Compressibility of Nanoconfined Fluids: Relating Atomistic Modeling to Ultrasonic Experiments

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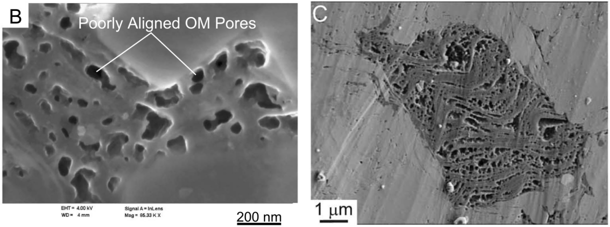
Motivation & Potential Industrial Needs

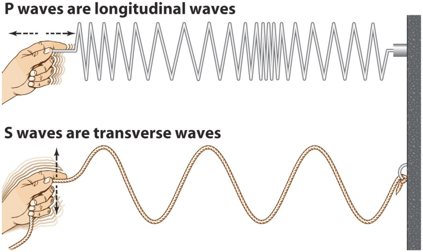
- ExxonMobil Research & Engineering Company
- Industrial need: exploration and development of unconventional hydrocarbons (shale gas, shale oil)
- One of the key difference with conventional hydrocarbons
- Nanoporous system with hydrocarbons in adsorbed state



Loucks, R. G.; Reed, R. M.; Ruppel, S. C. & Jarvie, D. M. *J. Sediment. Res.*, 2009, 79, 848-861.

Wave Propagation in an Elastic Medium

- Seismic waves – characterization of geological formations
- Sonic/utrasonic waves – characterization of rock samples



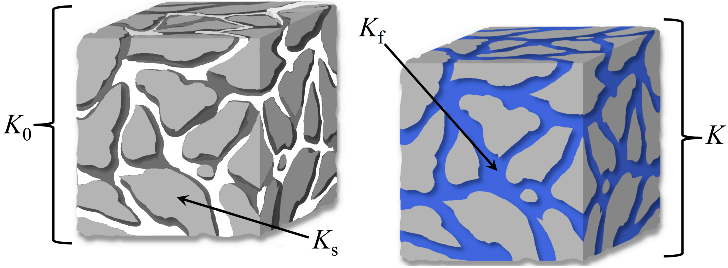
- Longitudinal waves $\leftrightarrow$ longitudinal modulus M

$$M = \rho v_M^2 \tag{1}$$

- Transverse waves $\leftrightarrow$ shear modulus G

$$G = \rho v_G^2 \tag{2}$$

Properties of Fluid-Saturated Porous Media



$$K = M - \frac{4}{3}G \quad (3)$$

$$K = f\left(K_s, K_0, K_f\right) \quad (4)$$

Properties of Composite and its Constituents

- Fluid does not affect the shear modulus $G_\mathrm{f} = 0 \Rightarrow G = G_0$
- Gassmann's equation (low frequency limit of Biot's theory):

$$K = K_0 + \frac{\left(1 - \frac{K_0}{K_\mathrm{s}}\right)^2}{\frac{\phi}{K_\mathrm{f}} + \frac{(1-\phi)}{K_\mathrm{s}} - \frac{K_0}{K_\mathrm{s}^2}}, \quad (5)$$

- Experimentally measured quantity: the longitudinal modulus M

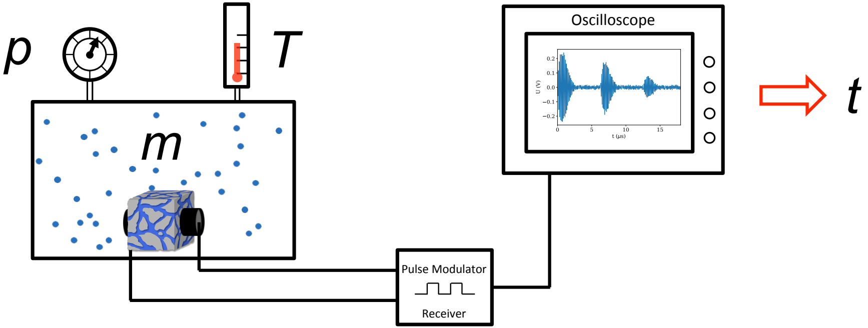
$$M = M_0 + \frac{(K_\mathrm{s} - K_0)^2 K_\mathrm{f}}{\phi K_\mathrm{s}^2 + \left[(1-\phi)K_\mathrm{s} - K_0\right] K_\mathrm{f}}. \quad (6)$$

- Derived for "classical" macroporous media (Gassmann, 1951)
- Does it work for nanoporous media?

