Calculating elastic properties of confined simple fluids

Christopher D. Dobrzanski
New Jersey Institute of Technology

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Confinement in nanoporous materials is known to affect many properties of the fluids confined within their pores. The elastic properties are no exception. This dissertation begins with an overview of the relevant literature on ways of obtaining elastic properties of confined fluids. It outlines some fundamental gaps in our understanding. The chapters following address some of these gaps in understanding elastic properties of the confined fluid, in particular, how the shape of the confining pore matters, how supercriticality effects the properties, how an equation of state designed for confined fluids can be used to calculate elastic properties, and if an effective medium theory can accurately describe the elastic properties of fluid-saturated nanoporous materials. This dissertation concludes with some of the potential future improvements that can further our understanding of confinement effects on elastic properties.
CALCULATING ELASTIC PROPERTIES OF CONFINED SIMPLE FLUIDS

by
Christopher D. Dobrzanski

A Dissertation
Submitted to the Faculty of
New Jersey Institute of Technology
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CALCULATING ELASTIC PROPERTIES OF CONFINED SIMPLE FLUIDS

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Science is the belief in the ignorance of experts.

When someone says, "Science teaches such and such," he is using the word incorrectly. Science doesn’t teach anything; experience teaches it. If they say to you, "Science has shown such and such," you might ask, "How does science show it? How did the scientists find out? How? What? Where?"

Richard Feynman, from “What is science?”, 1966
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CHAPTER 1
INTRODUCTION

1.1 Fluids Confined in Nanoporous Materials

According to the International Union of Pure and Applied Chemistry (IUPAC) convention, nanoporous materials are materials that have pore sizes (internal dimensions) below 100 nm [12]. Due to having extremely small pores and large surface areas, these materials are employed for many industrial applications such catalysis, separation processes, as adsorbents and dessicants, heat exchangers, membrane technology, electrodes in energy storage, for methane storage and more [13, 14, 15, 16]. Many of these processes focus on a specific desired effect on the fluids which are confined within the pores. This special confinement and the interactions between the solid and fluid are known to induce changes to both the solid structure of the nanoporous materials as well as produce changes to the properties of the fluids confined within the nanopores [17, 18]. The effects on the solid structure can also be rather complex such that it depends non-monotonically on the vapor pressure of an adsorbed gas. For example, a solid porous Vycor glass sample will go through stages of expansion and contraction with increased amount of adsorbed fluid [19]. The magnitude of such deformations corresponds to hydrostatic pressures of roughly 100 bar. For fluids in particular, it is known that the temperature at which fluids freeze is different when the fluid is confined in nanopores versus in the bulk [20]. Also, the self-diffusion of fluids differs under confinement [17]. There is a shift in the vapor-liquid equilibrium and a capillary condensation as a result of confinement in nanopores [21]. The focus of this work will in particular be on how the elastic properties of the adsorbates are affected by confinement.
Confinement has its largest effects for pore sizes of sizes below about 10 nm, which are the smallest pores capable of encasing an atom or molecule. For the sake of avoiding superfluous repetition, “confined fluids” and related phrases in the rest of this document will specifically refer to fluids confined in (or adsorbed onto the inner surfaces of) nanoporous materials, where the confinement effects thereof are greatest.

1.2 Elastic Properties

Elastic properties such as the compressibility, bulk modulus, longitudinal modulus, and shear modulus are fundamental properties of a material which describe how a material responds to various mechanical loads. Knowledge of the elastic properties of confined fluids is important for probing their behavior and effectiveness in various practical applications including high-pressure lubricants [22] and nanofluidics [23].

The shear modulus may be considered zero for a bulk liquid, but this may not be the case for a fluids under confinement at the same temperature and pressure. When a liquid film is sufficiently thin, it becomes anisotropic and its response to shear force becomes similar to that of a solid [24]. Therefore, care must be taken when designing mechanical devices with dimensions on the nanoscale. Such changes to the elastic properties of fluids can alter their ability to be effective lubricants [25].

The compressibility of a material also determine the speed at which sound travels through the material. The summarized literature in this chapter suggests that the fluids confined in nanoporous materials have their elastic properties modified. This can have obvious implications for wave propagation analysis including seismic wave propagation on geological formations and laboratory based ultrasonic experiments on nanoporous samples [26].

The compressibility is also related to several other properties of materials such as the heat capacities, thermal pressure coefficient, and thermal expansion coefficient via thermodynamic relations (e.g., Mayer’s equation). Thus, the change
of compressibility may result in a change of other derivative properties of fluids in confinement. Note that experimental evidence exists for departure of the thermal expansion coefficient from the bulk value when measured for confined fluids [27].

Changes in the compressibility of a fluid has implication for flow properties through a porous medium. A relevant example system is hydraulic fracturing in shale, whose matrix consists predominantly of nanopores. Confinement in shales can cause flow properties of hydrocarbon fluids to differ from in the bulk due to the elastic properties being affected. The fundamental behavior of these systems is not well understood. The understanding is complicated by the many factors that are involved that can influence the fluid behavior including flow and elastic properties such as the pore sizes, curvatures, morphologies, and various defects. Moreover, it is not straightforward to probe such systems to measure the elastic properties of confined fluids; the tiny length scales in nanoporous systems make it difficult to resolve some of the unknowns of these systems. There are only a few techniques that can shed some light on several of the fluid behaviors and elastic properties in nanoporous systems, but they also have limitations. The methods and limitations of these techniques will be discussed in the next sections, as well as some alternative approaches to experimental measurements.

1.3 Experimental Measurements

The elastic properties of monolithic solid samples can be measured in a relatively straightforward fashion by applying mechanical pressure on the material and measuring the change of materials dimensional lengths. Clearly such approaches cannot be applied to confined fluids directly; the measurements would have to be on a fluid-saturated nanoporous medium. Furthermore, interpreting stress-strain measurements on a nanoporous sample can be nontrivial due to complications with poroelastic behaviors [28, 29]. Therefore, the elastic properties of fluid-saturated nanoporous
media can be more straightforwardly extracted from measuring the velocity of elastic waves in the media, typically using ultrasonic frequencies. The key equations which determine the elastic moduli from sound wave propagation through a sample are

\[ c_t = \sqrt{\frac{G}{\rho}}, \quad \text{and} \quad c_l = \sqrt{\frac{M}{\rho}}, \quad (1.1) \]

where \( c_t \) is the velocity of transverse waves, \( c_l \) is the velocity of longitudinal waves, \( \rho \) is the mass density of the sample, \( G \) is the shear modulus, and \( M \) is the longitudinal modulus. The bulk modulus \( K \) is related to the longitudinal and shear moduli by

\[ K = M - \frac{4}{3} G. \quad (1.2) \]

The typical experimental set-up for determining the elastic properties via ultrasonics involves the pulse-echo method [30]. Short ultrasonic pulses are generated by applying voltage pulses to a piezo-electric crystal, such as LiNbO\(_3\), that is attached to the sample. The waves generated can be either longitudinal or transverse, depending on the crystal and its cut angle. The ultrasonic pulse propagates through the sample multiples times due to reflections normal to two parallel faces. The successive echos decrease in amplitude and the transit time is measured with an oscilloscope by comparing the time between pulses. Thus, the speed of sound \( c \) is calculated from the distance that the sound travels \( L \) (i.e., twice the sample length for reflections) and the transit time \( \Delta t \) as

\[ c = \frac{L}{\Delta t}. \quad (1.3) \]

Although the first ultrasonic measurements on fluid-saturated nanoporous samples have been carried out in the early 1980s, there have been relatively few studies of this kind since then. The first work was done by Murphy and was not focused on the confined fluid properties, but rather in properties of the solid [31]. Murphy measured sound velocity and attenuation on nanoporous Vycor relative to
humidity and compared the results to similar experiments on Massilon sandstone (10 - 100 µm pores). Murphy found that even though the sandstone is 88% quartz and only 4% amorphous silica, it had about 6 times greater losses than compared to attenuation on Vycor, which is 96% amorphous silica. Murphy attributed this difference due to differences in surfaces and pore properties of the materials: Massilon sandstone had flatter pores and rougher surfaces, thus being more compliant and generating more viscous losses compared to Vycor, which has smooth surfaces and spherically isotropic pores.

A transformational step was made later in that decade by Warner and Beamish, who used ultrasonic experiments to investigate fluid adsorption on nanoporous
materials and its surface area [1]. The speed of sound through a medium depends on its density, as stated in Equation (1.1). When a fluid is allowed to adsorb onto a porous solid, the speed of sound through the medium changes. Since the fluid does not contribute to the system’s shear modulus, the effective shear modulus of the system is the same as the shear modulus of the empty porous sample $G = G_0$. This allows straightforward and direct probing of the sample density using ultrasonics via Equation (1.1). Warner and Beamish utilized this concept to relate the amount of fluid adsorbed to the speed of sound, thus proposing an alternative way to measure an adsorption isotherm. They showed that the adsorption isotherms determined from sound velocity measurements are fully consistent with adsorption isotherms obtained through volumetric measurements and that the ultrasonic method is also applicable for calculation of the specific surface area. They found the ultrasonic method to have several key distinctions which translate to some advantages compared to conventional adsorption isotherm methods: 1 – no calibrated volumes or delicate balance needed; 2 – no need to know the mass of the sample nor dead volume of the container; and 3 – only measurements of the gas pressure and sound velocity are needed. Moreover, both the ultrasonic and volumetric methods to produce an adsorption isotherm can be used simultaneously and completely independently on the same experimental set up. This can be an viable alternative method or provide complimentary information for the system when both are used together. These early works set the stage for more developments in using ultrasound to understand nanoporous materials and fluids confined within them, in particular the elastic properties.

In the early 1990’s, Page et al. combined ultrasonic measurements during vapor adsorption in nanoporous media with optical measurements [32, 2]. The main focus of their work was the pore-space, in particular how the fluid fills the pore-space and how the filled pores are spacially correlated. However, additionally they were the first to report the longitudinal modulus of the fluid saturated nanoporous sample
as a function of vapor pressure. They showed that the longitudinal modulus is approximately unchanged as the vapor pressure increases up until the pores are completely filled, where there is a rapid increase in the longitudinal modulus. Their original data of this behavior is replotted and shown in Figure 1.2. They attributed this behavior to the vapor voids in the confined fluid, which plays a dramatic role in the effective modulus of the liquid-vapor mixture according to Wood’s approximation [33]

\[
\frac{1}{K_f} = 1 - \frac{\phi_{\text{vap.}}}{K_{\text{liq.}}} + \frac{\phi_{\text{vap.}}}{K_{\text{vap.}}},
\]  

(1.4)

where \(K_f\), \(K_{\text{liq.}}\), and \(K_{\text{vap.}}\) are the moduli of the fluid mixture, liquid, and vapor, respectively, and \(\phi_{\text{vap.}}\) is the volume fraction of vapor in the pores. According to Wood’s approximation, the compressibilities \((1/K)\) are added proportionally to their volume fraction. Thus, the effective modulus is dominated by the much smaller modulus of the vapor voids. Therefore, when the vapor fraction is very small (i.e., \(\phi_{\text{vap.}} < 10^{-3}\)), it makes negligible contribution to the effective modulus of the fluid-filled solid. Page et al. found that changes to the effective modulus of the fluid-saturated sample were almost entirely due to changes in the modulus of the fluid.

