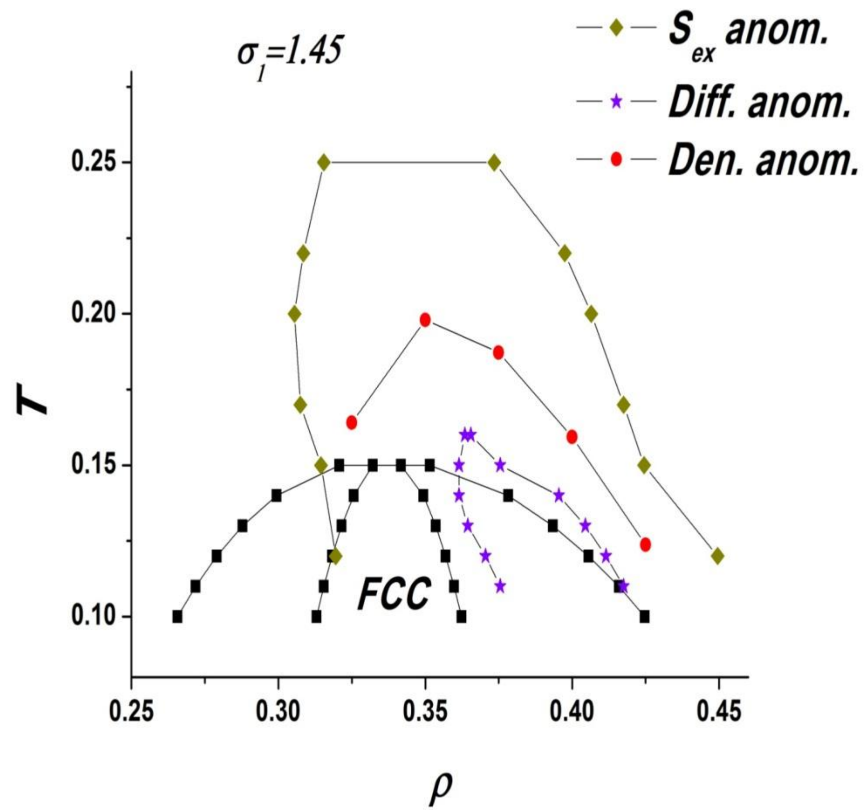
Pair entropy does not represent the full excess entropy in case of anomalous fluid