Gassmann, F. Über die Elastizität poröser Medien *Viertel. Naturforsch. Ges. Zürich*, 1951, 96, 1-23
Biot, M. A. *J. Acoust. Soc. Am.*, 1956, 28, 168-178

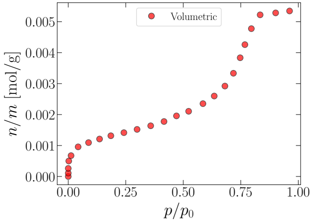
Experiments on Saturated Nanoporous Media

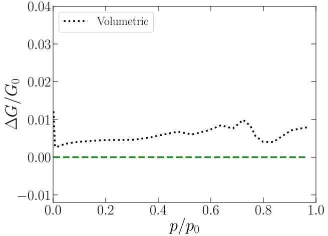
Gas adsorption + Ultrasound on Nanoporous Vycor glass

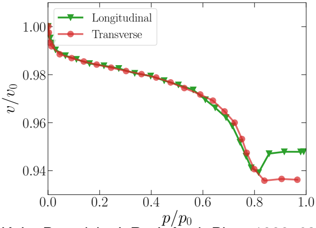


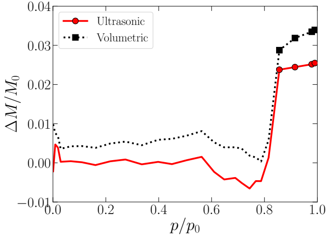
Schematic for the experimental setup from: Warner, K. L.; Beamish, J. R. *J. Appl. Phys.* 1988, 63, 4372-4376.
Dobrzanski, C. D.; Gurevich, B.; Gor, G. Y. *Appl. Phys. Rev.*, 2020, submitted

Experimental Data: Density and Velocities (N_2 at 77 K)





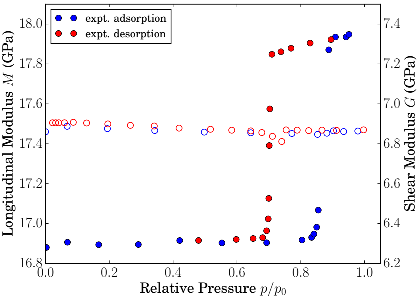




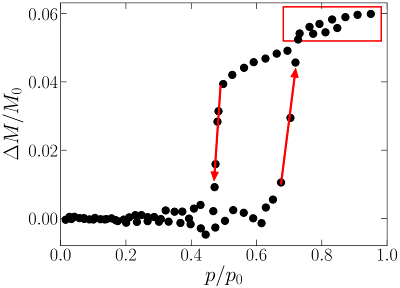
Warner, K. L.; Beamish, J. R. *J. Appl. Phys.* 1988, 63, 4372-4376.

Experimental Data: Other Fluids

Argon at 87 K



Hexane at 298 K

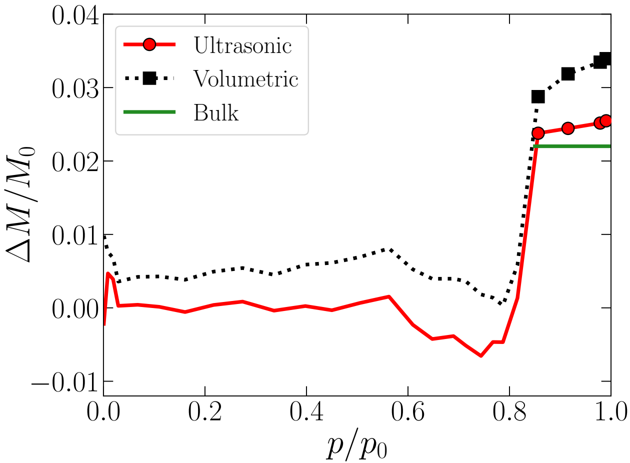


- Shear modulus does not appreciably change
- Longitudinal modulus changes at capillary condensation and continues to change beyond it

Page, J.H., Liu, J., Abeles, B., Herbolzheimer, E., Deckman, H.W. and Weitz, D.A., *Phys. Rev. E*, 1995, 52(3), 2763.
Schappert, K. and Pelster, R., *EPL (Europhysics Letters)*, 2014, 105(5), 56001.