From ultrasonic the transit time measurements with increasing gas pressure, they found that the longitudinal modulus of the sample is relatively constant (same as empty sample) until the pores are nearly all filled with fluid, where the effective modulus has a rapid increase to 5% higher than the empty sample modulus, which is followed by a gentler rise to a final modulus of about 6% higher than that of empty Vycor. This behavior can be seen in Figure 1.2 where at pressures below capillary condensation where there are significant vapor voids, the modulus is nearly zero.

Following those early works on nanoporous materials, various other researchers employed ultrasonic experiments to study phase transitions of confined phases [34, 35, 36, 37, 38, 39, 40]. When a fluid freezes in the pores its elastic properties noticeably
change, which is seen clearly in velocity of wave propagation measurements. This signature of phase transitions has been used in a number of works to monitor the freezing of fluids in confinement, such as helium or mercury, however these works did not quantify their elastic properties.

Figure 1.2 Gravimetric adsorption isotherm (left) of hexane in Vycor glass and the elastic longitudinal modulus (right) of the Vycor glass sample from ultrasonic measurements as a function of relative hexane vapor pressure. Source: [2].

More recently, Schappert and Pelster have undertaken a major role in experimental investigations of the elastic properties of confined phases with over a dozen publications studying the changes of elastic properties of fluid and solid phases of argon, nitrogen, and oxygen confined in nanoporous materials at low temperatures [3, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52].

In their first work, Schappert and Pelster investigated elastic and freezing properties of argon confined in nanoporous Vycor glass [3]. They used an ultrasonic set up very similar to that of Warner and Beamish with some minor differences in such as using a silver epoxy instead of silicone fluid to bind the transducer to the sample. Both used LiNbO₃ crystals (41° X-cut) for the shear wave transducers. They determine there are three regions of filling fraction which have differing behavior for argon below its normal freezing point. In the first region, using the ultrasonic measurements they found that the shear modulus of the Vycor with adsorbed argon
does not change when there are less than about 3 to 4 adsorbed layers of argon. When the pore is filled past this region of filling, there is a linear increase in shear modulus in the second region. In the third region, when the pores become completely filled, the shear modulus has an abrupt increase and becomes nearly constant at its maximum value. This behavior is displayed in Figure 1.3.

Figure 1.3 (a) Ultrasonic transit time (relative to the transit time of the unfilled sample), and (b) ratio of effective shear modulus \( G \) to the shear modulus of the empty sample \( G_0 \) on adsorption of argon at \( T = 72 \) K. The process of freezing starts above a filling fraction of 0.53. Source: [3].

Three years after their first work, Schappert and Pelster reported on using ultrasonics to study the shear moduli of argon confined in nanopores at temperatures well below the normal freezing point. They found the shear modulus of solid argon confined in nanopores to be about equal to the shear modulus of solid argon in bulk [41]. Schappert and Pelster used ultrasonic experiments combined with controlled
argon adsorption in nanoporous Vycor glass to show that ultrasonic measurements can be a useful method of determining the liquid-solid phase transition in nanopores [42]. They also found that the adsorbate only noticeably contributes to the effective longitudinal modulus when the pores are completely filled, and that partially filled pores have the same longitudinal modulus as a dry porous sample. They conducted more investigations on filled pores and found that the shear modulus shows a continuous freezing behavior for argon in Vycor glass at temperatures below 80 K and show that it is possible to calculate the amount of solid adsorbate from ultrasonic measurements during temperature cycles [43]. After that study, by using ultrasonic measurements of nitrogen adsorbing on nanoporous glass, Shappert and Pelster showed that the shear modulus of the confined solid nitrogen is significantly enhanced close to the pore walls [44]. They found that by filling the pores with approximately one layer of adsorbed nitrogen, corresponding to about 12% of the filled pore volume, the modulus was enhanced to 20% of its maximum, which occurs at complete pore filling.

Following that, Schappert and Pelster were able to measure the adsorption-induced deformation during the experiments using a capacitive distance sensor. They showed that the Laplace (capillary) pressure of the menisci at the pore ends causes deformation of the sample, and also influences the effective longitudinal modulus of the sample [45, 46]. They found that the changes in the modulus are due to changes in the longitudinal modulus of adsorbed argon. Although the longitudinal modulus was affected, the shear modulus of the sample was not affected by the Laplace pressure when the pores were filled.

Subsequently, they turned their focus to behaviors of more complex fluids under confinement [47]. They conducted ultrasonic experiments on n-heptane and n-nonane confined in Vycor glass. Above the melting temperatures, Schappert et al. found that the shear moduli of confined n-heptane and confined n-nonane was non-zero, which is
typically seen at temperatures below the melting temperature. They also found the shear modulus to increase continuously over a broad temperature range (more than 120 K for nonane), indicating that either a continuous change of molecular order is happening or that the fraction of crystalline parts is increasing.

Later, Schappert et al. studied solid oxygen in nanopores and its temperature dependence. They showed through the shear modulus of the confined oxygen in completely filled pores that the adsorbate exhibits the two abrupt phase changes (liquid-solid, solid-solid) seen in bulk oxygen experiments, but when the pores are not completely filled there is a continuous liquid-solid transition [48]. They also found that the extent of the modulus enhancement for the adsorbate does not have a simple dependence proportional to the strength of the adsorbate-solid interaction, and that further studies are needed to resolve the influencing factors that contribute to the changing structure of the adsorbate and its elasticity.

Schappert et al. used their experimental set up for measurements of elongation of the Vycor glass upon changes in the properties of the confined argon [53]. In particular, they found that the continuous crystallization of the confined argon with lowering of the temperature produces a continuous reduction of the adsorption-induced deformation. Schappert et al. suggest that this is due to the lowering of the so called solvation pressure from the continuous crystallization of the confined argon.

Based on experimentally-observed linear relationship between the measured elastic modulus of the fluid and the strain of the porous sample, Schappert and Pelster also proposed a method to determine changes of pressure and surface stress of the adsorbate in nanopores [49]. They based their method on theoretical works of Gor and Neimark [54, 55]. Assuming Hooke’s law applies, the strain $\varepsilon = \Delta V/V_0$ on the porous sample with adsorbed fluid results from the solvation pressure $P_s$ modulated
by the elastic modulus $K$
$$\varepsilon = \frac{P_s}{K} + \varepsilon_0. \quad (1.5)$$

The difference between the adsorption stress and the external gas pressure is known as the solvation pressure, that is $P_s = \sigma_{\text{Ads}} - p$. $\varepsilon_0$ is a strain offset due to the prestress of the porous matrix. A pore filled with an adsorbate has three contributions to the solvation pressure in the pores as
$$P_s = -\frac{\gamma_{sl}}{r_p} + P_L + (p_0 - p), \quad (1.6)$$
where $r_p$ is the pore radius, $\gamma_{sl}$ is the solid-liquid surface tension, $R_g$ is the gas constant, $V_m$ is the molar volume of the adsorbate, and $p_0$ is the saturation pressure of the adsorbate. The term $P_L = \frac{R_g T}{V_m} \ln\left(\frac{p}{p_0}\right)$ is the Kelvin equation form of the Laplace pressure. However, it is the change in the solvation pressure during pore filling from a reference pre-stress state such as empty pore that induces an elastic strain. For filled pores, the normal pressure exerted by the fluid is
$$\Delta P_s = \Delta P_{s}^{\text{sat}} + \frac{R_g T}{V_m} \ln\left(\frac{p}{p_0}\right) + (p_0 - p). \quad (1.7)$$
$\Delta P_s$ is zero for empty pores and takes its maximum value at saturation vapor pressure, which is also when the $(p_0 - p) = 0$. For large pores, the dependence $\Delta P_s^{\text{sat}}$ is proportional to $1/r_p$.

Their method relies on the dependence of the adsorbate’s longitudinal modulus $M_l$ on $\Delta P_s - \Delta P_{s}^{\text{sat}}$, which has been found experimentally to have a nearly linear relationship. Therefore,
$$M_l = \alpha \Delta P_s + M_{l,\text{bulk}} \quad (1.8)$$
holds with the slope $\alpha = \partial M_l/\partial \Delta P_s$. Thus by using data of the confined fluid modulus in the filled state with respect to $\Delta P_s - \Delta P_{s}^{\text{sat}}$, one can obtain the pore pressure by
extrapolating the linear relation. Schappert and Pelster found this method to match closely to the experimental solvation pressure at saturation for argon at temperatures of 80 and 86 K confined in silica nanopores [49]. Later, Schappert and Pelster also found that the slope of the proportionality constant $\alpha$ does not depend on temperature [51].

They also determined some missing pieces in the fundamental understanding of how fluids behave in nanoporous materials that are needed in order to more accurately analyze ultrasonic experiments on nanoporous materials: how the pore size affects the isothermal modulus, adsorption-induced pressure, and heat capacity ratio [52]. Thus, they outlined some clear goals for future works to tackle.

Schappert and Pelster performed several other investigations of the confined fluid elastic properties. They found that the temperature change produces linear dependence in the confined fluid modulus [50]. Through their analysis of the ultrasound data, they found that the modulus of the matrix material can significantly impact the accuracy of the determined fluid modulus. This is important and will be discussed further in Section 1.5

### 1.4 Theoretical Predictions

#### 1.4.1 Compressibility and Bulk Modulus

There are less than a handful of known experimental setups that can simultaneously measure extent of adsorption and elastic properties via ultrasonics, thus, there are not much experimental data available. Fortunately, molecular modeling techniques are available to simulate the adsorption and calculate elastic properties to fill in the gap in science. Moreover, molecular simulations have an advantage over experiments since they can be used to examine the local properties, anisotropies, and properties of individual materials down to a molecular level directly, which most experiments cannot. Experiments typically require measuring the average properties of some
inhomogenous material. The ability to examine the individual contributions of the fluid and of the solid directly is a distinct advantage of molecular modeling over experiments. Molecular modeling methods such as molecular dynamics (MD) and Monte Carlo (MC) simulations model atoms or groups of atoms as particles obeying classical mechanics with empirical interaction potentials representing the particle interactions. These methods allow obtaining great detail on the mechanics and thermodynamics of nanoscale systems [56]. In thermodynamics, the elastic properties of fluids are typically presented in terms of the isothermal compressibility $\beta_T$, the reciprocal of which is known as the isothermal elastic modulus $K_T = \beta_T^{-1}$.

For a macroscopic system, the isothermal compressibility $\beta_T$ is defined as

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

(1.9)

where $V$ is the system volume, $P$ is the fluid pressure, and $T$ is the absolute temperature. Here, following Refs. [57, 4, 58], we use the same definition of $\beta_T$ for the fluid confined in the pore.