Спасибо

за внимание

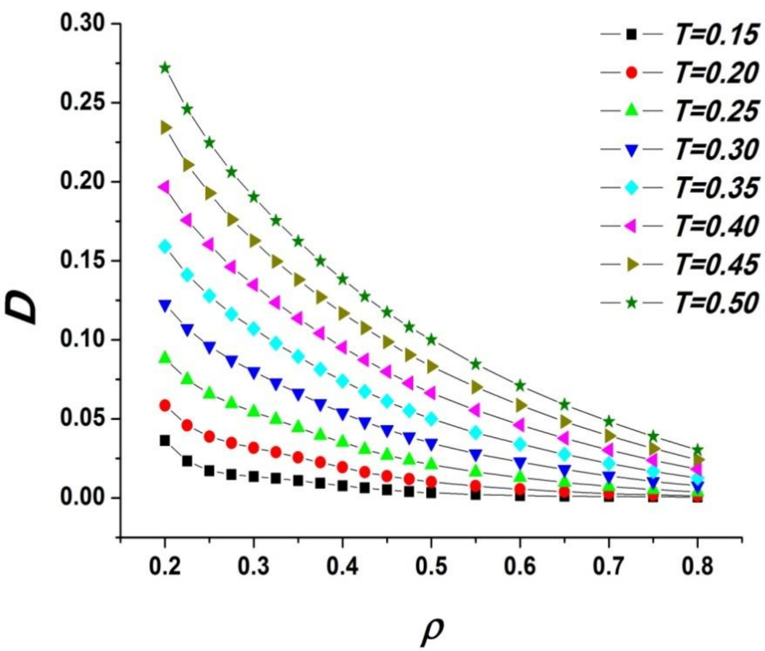
Anomalies for σ=1.45

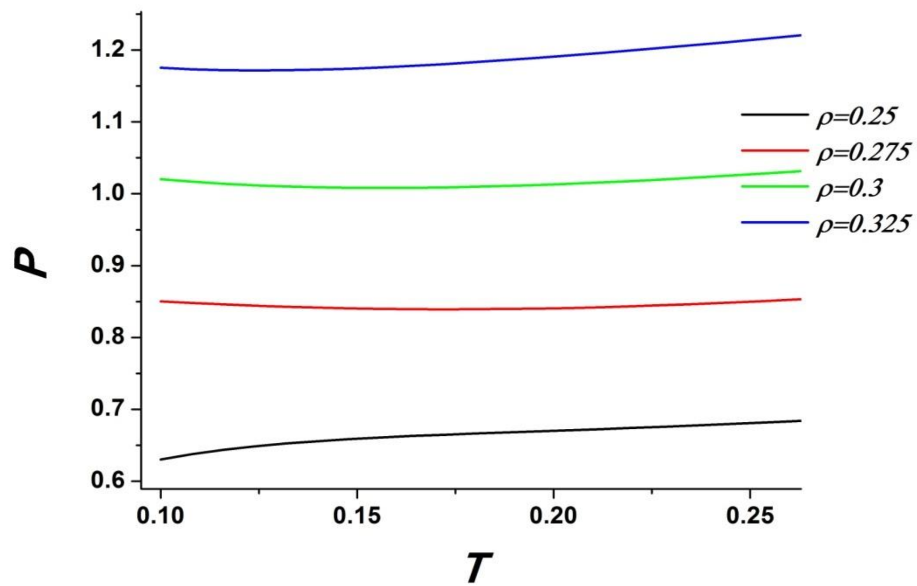




Smooth Repulsive Shoulder System

Diffusion and Density Anomalies for $\sigma = 1.55$

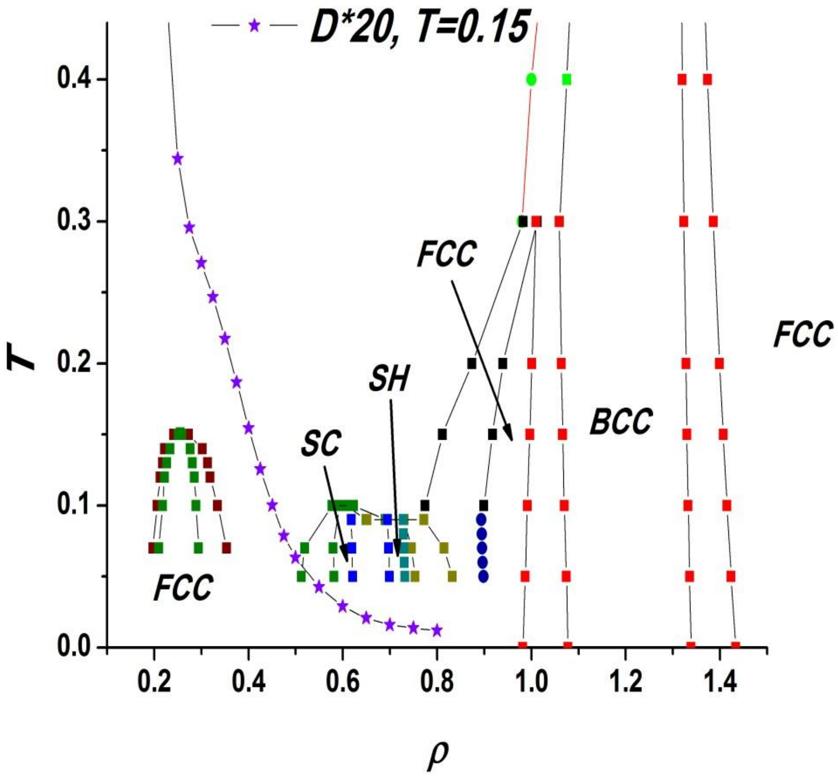


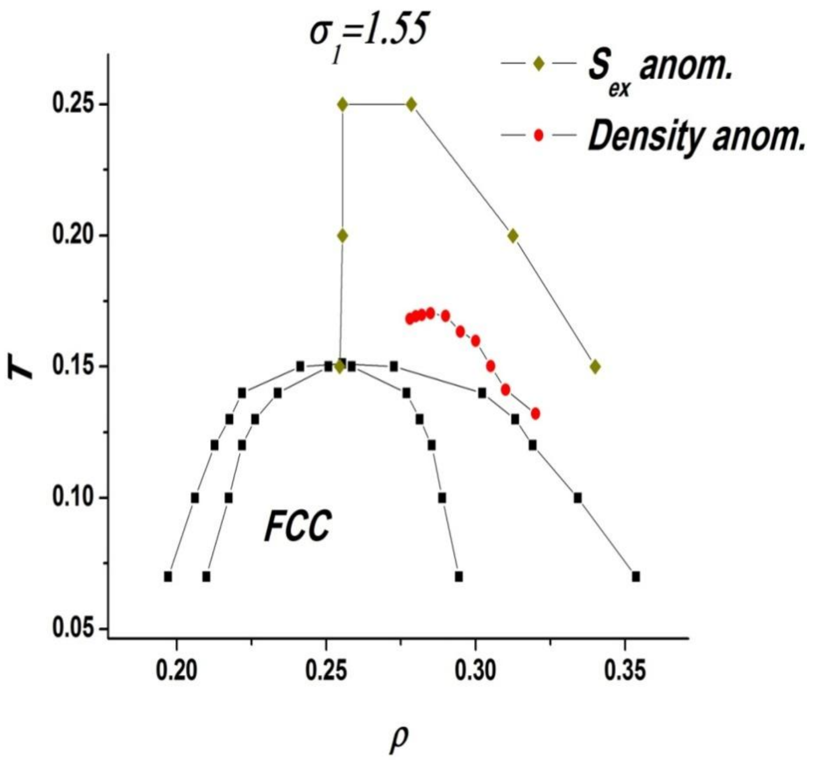


No diffusion anomaly!

Anomalies for σ=1.55

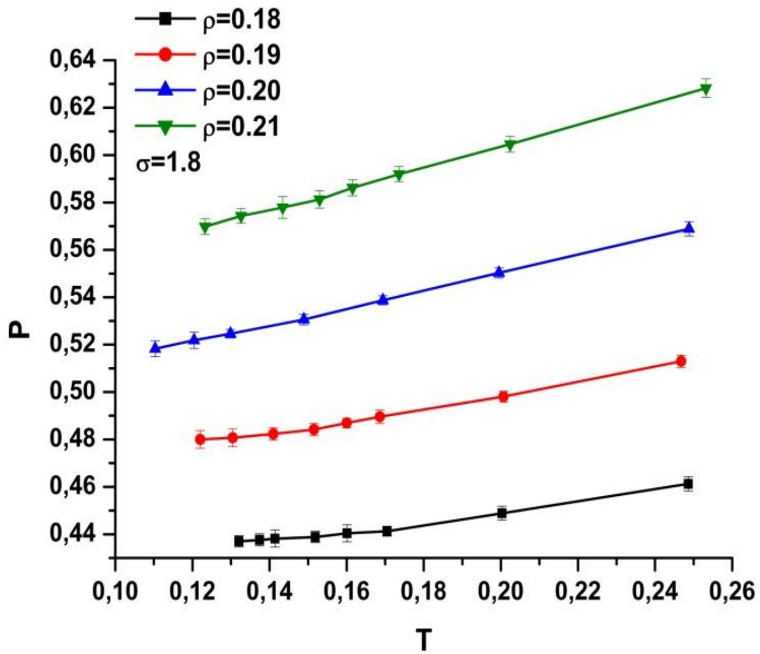
No diffusion anomaly!