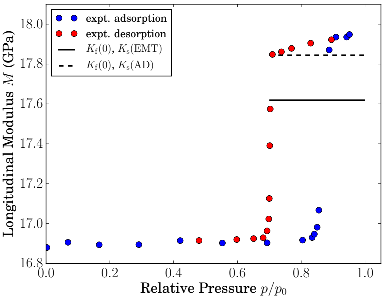
Experimental Data vs Gassmann Equation

$$K_0, K_{\rm s}, K_{\rm f}^{\rm bulk}, \phi \to K \text{ or } M$$



Experimental Data vs Gassmann Equation

Argon at 87 K



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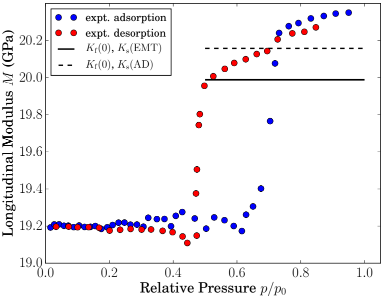


- The modulus changes with the vapor pressure p
- Even at $p = p_0$ the modulus of saturated sample differs from the modulus of the bulk-fluid saturated sample

Page, J.H., Liu, J., Abeles, B., Herbolzheimer, E., Deckman, H.W. and Weitz, D.A., *Phys. Rev. E*, 1995, 52(3), 2763.
Schappert, K. and Pelster, R., *EPL (Europhysics Letters)*, 2014, 105(5), 56001.

Calculating Fluid Modulus from Molecular Simulation

- Bulk (adiabatic) modulus and isothermal modulus: $K_\mathrm{f} = \gamma K_\mathrm{f}^T$
- Isothermal modulus and isothermal compressibility: $K_\mathrm{f}^T = 1/\beta^T$
- Isothermal compressibility (definition):

$$\beta^T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$$

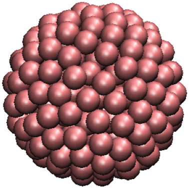
- Fluctuations of number of particles in the grand canonical ensemble (μ, V, T)

$$\beta^T = \frac{V\langle \delta N^2 \rangle}{k_\mathrm{B} T \langle N \rangle^2}$$

Bratko, D.; Curtis, R.; Blanch, D.; and Prausnitz, J. *J. Chem. Phys.* 2001, 115, 3873-3877.
Coasne, B.; Czwartos, J.; Sliwinska-Bartkowiak, M.; Gubbins, K. E. J. *Phys. Chem. B*, 2009, 113, 13874.
Strekalova, E.G., Mazza, M.G., Stanley, H.E. and Franzese, G., *Phys. Rev. Lett.*, 2011, 106(14), 145701.

Calculating Fluid Modulus from Molecular Simulation

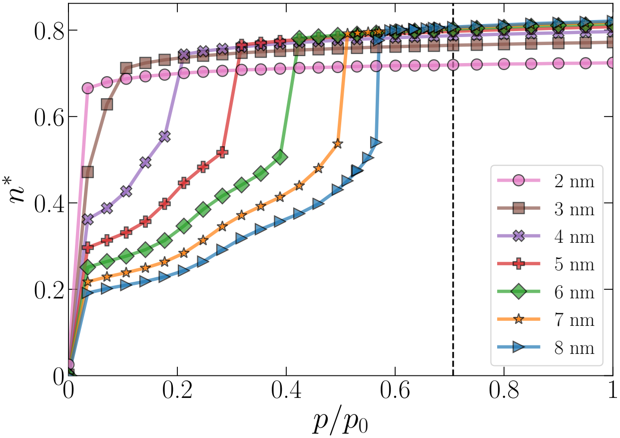
- Lennard-Jones nitrogen, spherical silica pores, $T = 77$ K, LJ solid-fluid interactions, integrated spherical potential
- Monte Carlo in the grand canonical ensemble (GCMC)
- 10^9 equilibration moves, then 3-5 series of 5×10^9 moves



Interaction	σ, nm	ϵ/k_B, K	n_s, nm^{-2}	r_{cut}, σ_{ff}
N_2-N_2	0.36154	101.5	-	5.0
SiO_2-N_2	0.317	147.3	15.3	-

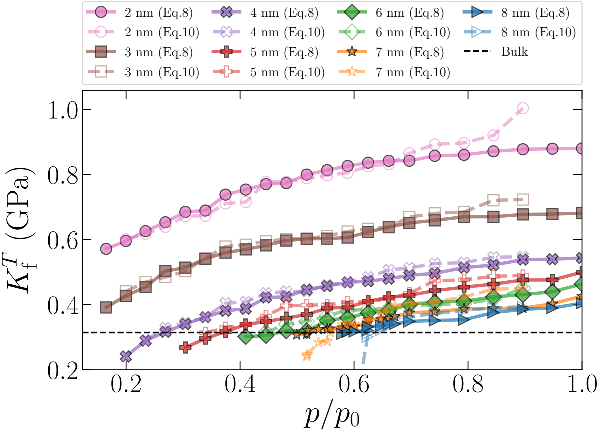
Allen, M. P. & Tildesley, D. J. Computer simulation of liquids. 1987. New York: Oxford, 385.
Norman, G. & Filinov, V. *High Temp.*, 1969, 7, 216
Rasmussen, C. J.; Vishnyakov, A.; Thommes, M.; Smarsly, B. M.; Kleitz, F.; Neimark, A. V. *Langmuir* 2010, 26, 10147-10157