The overall compressibility of the fluid in the pore which corresponds to the macroscopic average compressibility that can be extracted from experimental sound velocity measurements on fluid-saturated porous samples. But, by using theoretical techniques including molecular simulations, it is possible to also obtain more detailed information on the system. The elastic properties in the pore can vary based on the radial distance to the pore walls $r$. Certain techniques can calculate these “local” properties, such as a local isothermal compressibility $\beta_T(r)$ and will be discussed below.

1.4.2 Monte Carlo

There are various statistical mechanical ensembles and associated simulation techniques for molecular modeling, most of which hold the number of particles in the system
constant. Grand canonical Monte Carlo (GCMC) [59] algorithm is very useful for modeling adsorption of fluids in nanopores because it allows the number of particles in the pore (i.e., adsorbed) to change in accordance with the assigned chemical potential (or vapor pressure) of an external reservoir.

Classical statistical mechanics allows for the calculation of the compressibility of the fluid in the pore from the fluctuations in the number of particles in the pore $N$ in the grand canonical ensemble through the following relation

$$\beta_T = \frac{V \langle \delta N^2 \rangle}{k_B T (N)^2} \quad (1.10)$$

where $\langle \delta N^2 \rangle$ is the variance of $N$ and $k_B$ is the Boltzmann constant. Equation (1.10) can be applied to a small system as long as the fluctuations obey a Gaussian distribution [57, 4]. Thus, molecular simulation of a fluid in the pore performed in the grand canonical ensemble can provide data for calculation of $\beta_T$. Some of the first works to report confined fluid elastic properties utilized the GCMC simulation technique.

In 2001, Bratko et al. used GCMC to calculate an elastic property of fluid confined between two plates up to 6 nm apart [60]. The goal of the paper was to assess metastable water behavior in hydrophobic confinement beyond the point of evaporation, nevertheless in the process they also reported an elastic property. Using GCMC simulations of water in hydrophobic smooth parallel plates, they calculated the reduced isothermal compressibility $\beta^R_T = \frac{\beta_T V}{k_B T} = \frac{(N^2) - \langle N \rangle^2}{N}$ of a fluid between plates with separation distances ranging between 1 and 6 nm. They found that reduced compressibility was enhanced significantly as the separation distance decreases. They also found this enhancement of the reduced compressibility to be larger at lower values of the vapor pressure at the same pore size. Calculating the reduced compressibility is also convenient because it avoids the questionable nature of defining the volume $V$ used in calculating the compressibility of the confined fluid.
Bratko et al. later calculated the reduced compressibility for water in a 2.7 nm hydrocarbon slit pore and how it depends on electric field [61]. They found that applying an electrical field lowered the reduced compressibility of the confined water from about 0.2 to 0.05 when going from an electrical field of 0 to 0.4 V/Å. The higher electrical field suppressed the fluctuations of particles in the pore. They found that the effects of electrostriction on compressibility of the confined water are an order of magnitude higher than those of bulk water. Varying the direction of the applied electrical field (parallel or perpendicular to the wall) did not appear to produce a markedly different behavior in the reduced compressibility [61].

Vaitheeswaran et al. calculated the isothermal compressibility of water in the presence of an electric field and in the region between two plates. The plates were modeled by a “hard-wall-like” potential and separated by 1.64 nm at a temperature of 300 K. They calculated from the particle fluctuations in this region at a constant volume with respect to electrical field [62]. They applied electrical fields between 0 and 8.68 V/nm and found that the compressibility was a maximum at a field of 2.82 V/nm, which resembled a liquid-vapor phase transition.

Coasne et al. utilized Equation (1.10) to calculate the compressibility of argon and methane confined in graphene slit-like pores that were two molecular diameters of the fluid in width [63]. They found that the compressibility was about 50 and 33% of the bulk fluid values, respectively. They found that the pressure strongly controlled the freezing temperature of the confined fluid. But, because the compressibility was lower, they suggested that this significant pressure dependence of the freezing temperature of the confined fluid is not related its compressibility, but rather related to the pressure difference between the bulk and confined phase [63].

Shimoyama et al. used GCMC simulations of cyclohexane, oxane, 1,4-dioxane, and 1,3,5-trioxane confined in carbon slit pores of widths of 0.8, 1.0, and 1.2 nm at 298 K. They used calculations of the isothermal compressibility Equation (1.10)
to interpret the state of the adsorbed fluid and the transition from gas to liquid. Also, 1,4-dioxane was shown to have another sharp transition at higher pressure to a solid-like state where it packs in a square lattice structure for the 0.8 nm pore, but not the larger pores. They found that although it does not have such a sharp transition, 1,3,5-trioxane also packs in a solid-like state with a hexagonal lattice structure at saturation pressure. Cyclohexane and oxane, on the other hand, were found to remain liquid-like at saturation.

A different approach taken by Rickman [64] to calculate local elastic properties of confined fluids was based on correlations between components of the stress rate and the strain rate. Rickman used stress correlation functions first derived by Schofield. Schofield defined the elastic constant tensor components in k-space from an assumed linear relation between components of the stress rate and the strain rate [65]. Rickman used these to determine local elastic properties of Lennard-Jones (LJ) fluid confined in slit-shaped pores in MC simulations and related them to the fluid structure.

Urbic et al. took another approach using MC simulations of water confined in LJ disk matrix. They calculated compressibility of the water using a fluid-fluid correlation function [66]. They found that the compressibility was affected by the density of the LJ disk obstacles. At low disk density, the water compressibility increased relative to pure fluid due to an increased ordering and hydrogen bonding network formation, whereas high obstacle density reduces the compressibility of confined water, because the obstacles prevent the fluid from forming good hydrogen bonding networks.

Strekalova et al. took a similar approach and investigated water in hydrophobic confinement around nanoparticles [67, 68]. They performed MC simulations of water in a constant pressure ensemble, allowing volume to change. They calculated the compressibility from the volume fluctuations. They found that there is a first-order liquid-liquid phase transition (LLPT) associated with an over 90% decrease in the
compressibility in the region of the phase transition. They found that a nanoparticle concentration of just 2.4% is enough to prevent the LLPT and pressures above 0.16 GPa.

Although all the aforementioned works calculated compressibility of fluids in confinement, they used it as a qualitative criterion to deduce about the phase transition in the fluid. That is to some extent similar to some of the experimental works utilizing ultrasonic measurements to see qualitative changes in the transit time of sound and indicate the solid-liquid phase transition [37, 38, 39, 40]. Although, none of these molecular simulation works strived to relate the predicted values to the values extracted from experimental measurements on nanoporous samples. The first attempts on the matter were made by Gor et al. in the last five years.

In particular, they calculated the isothermal compressibility of argon confined in spherical silica pores using Equation (1.10) [4]. They varied the pore sizes from 2.5 to 6 nm in GCMC simulations. They found that the compressibility is significantly lowered by confinement and is much lower for the smaller pore sizes. They found it to be about 1 and 1.6 GPa$^{-1}$ at 2.5 and 6 nm, respectively, whereas the bulk value of argon is closer to 2.1 GPa$^{-1}$ [4].

Gor et al. used additional GCMC simulations and calculated the isothermal modulus (reciprocal of compressibility) of argon fluid confined in spherical nanopores [58]. They found that the confined fluid modulus dependence on pressure can be well described by the linear Tait-Murnaghan equation [69]

$$K(P) = K(P_0) + \alpha P.$$ (1.11)

This equation is known to apply well for bulk fluids and solids for wide ranges of pressures, but Gor et al. showed that it also describes confined fluids rather well over similar pressure ranges. They also varied the solid-fluid interaction strength to show how it influences the elastic modulus, finding that the higher interaction strengths
were associated with higher moduli. Also, the calculated slope $\alpha$ for the confined fluid was found to match the slope for the fluid in bulk, as long as the interaction was not solvophobic [58]. Although Gor et al. made these advances, there were still plenty of unanswered questions, in particular, how the pore shape can effect the confined fluid compressibility, considering fluids beyond argon, and relating elastic properties to values obtainable from an equation of state.

1.4.3 Density Functional Theory
Evans and coworkers took a different approach to calculating an elastic property of the confined fluid [70, 71]. They used an alternative definition of compressibility 
\[
\left(\frac{\partial \rho(z)}{\partial \mu}\right)_T,
\]
which was based from previous works [72]. This allowed investigating the compressibility as a function of distance to the adsorbent wall. They performed density functional theory (DFT) calculation of fluid near a single wall and confined between two walls and found that they have similar effects on their local compressibility of the confined fluid. They compared how different fluid-wall interactions affected the local compressibility and found that solvophobicity has a larger effect on the compressibility than the density of the fluid, indicating that compressibility can be a good indicator of the solvophobicity of a surface [70, 71]. Later, Evans et al. extended this method for GCMC simulations, which were found to be consistent with their DFT calculations [73]. They also showed how different forms of the wall-fluid interaction, short-ranged versus long-ranged, effect the wetting-drying conditions. They found from GCMC and DFT that for the long-ranged case, wetting is first-order, while for the short-ranged it is continuous (critical), while the drying is continuous in both cases [73].

Sun et al. used DFT to calculate the elastic properties of argon fluid in slit and later in spherical pores [74, 75, 76]. They formed the expressions for elastic moduli based on Hooke’s law. One can relate the elastic modulus to changes in the stress
tensor \( \Pi \) before and after deformation. Following the model of Fisher [77], Sun et al. calculated the change in the stress tensor

\[
\tilde{\Pi} - \Pi = G_T(T_{\alpha\beta} + T_{\beta\alpha}) + \left(K_T - \frac{2}{3}G_T\right)T_{\alpha\alpha}, \tag{1.12}
\]

where \( G_T \) and \( K_T \) are the isothermal shear and bulk moduli, respectively. The stress tensor can be obtained from the Irving-Kirkwood expression [78]

\[
\Pi = -k_B T \rho(r) I + \frac{1}{2} \int \frac{dr_{12}}{r_{12}} \frac{r_{12}}{r_{12}} U'(r_{12}) \times \int_0^1 d\xi \rho^{(2)}(r - \xi r_{12}, r - \xi r_{12} + r_{12}), \tag{1.13}
\]

where \( \rho \) and \( \rho^{(2)} \) are the singles and doublet pair density functions, respectively, \( I \) is the unit tensor, \( U(r_{12}) \) is the pair potential, and \( \xi \in (0,1) \) is a constant. Using this they calculated the isothermal shear and bulk moduli as

\[
G_T(r) = k_B T \rho(r) + \frac{4}{15} I_1(r) + \frac{1}{15} I_2(r) \tag{1.14}
\]

\[
K_T(r) = \frac{5}{3} k_B T \rho(r) - \frac{2}{9} I_1(r) + \frac{1}{9} I_2(r). \tag{1.15}
\]

They also obtained an average of this modulus in the pore over the length of the pore width \( D \)

\[
\bar{K}_T = \frac{2}{D} \int_0^{D/2} K_T(r) dr. \tag{1.16}
\]

They found that the elastic modulus has large deviations in the pore from the average and can have large negative spikes. But, the average value the calculated compared well to other similar theoretical predictions. Of note, Sun et al. took the spatial average over the length rather than the volume, which could have issues when considering geometries besides parallel slit pores.