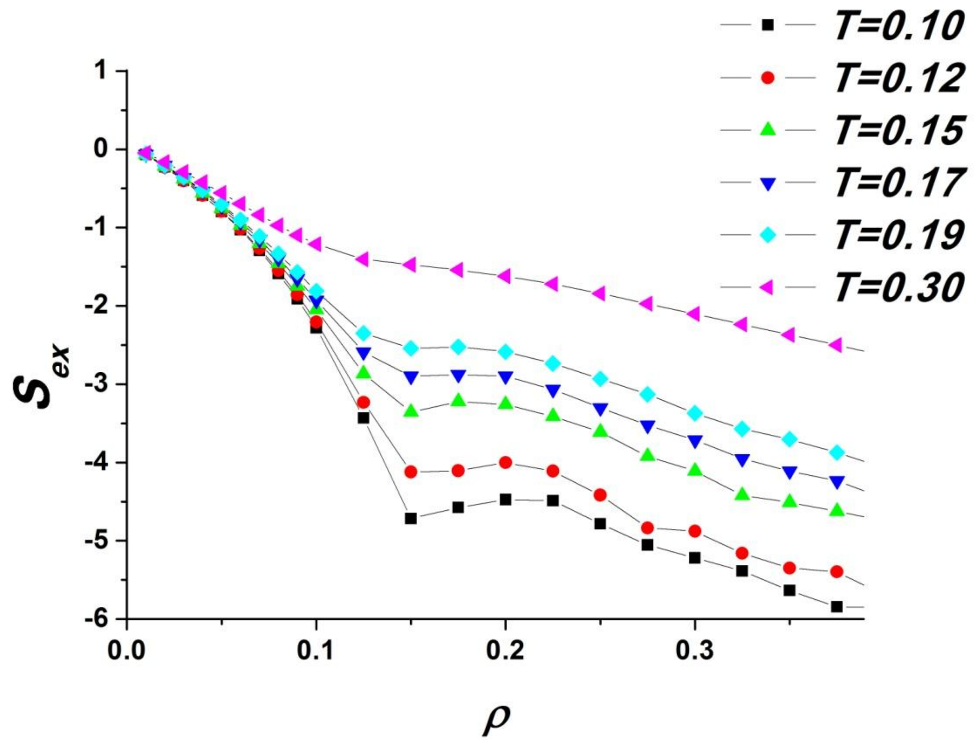




Smooth Repulsive Shoulder System

Density and Excess Entropy Anomalies for σ =1.8

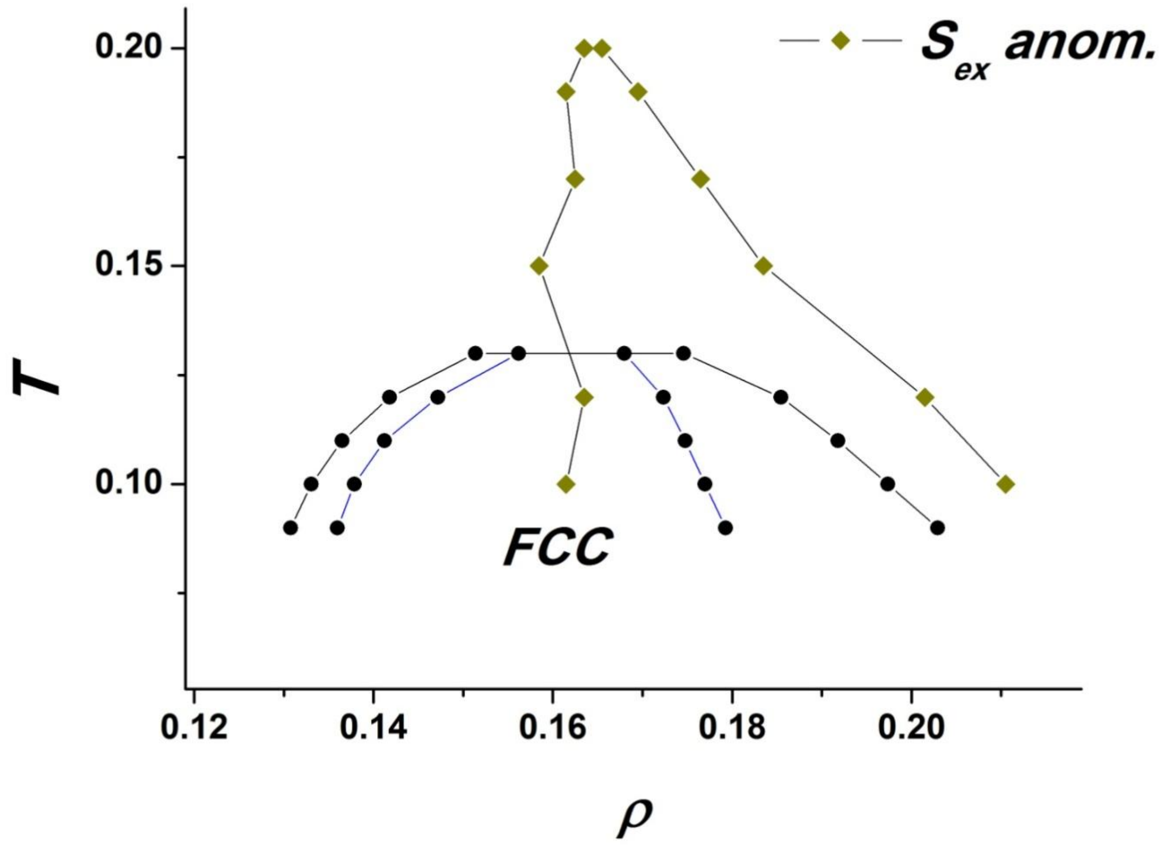




No density anomaly!