Results: Adsorption Isotherms

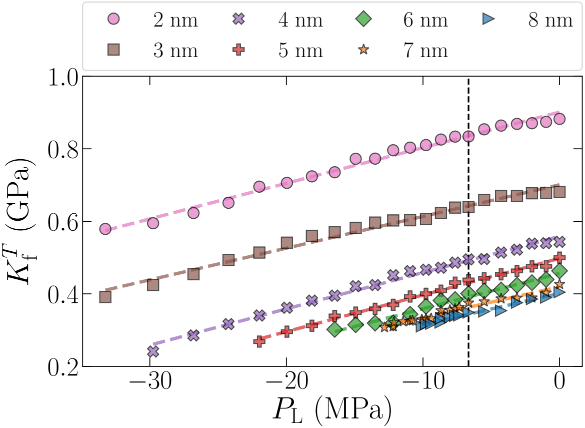


Maximov, M. A.; Gor, G. Y. *Langmuir*, 2018, 34 (51), 15650-15657 & 2020, 36 (17), 4853-4854

Results: Modulus Isotherms

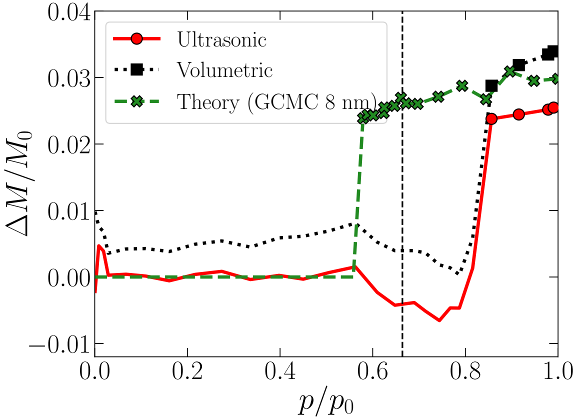


Results: Modulus vs Laplace Pressure



Laplace pressure: $$P_\mathrm{L} = \frac{R_\mathrm{g}T}{V_\mathrm{l}} \log\left(\frac{p}{p_0}\right) \quad (7)$$

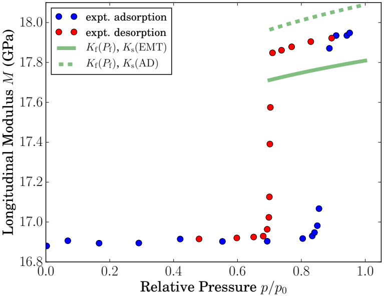
Results: Comparison with Experiment



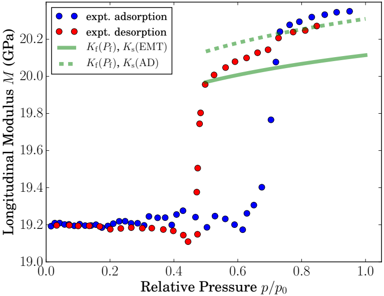
Maximov, M. A.; Gor, G. Y. *Langmuir*, 2018, 34 (51), 15650-15657 & 2020, 36 (17), 4853-4854

Experimental Data vs Gassmann Equation

Argon at 87 K



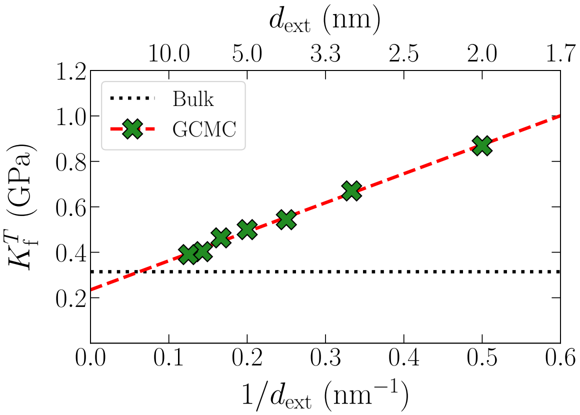
Hexane at 298 K



- Gassmann equation is applicable to nanoporous media
- The fluid modulus K_f has to be corrected for confined effects