Keshavarzi et al. [79] employed density functional theory to determine an elastic property of LJ fluid in slit pores of 2 to 8 multiples of \( \sigma \) (LJ distance unit) and at LJ reduced temperatures between 1.5 and 3. They calculated a reduced bulk modulus

20
similar to form of
\[ K_T^R = \frac{1}{T} \left( \frac{\partial P}{\partial \rho} \right)_T, \]
but modified to separate the normal and lateral components of the reduced modulus with respect to normal and lateral components of the pressure. They found that there is a common bulk modulus point as a function of density observed in slit pores of various sizes and at different temperatures. They attributed the existence of the common point for different isotherms of the the bulk modulus is due the attraction contribution being canceled out by the repulsion contribution. They also found that both the lateral and normal moduli agree with the linear Tait-Murnaghan Equation (1.11) for all temperatures and pore widths that they considered, with linear fits to their results having $R^2$ values of 0.996 or higher. The DFT calculation have shown to be useful for modeling simple pore structures and providing great detail on properties of the confined fluid, but DFT has difficulties for modeling more complex geometries such as rough surfaces with atomistic detail.

1.4.4 Molecular Dynamics
In addition to Monte Carlo and classical DFT, molecular dynamics (MD) can be also employed for calculating of confined fluid compressibility. Acharya et al. performed MD simulations to model protein hydrophobicity. They used an alternative definition of compressibility \( \frac{1}{\rho(z)} \left( \frac{\partial \rho(z)}{\partial P} \right)_{T,\Delta} \) where \( \Delta = 0.25 \text{ nm} \) is the thickness of the adsorbate layer considered. They used MD simulations of SPC/E water hydrating flat protein surfaces. Using that definition they found that the local compressibility near the most hydrophobic surfaces is about 12 times higher than that of bulk water. They found this local compressibility tracks well with another local compressibility based on particle number \( N \) fluctuations \( k_B T \frac{<N(z)^2>-<N(z)>^2}{<N(z)>^2} \) when larger observation volumes \( V \) are considered. The calculated compressibility depended on the size and shape
of the $V$ used. They also found a large asymmetry in the ability of hydrophobic and hydrophilic inhomogeneities to affect the local compressibility of water at the interface.

Another approach taken by Martini and Vadakkepatt, who studied thin film lubricant behavior in slit pores, is more straightforward [25]. They modeled hexadecane fluid confined in 5 nm wide alumina slit pores at different temperatures (300, 350, 400 K) using molecular dynamics (MD) simulation. They applied a small change in pressure via compressive load onto one of the pore walls and measured the resulting volume change and calculated the compressibility via the definition Equation (1.9). They compared their results to the Dowson and Higginson (DH) model [80], which is a pressure-density relation commonly used to describe elastohydrodynamic lubrication. They found that the MD results differ significantly from the DH model prediction at higher pressures. Their obtained density is close to DH at around ambient pressures, but is increased much more compared to DH as pressure increases. They argued that this difference could be due to layering effects in the simulations. They also compared the calculated $K_T$ from MD simulation to the Tait equation prediction [81]. They found good agreement with the Tait equation at all temperatures considered.

These authors later performed similar simulations using other fluids [82]. They simulated three lubricants [heptane, squalene, and pentaerythritol (2-ethylhexanonate)] in pores of various separation widths with loads between 0.2 and 2.5 GPa. The main points they wanted to address in that work were: 1 – how should density be defined for confined fluids in channels given that excluded volume near the walls can play a major role in the calculated properties; 2 – will the compressibility predicted by MD approach that of the bulk fluid as the film thickness is increased; and 3 – is the method applicable to other fluids with very different molecular structures. They found that the pressure-density relationship from MD calculations matches well to
the Tait equation for larger pores ($D = 9.6$ nm) for all fluid models. But the densities become increasingly overpredicted by the Tait equation at smaller pore sizes (6.4 and 3.2 nm). They recommend the center points of the inner most wall atoms to be used as the boundaries of the volume, because they found that this allows predicting the bulk density when simulations are performed on larger pores.

Mochizuki and Koga used another approach to calculate a linear isothermal compressibility [83]. They were studying the solid-liquid critical behavior of confined LJ fluid. They performed MD simulations of LJ fluid in a carbon nanotube pore of 1.2 nm in diameter and calculated diverging heat capacity and maximum linear isothermal compressibility $\frac{1}{L_z} \left( \frac{\partial L_z}{\partial P_{zz}} \right)_T$. They used the locus $P_{zz}(T)$ of the maximum isothermal compressibility and heat capacity to determine the boundaries of the phases. They found that as with the heat capacity, the locus of the maximum isothermal compressibility is smoothly connected to the first-order phase boundary. As such, the MD simulations can provide information on more complex fluids and pore structures, but it is also useful to connect some of these highly complex and computationally expensive systems to some macroscopic thermodynamic concepts.

1.4.5 Compressibility by Macroscopic Thermodynamics

Another derivation of the compressibility of a confined fluid was done by one of us [84] from the same starting point, Equation (1.9). By neglecting the anisotropy of pressure and considering only a macroscopic average, the pressure $P$ in the pore, which is also known as the solvation pressure, can be determined from the grand thermodynamic potential $\Omega$ [85, 54]

$$P = - \left( \frac{\partial \Omega}{\partial V} \right)_{\mu,T} .$$
Also, the pressure in the pore $P$ is related to the chemical potential $\mu$ of the fluid via the Gibbs-Duhem equation

$$dP = nd\mu \quad (1.19)$$

where $n$ is the average particle density in the pore defined as $n \equiv N/V$.

Assuming that the number of particles in the pore and the temperature are constant, Equation (1.19) can be used to rewrite Equation (1.9) as

$$\beta_T = \frac{1}{n^2} \left( \frac{\partial n}{\partial \mu} \right)_{N,T} . \quad (1.20)$$

Since, at constant temperature and when Equation (1.19) is valid, Equation (1.20) is only a function of intensive variables (i.e., it does not depend on $N$ nor $V$), we can write

$$\left( \frac{\partial n}{\partial \mu} \right)_{N,T} = \left( \frac{\partial n}{\partial \mu} \right)_{V,T} . \quad (1.21)$$

This transformation is important because in the grand canonical ensemble, the number of particles does indeed change while the volume of the system is kept constant.

Since the vapor pressure is low, the vapor can be considered an ideal gas. Then, the chemical potential is related to the vapor pressure in equilibrium with the fluid in the pore by the relation

$$\mu = k_B T \ln(p/p_0) + \mu_0(T) \quad (1.22)$$

where $p_0$ and $\mu_0(T)$ are the vapor pressure and chemical potential at saturation, respectively. Equation (1.20) can be rewritten using Equations (1.21) and (1.22) as [84]

$$\beta_T = \frac{1}{n^2} \frac{p}{k_B T} \left( \frac{\partial n}{\partial (p/p_0)} \right)_{V,T} . \quad (1.23)$$
Therefore, to calculate the compressibility of a confined fluid using the thermodynamic method, one only needs the density $n$ of the fluid in the pore as a function of the relative pressure $p/p_0$ which is known as the adsorption isotherm. The derivative in Equation (1.23) can be obtained from the slope of the isotherm.

### 1.5 Relating Experiment with Theory

![Figure 1.4](image)

**Figure 1.4** Schematic of the empty porous sample (left) and the fluid-saturated porous sample (right) with denotations for the constituent elastic moduli used in the Gassmann Equation (1.24). Graphic courtesy of Max Maximov.

When sound traverses a fluid-saturated nanoporous medium, the sound propagation is affected by the elastic properties of both the solid matrix and of the confined fluid. So there is a need to understand how these different properties affect the overall experimentally measured sound velocity. One can use an effective medium theory (EMT) to relate the individual elastic properties of the components of the fluid-saturated porous matrix to the composite sample. The early works by Warner and Beamish did not attempt to use any EMT, since their focus was on pore surface area calculated in the range of vapor pressures where the fluid contribution to sound propagation was negligible [1]. Page et al. were the first to use an EMT to interpret the elastic properties of fluid saturated media [2]. They used the Gassmann equation,
which can be written as

\[
K = K_0 + \frac{1 - \frac{K_s^2}{K_0}}{K_f + \frac{(1-\phi)K_s}{K_0}}^{2} + (1 - \phi)K_s - K_0K_s^2,
\]

(1.24)

where \(K\) is the effective elastic modulus of the composite, \(K_0\) is the modulus of the empty porous sample, \(K_s\) is the modulus of the solid, \(K_f\) is the modulus of the fluid, and \(\phi\) is the porosity. A schematic of these components is shown in Figure 1.5. Note that Equation (1.24) is a low-frequency case of Biot’s theory of wave propagation in porous materials, thus it is often referred to as the Biot-Gassmann equation [86, 87].

But in their calculations, Page et al. assumed that the elastic modulus of their confined fluid is the same as the fluid in the bulk, which has been evidenced to not be true as noted in the sections above. Later, Schappert and Pelster began using an EMT of their own [3, 41, 42]

\[
K = K_0 + \left(1 - \frac{K_0}{K_s}\right)K_f.
\]

(1.25)

Their method relies on the assumption that the modulus of the porous sample \(K_0\) has a linear dependence on porosity at the low porosity range \(\phi \lesssim 0.25\). Gor and Gurevich showed that the Gassmann equation can be applied to nanoporous materials. But, the calculations still have some uncertainties and unverified assumptions involved. In order to be able to apply Gassmann theory to a material, some knowledge of the properties of the solid nonporous sample must be known. The solid modulus \(K_s\) is complicated for nanoporous samples because the sizes of grains and thermal history of the material can impact the properties of the solid. Gor and Gurevich proposed a way to estimate this solid modulus based on the pore-load modulus obtained from measurements of adsorption-induced deformation [26]. They showed that the Gassmann equation can be used to accurately predict the saturated moduli of nanoporous glass. The problem is that the properties of the solid are known with a large degree of uncertainty. Therefore, it cannot be considered as confirmation of
the validity of the Gassmann equation. The porosity is small \( \phi \lesssim 0.25 \), the modulus of the solid is much higher than of the fluid \( K_s \gg K_f \), so the fluid contribution to the effective modulus of the composite is not as significant. Indeed, the method still needs more validation with more well-characterized solid-fluid systems for practical uses such as in coal or shale.

1.6 Open Questions

The changes in elastic properties can be an effective signal for phase changes. For this reason, many of the works discussed above were focused on the phase equilibria of the confined fluid. Therefore, even though significant number of works calculated the elastic properties of confined fluids, they lacked in developing an understanding of the causes of such changes due to confinement. This begets more questions on how the elastic properties of the confined fluid are affected by various materials and conditions, as well as how an effective medium theory applies to nanoporous materials, where all the constituent properties are not yet accurately quantified.