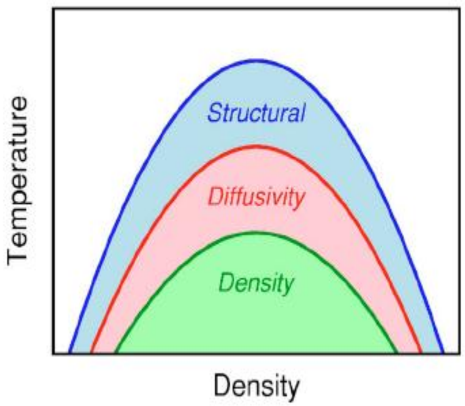
Anomalies for σ=1.8

No diffusion and density anomalies!

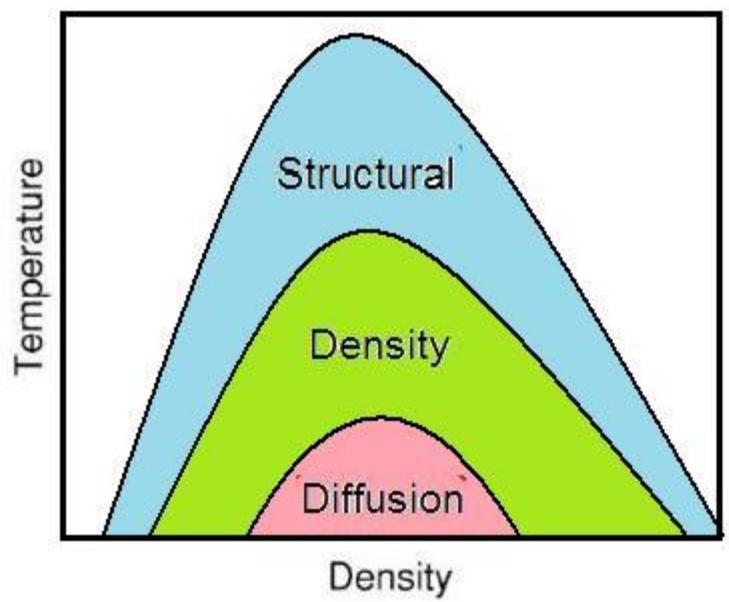


Range of Anomalies

Water



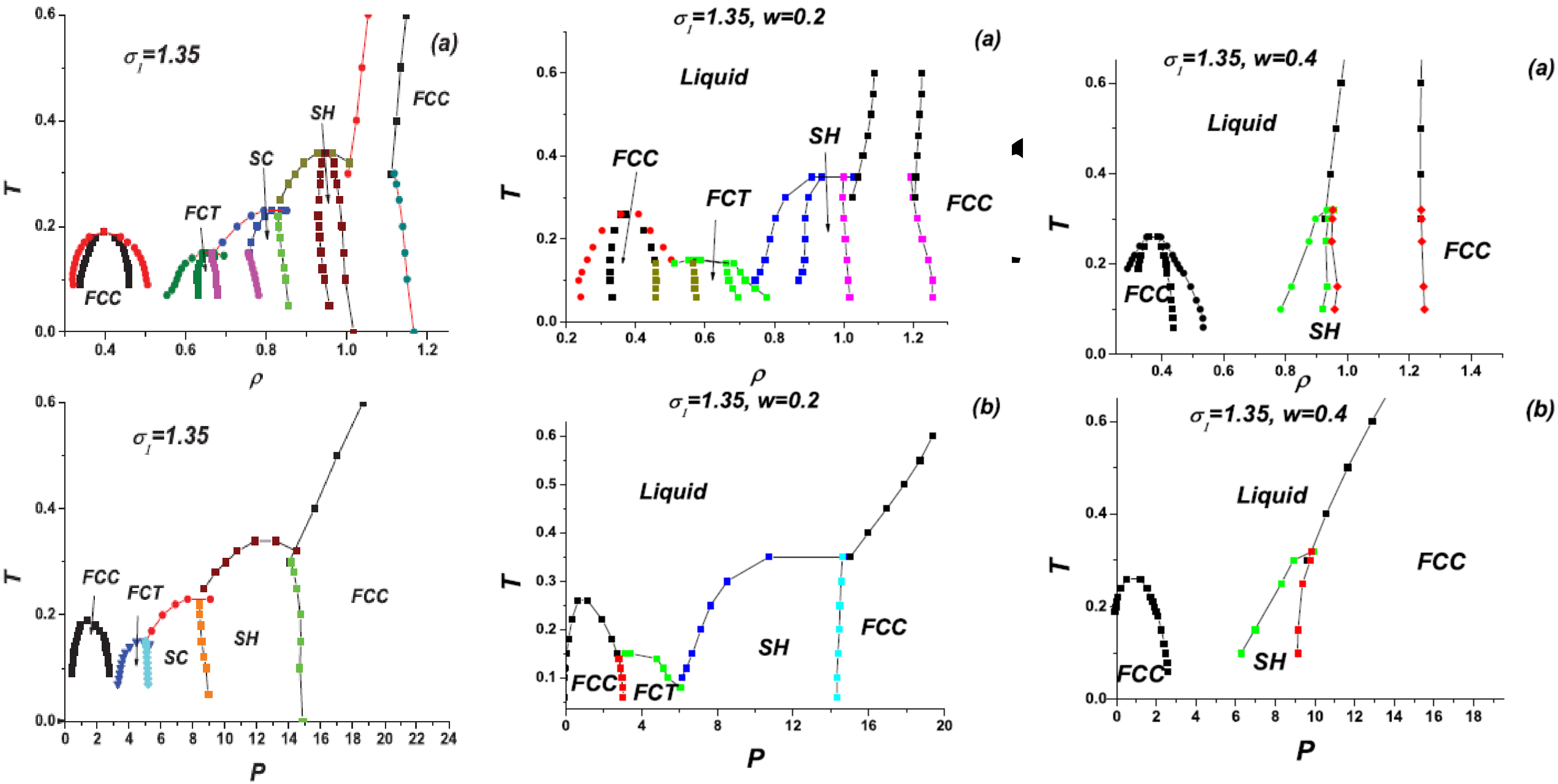
R. Errington and P. G. Debenedetti, Nature 409, 318 (2001) - water