Gor, G. Y. & Gurevich, B. *Geophys. Res. Lett.*, 2018, 45, 146-155

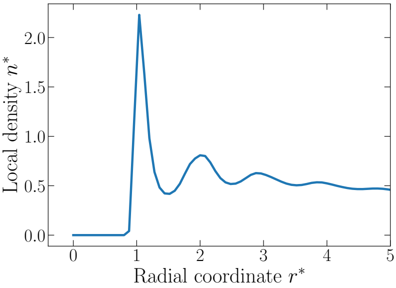
Results: Modulus vs Pore Size



- Modulus of confined nitrogen is a linear function of reciprocal pore size
- Modulus in small pores is higher than in bulk by a factor of three

Physical Mechanism

Density enhancement



Modulus-Pressure Equation

- Solvation pressure: $P_{\mathrm{f}} = P_{\mathrm{sl}} + P_{\mathrm{L}}$
- Laplace pressure: $P_{\mathrm{L}} = R_{\mathrm{g}} T / V_{\mathrm{l}} \log\left(p/p_0\right)$.
- Solvation pressure (solid-fluid interactions): $P_{\mathrm{sl}} \propto 1/d_{\mathrm{ext}}$
- Tait-Murnaghan Equation: $K(P_{\mathrm{f}}) = K(0) + \alpha P_{\mathrm{f}}$

Gor, G. Y.; Siderius, D. W.; Rasmussen, C. J.; Krekelberg, W. P.; Shen, V. K. & Bernstein, N. *J. Chem. Phys.*, 2015, 143, 194506
Gor, G. Y.; Siderius, D. W.; Shen, V. K. & Bernstein, N. *J. Chem. Phys.*, 2016, 145, 164505

Conclusions

- Analysis of experimental data suggests that the moduli of confined fluids differ from the bulk
- Isothermal compressibility (or modulus) of a confined fluid can be calculated using GCMC simulations
- The modulus is affected by the “solvation” pressure in the pore
- The modulus changes logarithmically with the vapor pressure
- The modulus is a linear function of the reciprocal pore size $1/d_{\mathrm{ext}}$
- The results are consistent with the ultrasonic data on porous glasses saturated with nitrogen (also argon and n-hexane)
- The modulus of supercritical methane is affected even stronger *

* Corrente, N. J.; Dobrzanski, C. D.; & Gor, G. Y. *Energy & Fuels*, 2020, 34 (2), 1506-1513

References

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- **Gor, G. Y.***; Siderius, D. W.; Rasmussen, C. J.; Krekelberg, W. P.; Shen, V. K; Bernstein, N. "Relation Between Pore Size and the Compressibility of a Confined Fluid", ***J. Chem. Phys.***, 2015, 143, 194506. DOI: 10.1063/1.4935430
- **Gor, G. Y.*** Siderius, D. W.; Shen, V. K.; Bernstein, N. "Modulus-Pressure Equation for Confined Fluids" ***J. Chem. Phys.*** 2016, 145, 164505. DOI: 10.1063/1.4965916
- Dobrzanski, C. D.; Maximov, M. A.; **Gor, G. Y.*** "Effect of Pore Geometry on the Compressibility of a Confined Simple Fluid" ***J. Chem. Phys.*** 2018, 148, 054503. DOI: 10.1063/1.5008490
- **Gor, G. Y.***; Gurevich, B. "Gassmann Theory Applies to Nanoporous Media" ***Geophys. Res. Lett.***, 2018, 45(1), 146-155. DOI: 10.1002/2017GL075321
- Maximov, M. A.; **Gor, G. Y.*** "Molecular Simulations Shed Light on Potential Uses of Ultrasound in Nitrogen Adsorption Experiments" ***Langmuir*** 2018, 34(51), 15650-15657 DOI: 10.1021/acs.langmuir.8b02909
- Corrente, N. J.; Dobrzanski, C. D.; **Gor, G. Y.*** "Compressibility of Supercritical Methane in Nanopores: a Molecular Simulations Study" ***Energy & Fuels***, 2020, 34(2), 1506-1513 DOI: 10.1021/acs.energyfuels.9b03592
- Dobrzanski, C. D.; Corrente, N. J.; **Gor, G. Y.*** "Compressibility of Simple Fluid in Cylindrical Confinement: Molecular Simulation and Equation of State Modeling" ***Ind. Eng. Chem. Res.***, 2020, 59(17), 8393-8402. DOI: 10.1021/acs.iecr.0c00693