The studies of confined fluids have left many gaps in our understanding of the behaviors and ways to calculate the elastic properties of confined fluids. The goal of this dissertation is to address some of the fundamental questions that can improve our understanding of confined fluids. In particular this dissertation addresses: how the elastic properties of the confined fluid are affected by the geometrical shape of the pore, how the elastic properties of supercritical fluids are affected by confinement, whether or not completely different molecular simulation techniques (i.e., MD, GCMC) for the same system can predict the same values for the confined fluid, if we can use an equation of state that calculates adsorption to predict elastic properties of confined fluids across different pore sizes, and if molecular simulations can provide insights on the technical underpinnings the Gassmann equation applied
to fluid-saturated nanoporous media. These topics, will be addressed in the chapters following.
CHAPTER 2

EFFECT OF PORE GEOMETRY ON THE COMPRESSIBILITY OF A
CONFINED SIMPLE FLUID

2.1 Introduction

The thermodynamic properties of a confined fluid differ from that of a fluid in bulk at the same temperature and pressure [88, 17]. Ultrasonic experiments on fluid-saturated nanoporous materials provide the way to probe one of those thermodynamic properties: compressibility or elastic (hydrostatic) modulus of the confined fluid [2, 45, 26]. Although the first ultrasonic measurements on fluid-saturated nanoporous samples have been carried out in the early 1980s [31], there have been relatively few studies of this kind since then. Warner and Beamish used ultrasonic experiments to investigate the surface area of nanoporous materials [1]. Page et al. studied pore-space correlations with adsorption on Vycor glass and effects of pore connectivity and were the first to report the elastic modulus of confined fluid (n-hexane) [32, 2]. Many works have employed ultrasonic experiments to study phase transitions of confined fluids [34, 35, 36, 37, 3, 89, 39, 40, 38], but did not quantify the elastic properties of confined phases.

Recently, Schappert and Pelster used ultrasonic measurements to study the changes of elastic properties of fluid and solid phases of argon, nitrogen, and oxygen confined in nanoporous materials at low temperatures [42, 44, 45, 46, 48]. Since argon is one of the simplest systems for molecular simulations, these works stimulated the development of macroscopic [84], and molecular modeling approach to the calculation of elastic properties of confined fluids [4, 58, 5].

References [4, 58, 5] presented the calculations of the elastic modulus of argon confined in spherical silica pores. The model used in those calculations is suitable to represent many nanoporous materials, such as SBA-16 silica [90], 3DOM carbon
The experimental data available in the literature is mainly for Vycor glass [1, 2, 45], which has different morphology. Pores in Vycor form a network of interconnected channels [93]. Since the length of these pores significantly exceeds its diameter and the diameter does not vary much along the length of the pores, the behavior of fluids in Vycor glass is often simulated in a cylindrical pore model [94]. Thus, we expect that simulations of argon in cylindrical pores would be a more rigorous representation of the experimental system studies in References [1, 2, 45].

Note that the References [4, 58, 5] are not the only theoretical works studying the compressibility of confined fluids. Rickman used conventional Metropolis Monte Carlo simulations and stress correlation functions to determine the elastic properties of Lennard-Jones (LJ) fluid in a slit pore [64]. Sun and Kang [74] and Keshavarzi et al. [79] employed density functional theory to determine the elastic properties of LJ fluid in spherical and slit pores respectively. Vadakkepatt and Martini investigated the compressibility of fluids confined in slit pores using molecular dynamics simulations [82, 25]. However, none of these works calculated the moduli in the context of adsorption experiments and ultrasonics.

The primary goal of this research is to investigate the elastic properties of a simple fluid in cylindrical confinement, which is assumed to be a more realistic representation of the system used in ultrasonic experiments by several groups [1, 2, 45]. Here we consider the same system and use the same methods as in [4]: we model argon at its normal boiling temperature confined in silica mesopores using conventional grand canonical Monte Carlo (GCMC) simulations [59]. However, while Reference [4] dealt exclusively with the spherical pore model, here we consider both spherical and cylindrical pore models. Therefore, we investigate the effect of the pore shape on the elastic properties of confined fluids and examine the validity of the relations between
modulus and pore size (diameter) [4] and between modulus and pressure [58] for the cylindrical pore model.

2.2 Methods

2.2.1 Compressibility and Bulk Modulus

In thermodynamics, the elastic properties are typically presented in terms of the isothermal compressibility $\beta_T$. We start from introducing equations for compressibility, but the results of the calculations are more convenient to represent in the form of the isothermal elastic modulus $K_T = \beta_T^{-1}$ which is more relevant to ultrasonics.

For a macroscopic system, the isothermal compressibility $\beta_T$ is defined as

$$\beta_T \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{N,T}, \quad (2.1)$$

where $V$ is the system volume, $P$ is the fluid pressure, and $T$ is the absolute temperature. Here, following References [57, 4, 58], we use the same definition of $\beta_T$ for the fluid confined in the pore. We determine the overall fluid compressibility in the pore which corresponds to the macroscopic average compressibility that can be extracted from the experimental data on fluid-saturated porous samples using effective medium analysis.

2.2.2 Compressibility by Statistical Mechanics

Classical statistical mechanics allows for the calculation of the compressibility of the fluid in the pore from the fluctuations in the number of particles in the pore $N$ in the grand canonical ensemble through the following relation [63]

$$\beta_T = \frac{V \langle \delta N^2 \rangle}{k_B T \langle N \rangle^2}, \quad (2.2)$$

where $\langle \delta N^2 \rangle$ is the variance of $N$ and $k_B$ is the Boltzmann constant. Equation (2.2) can be applied to a small system as long as the fluctuations obey a Gaussian
distribution [57, 4]. Thus, molecular simulation of a fluid in the pore performed in the grand canonical ensemble can provide data for calculation of $\beta_T$.

### 2.2.3 Compressibility by Macroscopic Thermodynamics

Another derivation of the compressibility of a confined fluid was done by one of us [84] from the same starting point, Equation (2.1). By neglecting the anisotropy of pressure and considering only a macroscopic average, the pressure $P$ in the pore, which is also known as the solvation pressure, can be determined from the grand thermodynamic potential $\Omega$ [85, 54]

$$P = -\left( \frac{\partial \Omega}{\partial V} \right)_{\mu,T}.$$  \hspace{1cm} (2.3)

Also, the pressure in the pore $P$ is related to the chemical potential $\mu$ of the fluid via the Gibbs-Duhem equation

$$dP = nd\mu$$ \hspace{1cm} (2.4)

where $n$ is the average particle density in the pore defined as $n \equiv N/V$.

Assuming that the number of particles in the pore and the temperature are constant, Equation (2.4) can be used to rewrite Equation (2.1) as

$$\beta_T = \frac{1}{n^2} \left( \frac{\partial n}{\partial \mu} \right)_{N,T}. \hspace{1cm} (2.5)$$

Since, at constant temperature and when Equation (2.4) is valid, Equation (2.5) is only a function of intensive variables (i.e., it does not depend on $N$ nor $V$), we can write

$$\left( \frac{\partial n}{\partial \mu} \right)_{N,T} = \left( \frac{\partial n}{\partial \mu} \right)_{V,T}. \hspace{1cm} (2.6)$$
This transformation is important because in the grand canonical ensemble, the number of particles does indeed change while the volume of the system is kept constant.

Since the vapor pressure is low, the vapor can be considered an ideal gas. Then, the chemical potential is related to the vapor pressure in equilibrium with the fluid in the pore by the relation

\[
\mu = k_B T \ln \left( \frac{p}{p_0} \right) + \mu_0(T),
\]

(2.7)

where \( p_0 \) and \( \mu_0(T) \) are the vapor pressure and chemical potential at saturation respectively. Equation (2.5) can be rewritten using Equations (2.6) and (2.7) as \[84\]

\[
\beta_T = \frac{1}{n^2} \frac{p/p_0}{k_B T} \left( \frac{\partial n}{\partial (p/p_0)} \right)_{V,T}.
\]

(2.8)

Therefore, to calculate the compressibility of a confined fluid using the thermodynamic method, one only needs the density \( n \) of the fluid in the pore as a function of the relative pressure \( p/p_0 \) which is known as the adsorption isotherm. The derivative in Equation (2.8) can be obtained from the slope of the isotherm.

### 2.2.4 Grand Canonical Monte Carlo Simulations

The fluid used for our simulations was argon; interactions between argon atoms were modeled by LJ pair potentials. We considered two temperatures: the normal boiling point \( T = 87.3 \text{ K} \), which is typical for argon adsorption experiments and close to the temperature in the ultrasonic experiments of Schappert and Pelster [45], and at \( T = 119.6 \text{ K} \), which corresponds to the reduced temperature \( T^* = 1 \). The reason for using this higher temperature in the simulations is discussed below. The simulations were performed at LJ reduced chemical potentials \( \mu^* = \mu/\epsilon_{\text{ff}} \) ranging from \(-15.0\) to \(-9.6\) for 87.3 K and \(-23.0\) to \(-11.6\) for 119.6 K; the upper limits of \( \mu^* \) correspond to the
saturation pressure $p_0$ of the fluid. The parameter $\epsilon_{ff}$ along with other Lennard-Jones parameters and physical properties used in the simulations are summarized in Table 2.1. The simulations were performed using the conventional GCMC method [59] based on the Metropolis algorithm [95]. The adsorptive potentials between the fluid atoms and the pore wall were modeled by spherically [96] or cylindrically [97] integrated, site-averaged interaction potentials. For the cylindrical pore model, we used a pore length of $40\sigma_{ff}$ and applied periodic boundary conditions along the direction of the cylinder axis. For the 2 nm pore, we used a length of $80\sigma_{ff}$ to even further increase the number of atoms in the system. Figure 2.1 shows the calculated solid-fluid interaction potentials for spherical and cylindrical pores of the 2, 3, 4, and 5 nm pore sizes that were used in simulations. For each pore size, the potential for the sphere has a deeper well which corresponds to the higher degree of attraction between the fluid and the wall in the sphere than in the cylinder.

![Solid-fluid potential for spherical and cylindrical pores](image)

**Figure 2.1** The solid-fluid potential for spherical and cylindrical pores. The potential from each individual wall atom is integrated over the surface of the pore. For each of the pore sizes, the deeper potential of the spherical pore is consistent with the higher degree of confinement due to the closer interactions with the pore walls. The point at which the potential is zero corresponds to the distance from the center of the pore to the center of the outermost fluid atoms, from which one can determine the internal diameter given by Equation (2.9).
Table 2.1 Parameters for the Fluid-fluid (ff) and Solid-fluid (sf) Interactions for the Argon-silica System

<table>
<thead>
<tr>
<th>Interaction</th>
<th>σ, nm</th>
<th>ϵ/k_B, K</th>
<th>ρ_s, nm^{-2}</th>
<th>r_{cut, sf}</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-Ar</td>
<td>0.34</td>
<td>119.6</td>
<td>-</td>
<td>5</td>
<td>[98]</td>
</tr>
<tr>
<td>Silica-Ar</td>
<td>0.30</td>
<td>171.24</td>
<td>15.3</td>
<td>10</td>
<td>[99]</td>
</tr>
</tbody>
</table>

Note: σ is the LJ diameter, ϵ is the LJ energy, ρ_s is the number density of solid LJ sites on the surface, and r_{cut} is the cut-off distance where interactions were truncated; no tail corrections were used.