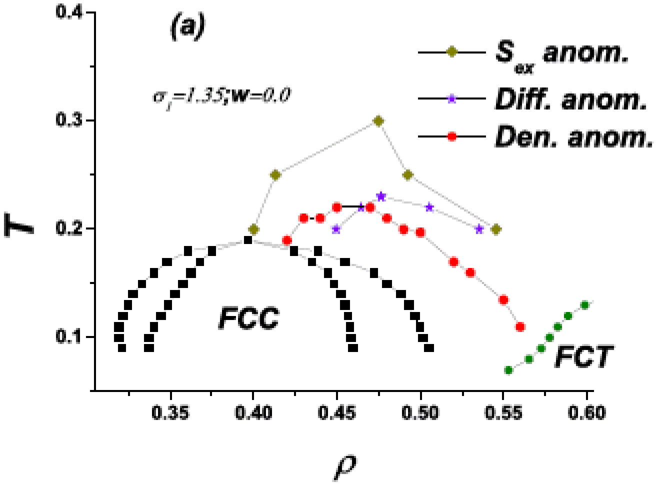
Yu. D. Fomin, V. N. Ryzhov, E.N. Tsiok, Inversion of Sequence of Diffusion and Density Anomalies in Core-Softened Systems, J. Chem. Phys. 135, 234502 (2011)

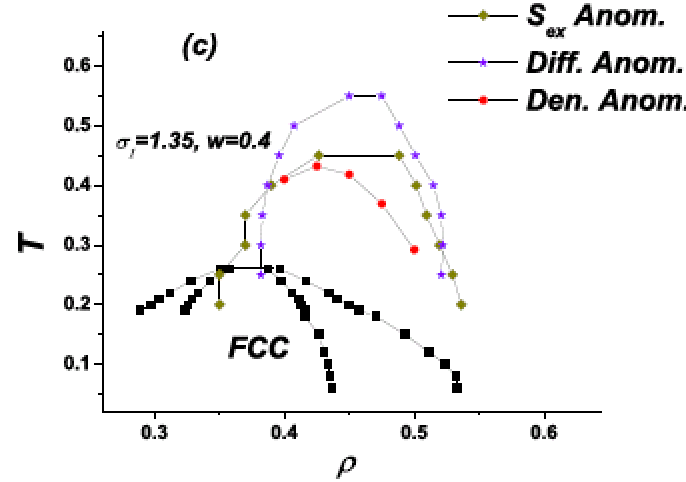
Phase diagrams for SRSS and SRSS-AW (Yu. D. Fomin, N.V. Gribova, V.N.Ryzhov, S.M. Stishov, and Daan Frenkel, J. Chem. Phys. 129, 064512 (2008); Yu.D. Fomin, V.N. Ryzhov, and E.N. Tsiok, J. Chem. Phys. 134, 044523 (2011)).

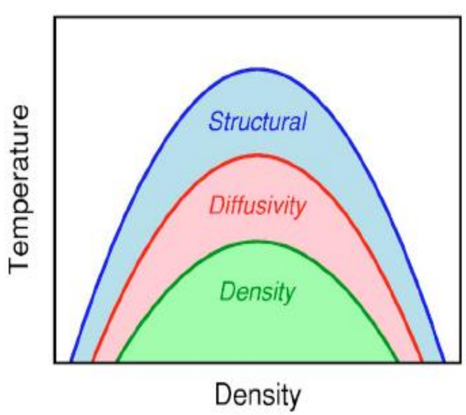
Phase diagrams for σ =1.35 with attractive well depth *W*



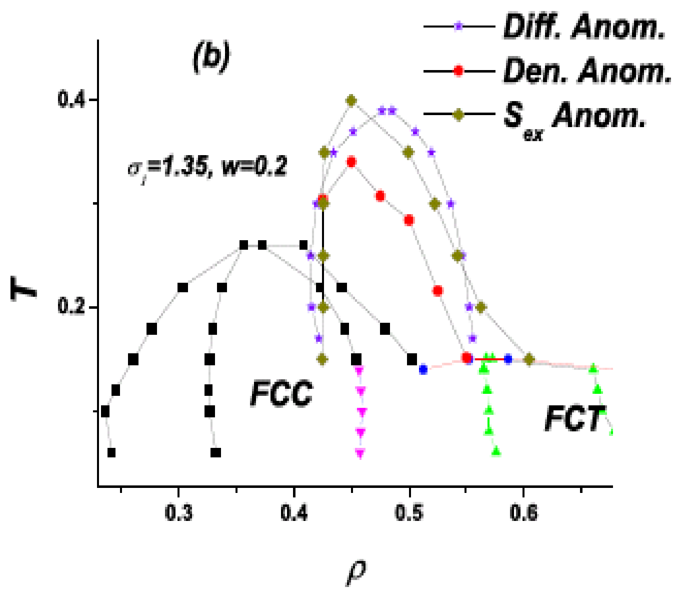
Location of anomalous regions at the low density part of the phase diagram of the system with $\sigma = 1.35$ and attractive well

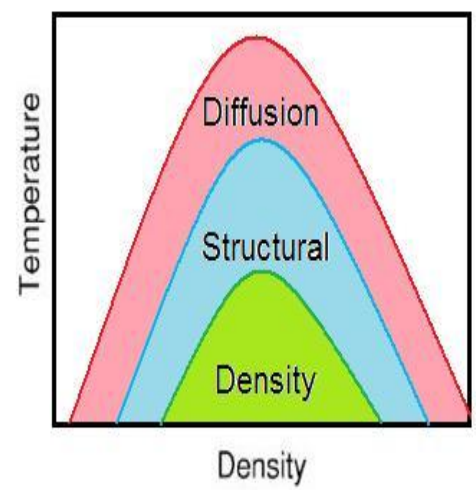






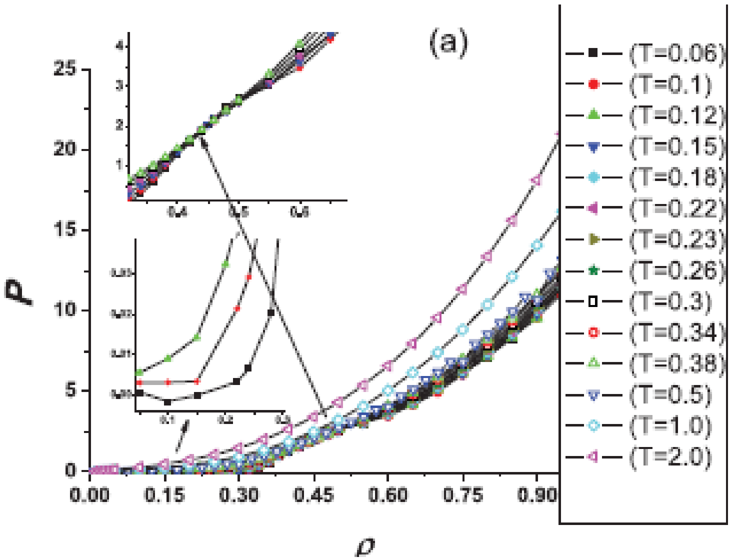
Water

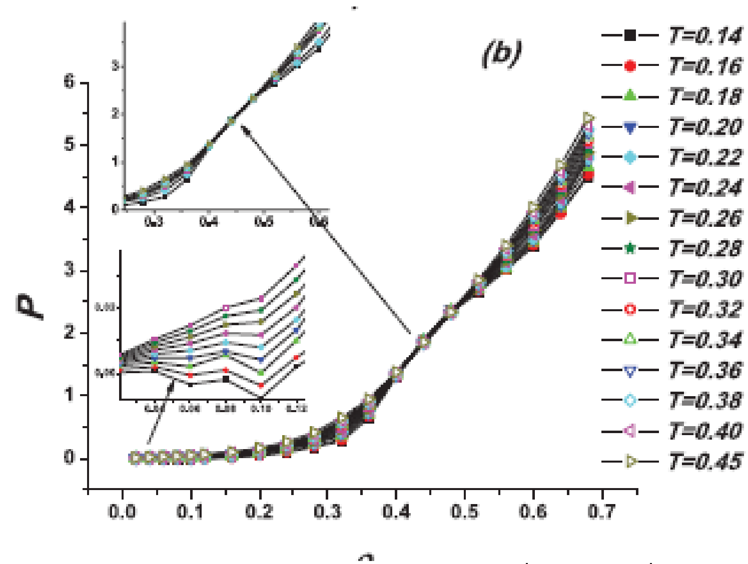


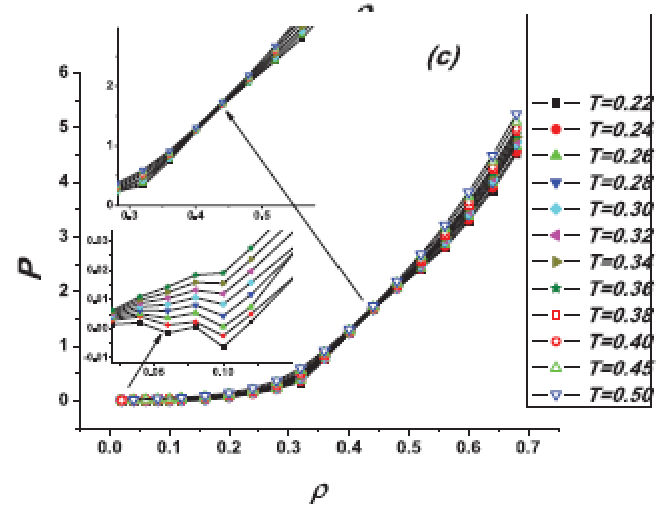


Silica

Isotherms for the systems with *σ = 1.35* and attractive well (Yu.D. Fomin, V.N. Ryzhov, and E.N. Tsiok, J. Chem. Phys. 134, 044523 (2011)).