Simulations were done with pore sizes ranging from 2 nm to 6 nm. The pore size refers to the external diameter d_{ext} which is taken as the center-to-center distance from one pore wall molecule to the molecule on the opposite side of the pore (see Figure 2.2). The volume of the pore that is accessible to the fluid atoms V is different from the volume calculated using the external diameter of the pore. To calculate the internal diameter d_{int} we used the approach from References [92, 100] and extended it to cylindrical geometry, which gives

\[
d_{int} \approx d_{ext} - 1.7168\sigma_{sf} + \sigma_{ff}.
\]

This internal volume can be calculated based on the positions of the outer-most fluid atoms in the pore. The center of such an atom corresponds to the zero of the integrated solid-fluid potential U_{sf} (shown in Figure 2.1) [92]. Since the volume needs to be taken up to the outer edge of those fluid atoms, an additional \(\sigma_{ff}\) needs to be added to the distance between the centers of such atoms (Figure 2.2).

The right panel of Figure 2.2 plots the internal diameters d_{int} calculated from the root of U_{sf} for the cylindrical pores with \(d_{ext} = 2, 3, 4,\) and 5 nm. The dashed line is the linear fit, which provides Equation (2.9). Note that this equation does not differ from the equation for spherical pores [92, 100].
At each pore size and each chemical potential, simulations were run for at least $5 \times 10^9$ trial Monte Carlo moves. Each simulated data point was first equilibrated with at least $10^9$ trial moves that were not considered in calculations. The reduced chemical potential $\mu^*$ was mapped to the relative vapor pressure $p/p_0$ using the Johnson et al. equation of state [101], from which we calculated the reduced chemical potential at vapor-liquid equilibrium to be $\mu^* = -9.6$ at $T = 87.3$ K and $\mu^* = -11.6$ at $T = 119.6$ K. Considering the vapor to be an ideal gas, we calculated the pressures at other values of chemical potential using Equation (2.7).

### 2.3 Results

We constructed GCMC adsorption isotherms from simulations of various pore sizes for both spherical and cylindrical pores at $T = 87.3$ K. The complete adsorption isotherms for spherical and cylindrical pores of 2, 3, 4 and 5 nm in size are shown in Figure 2.3. These isotherms display the typical behavior of monolayer formation at very low relative pressures, followed by multilayer formation, after which the pores...
are rapidly filled via capillary condensation. The spherical pores exhibit capillary condensation at lower pressures than the cylindrical pores, e.g., for 3 nm pores the capillary condensation takes place at \( p/p_0 \approx 0.1 \), while for cylindrical pore at \( p/p_0 \approx 0.2 \). This suggests that the confinement effects in spherical pores are stronger than in cylindrical, which is consistent with the deeper potential wells in spheres for the \( U_{sf} \) potential shown in Figure 2.1. The simulation data for the cylindrical pore of 3 nm size show another interesting feature: soon after the capillary condensation there is a second step on the adsorption isotherm, corresponding to small but noticeable densification. A similar feature has been recently reported by Siderius et al. for the simulation of Lennard-Jones methane in cylindrical pores using transition-matrix Monte Carlo simulations and attributed to a phase-transition to a more ordered phase [102].

The error bars in Figure 2.3 are twice the standard deviation error, related to the fluctuation or variance of the number of atoms \( N \) in the pores. The variance in the number of atoms is proportional to the compressibility of the fluid in the pore by Equation (2.2); therefore, the data shown in Figure 2.3 can be used for calculation of the compressibility (or elastic modulus of the fluid).
Figure 2.3  GCMC adsorption isotherms for argon at 87.3 K in spherical and cylindrical pores shown as the average reduced fluid density $n^* = N\sigma^3_{ff}/V$ plotted versus relative pressure. The top plot is in linear scale and the bottom has pressure in log scale. The horizontal dotted line at $n^* = 0.827$ represents the bulk density. Error bars represent a twice standard deviation error in the fluid density in the pore.

We calculated the isothermal elastic modulus of the fluid in the pores based on Equation (2.2), which is relevant for the pressures above the capillary condensation, when the pores are filled with a liquid-like condensate. The modulus $K_T$ as a function of relative vapor pressure $p/p_0$ is shown in Figure 2.4 for filled pores of 2, 3, 4 and 5 nm size and of both spherical and cylindrical geometry. The upper panel shows the results for the 3, 4, and 5 nm pores. The data for spherical pores show a clear trend: the
modulus of fluid exhibits monotonic increase as a function of relative vapor pressure \( p/p_0 \). The data for the cylindrical pores are so scattered that it is hard to make a similar conclusion; yet the values of moduli are of the same order of magnitude. The lower panel shows the same data along with the results of the modulus of argon in the 2 nm pore, which exceeds the moduli for the fluid in larger pores by an order of magnitude. Note that the methods used here for the calculation of the elastic moduli are applicable only when the pores are filled with capillary condensate. Even if one could come up with a method to calculate the modulus of the adsorbed fluid at pressures below capillary condensation, it could not be accessed via ultrasonic experiments [26].
Figure 2.4  (Top) Isothermal modulus \( K_T \) of argon in spherical and cylindrical pores of 3, 4, and 5 nm at 87.3 K calculated using Equation (2.2) from GCMC simulations as a function of reduced pressure. (Bottom) The same data shown together with the calculations for the 2 nm pore. The error bars represent the correlation error estimated by the method described by Gor et al. [4].

The isothermal modulus is calculated based on the fluctuation of the number of atoms in the pores, so it is worth looking at the histograms for the systems giving such drastically different elastic moduli. Figure 2.5 gives the histograms for argon atoms in four systems: 5 nm spherical and cylindrical pores and 2 nm spherical and cylindrical pores. While the 5 nm pore systems of both morphologies exhibit normally-distributed fluctuations in \( N \), the 2 nm spherical micropores do not. The
other mesopores not shown here were also normally distributed. The problem with the
distribution in the 2 nm spherical pore is related to the smallness of the fluid system: the
mean number of atoms in this pore is only around 60. The 2 nm cylindrical pore
can be made arbitrarily long so that the number of atoms is sufficient to have normal
distribution. Nevertheless, the cylindrical 2 nm pore does not provide reasonable
values for the modulus. This is discussed below in Section 2.4.

Figure 2.5 (Top) 5 nm spherical pore (left) and 40σ length cylindrical pore (right).
(Bottom) 2 nm spherical (left) and 80σ length cylindrical pore (right). The fluctuation
in the number of molecules at \( T = 87.3 \) K in both of the 5 nm pores and the 2 nm
cylindrical pore exhibit a Gaussian distribution, whereas for the 2 nm spherical pore,
the fluctuations do not fit well into a Gaussian distribution. The cylindrical pores
can fit many more molecules, allowing larger fluctuations.

The slopes of the isotherms in Figure 2.3 along the filled pore region allows for
the calculation of the compressibilities (or elastic moduli) by Equation (2.8). Figure
2.6 shows the isothermal modulus of the fluid in spherical pores of three sizes as
a function of vapor pressure \( p/p_0 \) calculated based on two different methods: the
method based on statistical mechanics, Equation (2.2), and the macroscopic method,
Notably, although the methods are very different, they produce very similar results. We do not show the calculations based on Equation (2.8) for cylindrical pores because of the scattered points on the isotherms for those systems. The application of Equation (2.8) for the calculation of the fluid modulus in cylindrical pores is discussed below for simulations at higher temperature.

Figure 2.6 The isothermal modulus at $T = 87.3\, \text{K}$ calculated using Equation (2.8), i.e., from the slope of the adsorption isotherm, along with the modulus calculated using Equation (2.2) for confined argon in spherical pores of 3, 4, and 5 nm pore width.

The upper panel of Figure 2.7 displays the isothermal modulus of a fluid at full saturation $p = p_0$ plotted as a function of the pore size. For spherical pores, the results obtained here agree well with data from References [4, 5]. These points show a linear dependence, approaching the bulk modulus value of 0.47 GPa [6] as the pores get larger than 10 nm. The cylindrical pores show the modulus which is close to the spherical one, yet the significant scatter in the data does not allow to draw a conclusion about the trend.

The lower panel of Figure 2.7 displays the average fluid density in the pore at saturation as a function of reciprocal pore size. The density of bulk liquid argon at 87.3 K is 1.395 g/cm$^3$, which corresponds to a LJ reduced density of about $n_\text{bulk}^*$ =
0.827 [6], is shown with the dotted line. There are two pronounced trends seen in this figure. First, the density of the confined fluid in spherical pores is lower than the bulk density, and it increases with the pore size trending towards the bulk value as the pore size increases above around 10 nm. The second trend is that for the same pore size, the density of fluid in cylindrical pores exceeds that in the spherical pores. Both of these trends were earlier discussed by Keffer et al. [103] for a LJ fluid in smaller pores. Recently densification of LJ fluid in the cylindrical pores was studied by Siderius et al. [102], they found that the higher density of fluid in the cylindrical pores is related to its ordering, which does not take place in the bulk.
<table>
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<th>Bulk Value</th>
<th>Cylinder</th>
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<td>$d_{ext}$ [nm]</td>
<td>0.0</td>
<td>0.2</td>
<td>0.4</td>
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<td>$K_T$ [GPa]</td>
<td>0.0</td>
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Figure 2.7  (Top) Isothermal elastic modulus $K_T$ of argon in spherical and cylindrical pores at saturation pressure $p/p_0 = 1$ and 87.3 K as a function of reciprocal pore size $1/d_{ext}$ for $d_{ext}$ values of 3, 3.5, 4, 5, and 6 nm. Also included are the data for spherical pores from Gor et al. [5] covering the range of pore sizes between 2.5 and 9.0 nm. Error bars are correlation error estimated by the method described by Gor et al. [4]. The dotted line shows the isothermal elastic modulus for the bulk liquid argon at saturation at $T = 87.3$ K [6]. (Bottom) Average fluid density at saturation point in a spherical and cylindrical pore as a function of the pore size. The dotted line shows the density of bulk fluid at the same thermodynamic conditions ($\mu$ and $T$). We find that the density of the cylindrical pores is higher than for the spherical pores, even though the well of the spherical interaction potential is deeper than for cylinders, as shown in Figure 2.1.
The density of the fluid confined in a nanopore is not uniform. The interaction of the fluid atoms with the solid wall significantly alters the density and leads to the appearance of the dense layers in the vicinity of the solid walls. The density profiles for 5 nm pores of both spherical and cylindrical geometry are shown in Figure 2.8. These density profiles can explain some of the effects we observed for the elastic modulus $K_T$; a more detailed discussion is given in Section 2.4.

![Density profiles](image)

**Figure 2.8** Density profiles for argon confined in 5 nm spherical (solid red line) and cylindrical (dashed blue line) pores at saturation ($T = 87.3$ K, $\mu^* = -9.6$). The dotted lines of corresponding colors represent the average densities for each of the systems. The first several density peaks and wells near the adsorbing wall are more pronounced for the cylindrical pore than for the spherical one. This suggests that the cylindrical pore has a more ordered fluid phase.

Since our simulations of argon in cylindrical pores lead to inconclusive results on the elastic modulus, we ran additional simulations at higher temperature. We chose $T = 119.6$ K (corresponding to $T^* = 1$), which is noticeably higher than the normal boiling point of argon, yet is still far from the critical point ($T = 150.7$ K). Figure 2.9 shows the adsorption isotherms for cylindrical ($40\sigma_f$ length) and spherical pores with sizes 2, 3, 4, and 5 nm.
Similarly to the data at $T = 87.3\ \text{K}$ we carried out the calculation of isothermal elastic modulus based on the fluctuations of number of atoms in the pores using Equation (2.2). The resulting curves for the moduli as a function of vapor pressure $p/p_0$ are shown in Figure 2.10. The curves for both spherical and cylindrical pores show the clear monotonic trend, observed above in Figure 2.4 for the data in the spherical pores. The only curve showing a less pronounced increase of the elastic modulus with the vapor pressure is for the 2 nm spherical pore, which, as discussed above, might be too small for application of our method.

Figure 2.11 shows the isothermal moduli calculated for argon at $T = 119.6\ \text{K}$ in spherical (top panel) and cylindrical (bottom panel) pores using the two different methods: the fluctuation method, Equation (2.2), and thermodynamic method, Equation (2.8). Similarly to Figure 2.6 showing the agreement between the two methods for calculating the modulus for the simulation data for spherical pores at $T = 87.3\ \text{K}$, Figure 2.11 suggests that the two methods are fully consistent. Note
that all of the data series, except for the curve for the 2 nm spherical pore, show a logarithmic dependence of the modulus on the vapor pressure.

Figure 2.10  The isothermal modulus $K_T$ of argon in spherical and cylindrical pores of 2, 3, 4, and 5 nm at 119.6 K calculated using Equation (2.2) from GCMC simulations as a function of reduced pressure.
Figure 2.11  The isothermal modulus of confined argon at $T = 119.6 \text{ K}$ calculated using Equation (2.8), i.e., from the slope of the adsorption isotherm, along with the modulus calculated using Equation (2.2) for confined argon in spherical (top) and cylindrical (bottom) pores of 2, 3, 4, and 5 nm diameter.

Figure 2.12, similarly to Figure 2.7, shows the moduli at temperature $T = 119.6 \text{ K}$ at the saturation point ($p = p_0$). Unlike at the lower temperature, the elastic modulus of argon in cylindrical pores as a function of the pore size shows here the same linear monotonic trend as the modulus of argon in spherical pores. The linear fit is shown by the dash-dotted lines; the point corresponding to the 2 nm spherical pore is excluded from the linear fit.
Figure 2.12  Isothermal elastic modulus $K_T$ of argon in spherical and cylindrical pores at saturation pressure $p/p_0 = 1$ and $T = 119.6$ K as a function of reciprocal pore size $1/d_{\text{ext}}$ for $d_{\text{ext}}$ values of 2, 3, 4, and 5 nm. The dash-dotted lines of the corresponding colors show the linear fit. The horizontal dotted line represents the bulk value of the elastic modulus.

2.4 Discussion

We presented the GCMC simulations of argon adsorption in spherical and cylindrical pores of various sizes. In addition to the adsorption isotherms, we calculated the elastic properties of adsorbed argon and compared the results for the two different pore morphologies. The main quantity we chose for consideration is isothermal (bulk) modulus of the fluid, a scalar thermodynamic property describing confined fluid as a macroscopic thermodynamic property. The rationale for introducing such modulus is driven by its accessibility in ultrasonic experiments [26].

Since one of our central goals was to investigate the difference in elastic properties of the confined fluid, related to the morphologies of the confining pores, we started from the comparison of the solid-fluid interaction potentials $U_{sf}$ for the spherical and cylindrical pores. We found that despite the difference in analytical forms for the integrated solid-fluid potentials for spherical and cylindrical pores, they have the same roots and therefore the internal diameters of cylindrical pores can...
be calculated from the external diameters using the same Equation (2.9), which was initially written by Rasmussen et al. for spherical pores only [92, 100]. Comparison of the depth of the potential wells for these two cases shows that the attractive potential for the spherical pore is stronger than for the cylindrical pore of the same size. This discrepancy between the potential depths explains the difference in the adsorption isotherm: capillary condensation in a spherical pore takes place at a lower pressure than in a cylindrical pore, in line with what has been discussed by Keffer et al. [103].

Since spherical and cylindrical pore geometries are related to the two different solid-fluid interaction potentials, we carried out an additional test aiming to reveal the effect of the solid-fluid potential on the adsorption isotherms and elastic modulus. For this purpose we simulated the “hybrid” model: while using the spherical geometry we used the cylindrical potential. The resulting adsorption isotherms are shown in Figure 2.13. The adsorption isotherms show that the capillary condensation in the spherical pores of each size take place at lower pressures than in hybrid model of the same size (which has the shallower potential well). The capillary condensation in the cylindrical pore takes place at even higher pressure than in the hybrid model, showing that the geometry itself reduces the confinement effects in addition to the solid-fluid interaction potential. Qualitatively similar effect of the solid-fluid potential on the elastic properties of the fluid is seen in Figure 2.14. The scatter on the modulus curve for the 4 nm cylindrical pore is relatively small, so this series can be compared to the two other models at the same pore size. The modulus of the fluid in cylindrical pore is lower than in hybrid model, and the hybrid is lower than in spherical. This trend is fully consistent with the trend for the capillary condensation point.
**Figure 2.13** GCMC adsorption isotherms for spherical, cylindrical and hybrid pores at $T = 87.3$ K shown as the average reduced fluid density $n^* = N\sigma_f^3/V$ plotted versus relative pressure. The horizontal dotted line displays the bulk density.

**Figure 2.14** Moduli calculated for argon confined in spherical, cylindrical, and the hybrid pores using Equation (2.2) at $T = 87.3$ K as a function of relative pressure.

The calculated elastic moduli for various systems is the central part of this work. Our calculations of the elastic modulus for the confined fluid confirmed the trends reported earlier in References [4, 58, 5]. The first trend is the change in elastic modulus with the vapor pressure for each of the pore sizes, shown in the top panel of Figure 2.4
and 2.10. For both pore morphologies, there is a clear increase of the modulus with the increase of the relative vapor pressure \( p/p_0 \). The data for cylindrical pores at the normal boiling temperature are too scattered to make quantitative predictions, but for the spherical pores, it can be seen that the modulus changes as a logarithm of the vapor pressure. This logarithmic dependence has been observed in experiments [2, 45] and in molecular simulations using different techniques, DFT [84] and transition-matrix Monte Carlo [58]. The origin of this dependence is the stretching of fluid by the negative Laplace pressure in the pore at \( p < p_0 \) [45, 58]. Note that in the simulations we do not model the curved liquid-vapor interface explicitly. Nevertheless, at any vapor pressure below \( p_0 \), the negative Laplace pressure acts on the fluid due to the difference in the chemical potential. The isothermal elastic moduli of many fluids display a linear dependence on pressure for a wide range of pressures (Tait-Murnaghan equation) [58, 104]:

\[
K_T(P) \simeq K_T(P_0) + K_T' \cdot (P - P_0),
\]

(2.10)

where, in our case, \( P \) is the solvation pressure in the fluid phase, \( P_0 \) is some reference pressure, and \( K_T' = dK_T/dP \), which is constant in the first approximation. This dependence holds for confined fluids as well [84, 79], moreover with the same slope \( K_T' \) [58]. The solvation pressure \( P \) in the confined fluid (not to be confused with vapor pressure \( p \)) consists of two terms [18]: the solid-fluid interaction term and Laplace pressure

\[
P = P_{sl} + \frac{R_g T}{V_l} \ln \left( \frac{p}{p_0} \right).
\]

(2.11)

The logarithmic behavior of the second term in Equation (2.11) together with Equation (2.10) explains the logarithmic dependence of the fluid modulus on vapor pressure seen in Figures 2.4 and 2.10 and observed experimentally [2, 45].
The second trend, which is clearly seen from the simulation data, is the dependence of the elastic modulus on the pore size, shown in the top panel of Figures 2.7 and 2.12 for the modulus of fluid at saturation. For the spherical pores, as it was revealed earlier [84], the modulus $K_T$ is a linear function of the reciprocal pore size $1/d_{\text{ext}}$. Similarly to the dependence on the vapor pressure, this dependence can be explained in terms of Tait-Murnaghan Equation (2.10) and the equation for solvation pressure Equation (2.11). When the vapor is saturated ($p = p_0$) and the second term in Equation (2.11) vanishes, the pressure in the fluid is determined by the $P_{\text{sl}}$ term, which scales like $1/d_{\text{ext}}$ [18]. Therefore, Equation (2.10) also gives the $1/d_{\text{ext}}$ scaling for the elastic modulus $K_T$.

It is insightful to consider the trends observed for the moduli along with the trends for the fluid density. All the isotherms shown in Figure 2.3 display a well-known behavior: after capillary condensation, there is still a slow increase in the density of the fluid in the pore with the increase of vapor pressure $p/p_0$. This gradual densification of fluid in pores of all the sizes and morphologies corresponds to the gradual stiffening of the fluid – an increase of its elastic modulus for each of the systems, as shown in Figure 2.4. A similar comparison of the trends for densities and elastic moduli for different systems (pore sizes and morphologies) can be made based on the data shown in Figure 2.7. The clear trend for modulus of the fluid in spherical pores corresponds to the clear trend for the density. This trend, however, is counter-intuitive: while the fluid is stiffer in smaller pores, its density in smaller pores is lower than in larger pores. This dependence of density of confined fluid on the pore size has been reported earlier by Keffer et al. [103] and is related to the packing effects.

The significant scatter in the results for argon modulus in cylindrical pores at 87.3 K complicated the comparison between the different pore morphologies. The likely reason for the scattering in the data for cylindrical pores is the layering of the
fluid atoms along the straight pore walls. This layering causes the dense packing of the fluid in the pores. Figure 2.7 shows that the density of the fluid in cylindrical pores is noticeably higher than the density in spherical pores of the same size and even exceeds the bulk density. The dense packing in cylindrical pores makes the removal and insertion of atoms in GCMC very inefficient; therefore, the fluctuations of number of atoms in the pores may be lowered. Since the elastic modulus of the fluid is calculated based on the molecule fluctuations, lowering of the fluctuations will cause the apparent increase of the elastic modulus. This is indeed what we observed in our simulations for the smallest cylindrical pores: the fluid confined in a 2 nm cylindrical pore exhibited an extremely high elastic modulus (lower panel of Figure 2.4). Such high values of the modulus exceed even the modulus of solid argon by an order of magnitude [105, 106, 107, 108], so it cannot be explained by the freezing of the fluid.