(a) w=0.2

(b) w=0.3

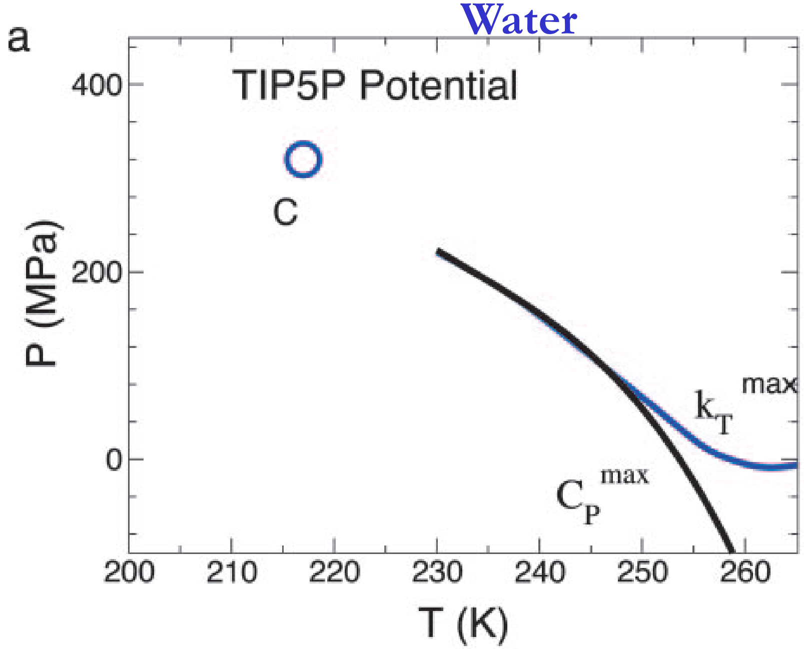
(c) w=0.4

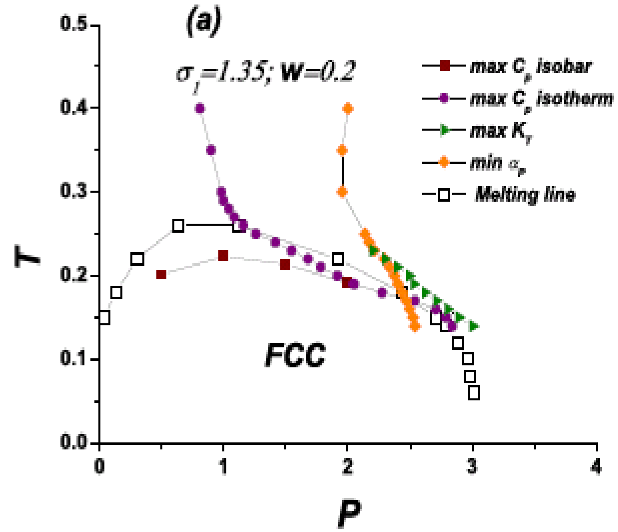
Tendency to the liquid-liquid phase with the increasing of the attractive well depth

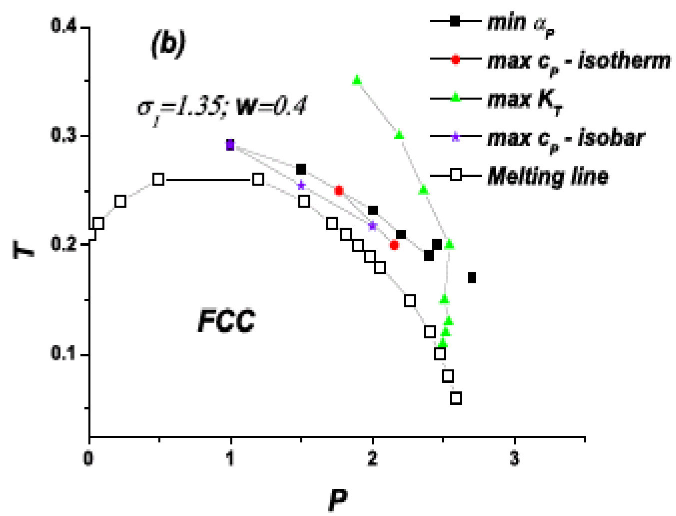
Location of anomalous regions at the low density part of the phase diagram of the system with $\sigma = 1.35$ and attractive well

It is now widely believed that the water anomalies arise from crossing the Widom line emanating from the hypothesized liquid-liquid critical point (LLCP) (L. Xu, P. Kumar, S.V. Buldyrev, S.-H. Chen, P.H. Poole, F. Sciortino, and H.E. Stanley, PNAS **102**, 16558 (2005)).

Water







Conclusions

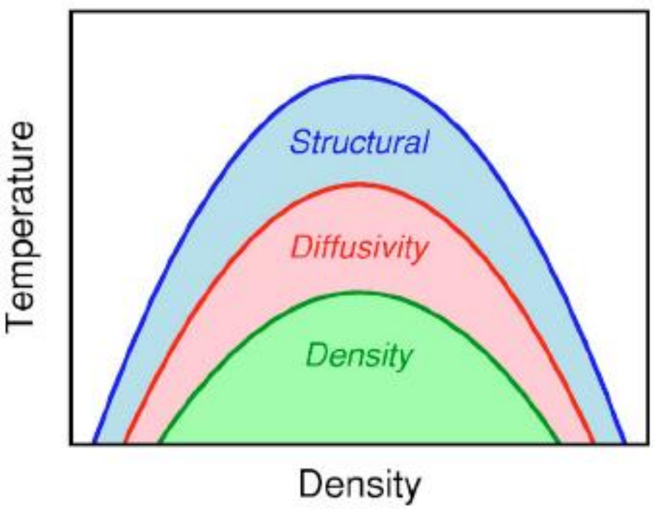
- A systematic simulation study of a core-softened system is carried out. Phase diagrams of Smooth Repulsive Shoulder system with different potential parameters are computed.
- Waterlike anomalies in the SRS system are found. The evolution of the anomalies with the potential parameter is studied.
- Relation of anomalous behavior and phase diagram was shown. It is demonstrated that with increasing the step width both low-density FCC phase and all anomalous regions move to lower densities – lower temperatures region. However, the rate of displacement is different which brings to disappearance of anomalies under the melting line.
- We prove that diffusion anomaly can occupy any place in the sequence of anomalous domains. In particular, for the first time we observe inversion of diffusion and density anomalies regions

Спасибо

за внимание

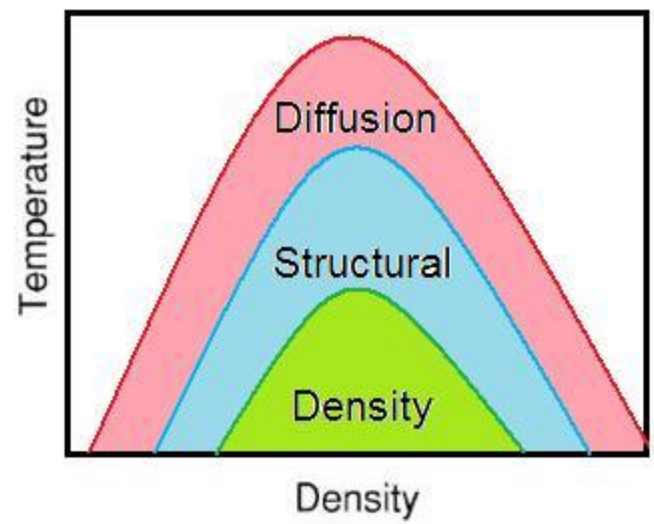
Range of Anomalies

Water



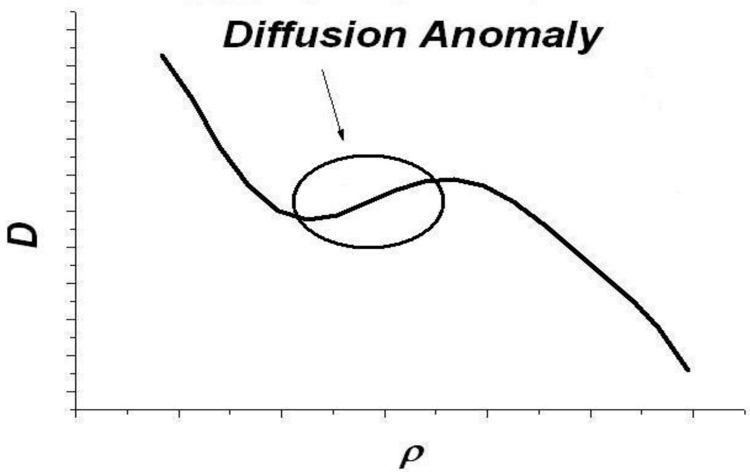
R. Errington and P. G. Debenedetti, Nature 409, 318 (2001).

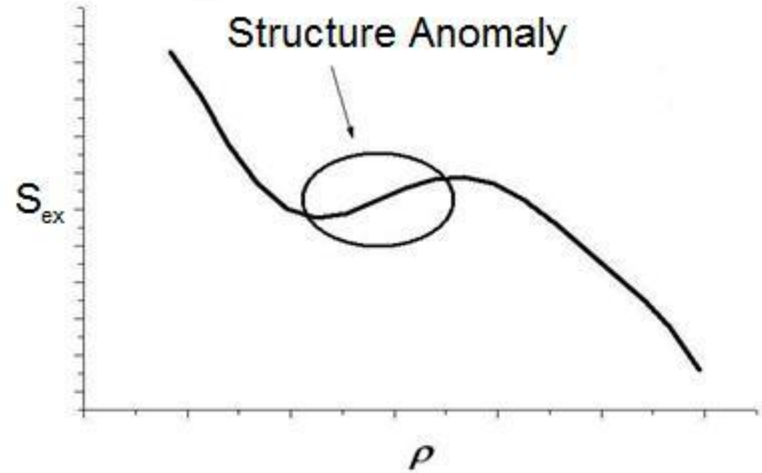
Silica

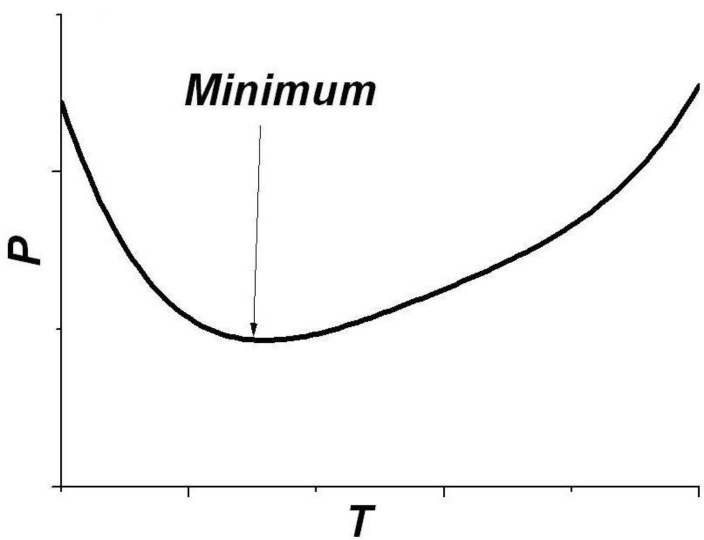


M. S. Shell, P. G. Debenedetti, A. Z. Panagiotopoulos Phys. Rev. E 66, 011202 (2002)

Waterlike Anomalies







Density Anomaly

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha_P}{\kappa_T}$$

$\alpha_P < 0$ *-thermal expansion coef.*

$\kappa_T > 0$ *-isothermal compressibility coef.*