Simulations at higher temperatures, when Monte Carlo moves such as insertions and removals become more efficient, provide more reliable data for elastic moduli in cylindrical pores. As it is seen in Figures 2.10, the simulation results at $T = 119.6 \text{ K}$ fall on smooth curves, which are suitable for comparison between spherical and cylindrical confinement. Moreover, the adsorption isotherms at $T = 119.6 \text{ K}$ in both pore geometries are sufficiently smooth for the calculation of the modulus using the thermodynamic route, i.e., by numerical differentiation of adsorption isotherms. Figure 2.11 shows that at a higher temperature, the predictions of two methods for calculation of elastic modulus match perfectly.

Unfortunately, we should conclude that at the normal boiling point of argon, the pores of 2 nm in diameter and smaller (i.e., micropores) remain challenging irrespective of their morphology. The calculation of the fluid modulus in the 2 nm spherical pore was not feasible because of the smallness of the system: the average number of atoms at saturation pressure is ca. 60 and the fluctuations are not normally
distributed (see the top right panel in Figure 2.5). The cylindrical pore can be made arbitrarily long, so that the number of atoms at saturation in cylindrical pores is sufficiently large. For the 2 nm cylindrical pore of $L = 80\sigma$ the average number of atoms is ca. 1460, and the fluctuations are normally distributed. Nevertheless, the strong attractive potential of the narrow confinement makes the GCMC insertions and removals very inefficient, so that the fluctuations are damped. These damped fluctuations result in an apparent high modulus, which is a computational artifact rather than the real behavior. However, at higher temperature, while the 2 nm spherical pore still remains a challenge, the calculation of the modulus in the 2 nm cylindrical pore gives results similar to other pore sizes.

Both the high scattering in the results for the modulus of the fluid in cylindrical pores and the apparent high modulus in the smallest pores, suggest that while the model for cylindrical pores used here is suitable for calculation of adsorption isotherms, it is not efficient for the calculation of the elastic modulus at the temperature typically used in argon adsorption experiments. It is likely that the main drawback of the model is the smooth structureless cylindrical pore wall, which stimulates the fluid atoms to arrange in tightly packed layers along it (see Figure 2.8). There could be two possible solutions to this problem. The first solution is to consider the pores with atomistic details, representing molecularly rough surfaces of real amorphous materials, e.g., mesoporous silicas or Vycor glass. This approach will require explicit modeling of the solid atoms, increasing the computational cost. The second solution is to use one of the approaches that take into account the heterogeneity or molecular roughness of the pore walls, yet do not explicitly mimic the atomistic structure of the walls. Among such approaches, the two versions of DFT could be mentioned: the quenched solid DFT by Ravikovitch and Neimark [85] and two-dimensional DFT by Jagiello and Olivier [109, 110]. Note that recent DFT calculations, showed that another thermodynamic property of confined fluid,
the heat of adsorption has been shown to be strongly influenced by the degree of surface roughness [111]. Therefore, we expect that introducing the surface roughness in the calculation of elastic properties of confined fluids might have a noticeable effect.

Last but not least, our simulations show that the thermodynamic route for calculation of elastic properties is fully consistent with the fluctuation route. This justifies the earlier results obtained by one of us using the thermodynamic route, where the average density of the fluid was calculated based on the density functional theory [84]. Those calculations showed in particular that the logarithmic dependence of the fluid modulus on vapor pressure is valid, even at vapor pressures above $p_0$.

2.5 Conclusion

Fluids confined in nanopores exhibit properties different from the properties of the same fluids in bulk. In this research, we focused on exploring the elastic properties of confined fluids: isothermal compressibility or elastic modulus. We calculated the modulus of liquid argon at its normal boiling point ($T = 87.3$ K) adsorbed in model silica pores of two different morphologies and various sizes. The main goal was to investigate the effect of the pore morphology on the elastic properties of confined fluid. We used conventional Monte Carlo simulations in the grand canonical ensemble to calculate argon adsorption isotherms for spherical and cylindrical pores with diameters of 2 nm and above. From the fluctuation of the number of fluid atoms in the pores at each given chemical potential, we calculated the elastic modulus of the fluid. Thus, for each of the considered systems, we obtained the elastic modulus as a function of vapor pressure.

For spherical pores, for all the pore sizes exceeding 2 nm, we obtained a logarithmic dependence of fluid modulus on the vapor pressure. Calculation of modulus at saturation showed that the modulus of the fluid in the spherical pores is a linear function of the reciprocal pore size. The calculation of the modulus of the
fluid in cylindrical pores appeared too scattered to make quantitative conclusions. Therefore, we performed additional simulations at higher temperature ($T = 119.6 \text{ K}$), at which Monte Carlo insertions and removals become more efficient. The results of the simulations at higher temperature confirmed both regularities for cylindrical pores and showed quantitative difference between the fluid moduli in pores of different geometries. Both of the observed regularities for the modulus stem from the Tait-Murnaghan equation applied to a confined fluid.

For the fluid in spherical pores at $T = 87.3 \text{ K}$ and for the fluid in both geometries at $T = 119.6 \text{ K}$, we calculated the elastic moduli from the numerical differentiation of adsorption isotherms and the results appeared very close to the method based on the fluctuations of number of atoms. At the normal boiling temperature of argon, both methods of calculation of elastic modulus of the fluid showed themselves inefficient for pores of 2 nm (and smaller), therefore calculation of the elasticity of the fluid in micropores still remains a challenge, and will likely require the use of different simulation techniques.

Our results, along with the development of the effective medium theories for decoupling elastic properties in nanoporous systems, set the basis for analysis of the experimentally-measured elastic properties of fluid-saturated nanoporous materials. In particular, the relation between the pore size and the fluid modulus could serve as a groundwork for determination of pore sizes from the ultrasonic measurements.
3.1 Introduction

In recent decades, coalbed methane (CBM) has emerged as a promising source for natural gas recovery [112, 113]. Unmineable coal seams provide an abundant source for natural gas because they are composed of extensive micro- and mesoporous\(^1\) systems containing large surface areas, which allow for a significant portion of methane to be trapped in the adsorbed state [114]. Some estimates are that over 90\% of the methane content is adsorbed onto the inner structures of the coal [115]. Standard CBM recovery techniques utilize the reduction of reservoir pressure in order to stimulate desorption of methane confined in the coal nanopores. However, such techniques are considered inefficient, yielding approximately 50\% CBM recovery according to some estimates [116]. Recently, enhanced CBM recovery techniques have been developed that can extract CBM using a fluid injection method. Particularly, the methods utilizing CO\(_2\) injection operate on the basis that coal adsorption selectively favors CO\(_2\) over methane by a factor of 10:1 molecules [117, 118]. As such, the CBM recovery process provides both a source for natural gas as well as a receptacle for carbon gas sequestration, which makes CBM use even more practical and environmentally conscious [116, 119, 112].

In order to make efficient utilization of CBM, there is a major need for direct hydrocarbon detection techniques and the ability to estimate the harvestable methane content in a given coal seam for CBM recovery [115]. The state of CBM systems is completely different from that of conventional gases in sands, therefore it is difficult to transfer direct hydrocarbon detection techniques used on conventional reservoirs

\(^1\)According to IUPAC convention, mesoporous materials have pores with internal dimensions of 2 to 50 nm; microporous materials have pores under 2 nm [12].
to CBM. Recently, several researchers have focused on studying the elastic properties of coalbeds, which is important for gauging the potential of estimating gas content in coal via seismic waves [119, 118, 120, 121, 115, 122, 123, 124].

Because of how heterogeneous CBM is, one of the challenges of interpreting related wave propagation experiments is understanding how the wave propagation is affected by the properties of CBM. Wave propagation behavior in CBM can be related directly to properties of the individual constituents of the CBM composite fluid-saturated porous medium via an effective medium theory such as the Gassmann equation [125].

The Gassmann equation

\[
K = K_0 + \frac{\left(1 - \frac{K_0}{K_s}\right)^2}{\frac{\phi}{K_f} + \frac{1-\phi}{K_s} - \frac{K_0}{K_s^2}}
\]

(3.1)

relates the effective bulk modulus of the fluid saturated rock \(K\), the bulk modulus of the dry rock \(K_0\), the bulk modulus of the solid \(K_s\), the bulk modulus of the fluid \(K_f\), and the porosity \(\phi\). There have been recent works which attempted to utilize Gassmann equation for insights relevant for CBM. McCrank and Lawton found a reduction of acoustic impedance due to CO\(_2\) injection in coal, which could not be explained solely by the Gassmann fluid substitution model, suggesting an interaction of the fluid and wall affects the properties of the CBM constituents [120]. Lespinasse et al. used the Gassmann equation with their simulations of CBM wells [119, 118]. Chen et al. correlated methane content with elastic parameters in CBM and noted that the elastic parameters of CBM play a similar role in the Gassmann equation as in amplitude-versus-offset (AVO) technology [115]. Huang et al. combined the Gassmann equation and a differential effective medium model to describe the relationship between methane content and P-wave velocity in CBM [123].

Gor and Gurevich showed that by combining molecular simulations with data from gas adsorption experiments, the Gassmann equation can be used for nanoporous materials [26]. They cautioned that care must be taken when utilizing the Gassmann
equation for nanoporous materials, because the fluid modulus in nanopores differs from the modulus of the same fluid in bulk [84, 4]: the parameter \( K_r \) in Equation (3.1) becomes dependent on the pore size and the pore pressure. However, since their study was conducted using argon and \( n \)-hexane at subcritical temperatures and pressures, it is not certain whether the effects they observed would hold for supercritical methane confined in nanopores, whose critical temperature and critical pressure are 190.55 K and 4.595 MPa, respectively.

In this research, we consider methane at supercritical conditions confined in model carbon slit nanopores of various sizes. In recent years, molecular simulations became widely used for studying confined hydrocarbons, and despite its simplicity the classical slit pore model showed to work efficiently for capturing a lot of properties of confined fluids [8, 126, 127, 128, 129, 130]. However, while adsorption [8, 129, 130] and transport properties [127, 130] on nanoconfined methane have been studied extensively, the elastic properties of confined methane are rarely considered. In addition to wave propagation in methane-saturated porous media, the departure of methane compressibility from the bulk value due to confinement needs to be take into account when estimating methane storage by adsorption.

We utilize the same system parameters and conditions as in the recent study by Mosher et al. [8]. We calculate the compressibility of the confined fluids following the approach which has been used recently for subcritical adsorption of simple gases in nanopores based on Monte Carlo (MC) molecular simulations [4, 58, 10, 131]. Additionally, we employed molecular dynamics (MD) simulations, which confirmed the MC results.

We calculate the elastic modulus of confined methane and show that it is significantly increased in nanopores compared to bulk methane at the same conditions. We also show that the behavior of the elastic modulus as a function of pressure or pore size is different for supercritical methane than what was previously reported.
for subcritical fluids. This increase of the modulus contributes to the parameters of the Gassmann Equation (3.1), thus affecting the analysis of wave propagation in methane-saturated coal seams.

3.2 Methods

For a bulk fluid system the isothermal compressibility $\beta_T$ is defined as

$$\beta_T \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{N,T},$$  \hspace{1cm} (3.2)

where $P$ is the pressure of the fluid, $V$ is the volume of the system, $N$ is the number of particles in the system, and $T$ is the temperature. We assume that this definition is applicable for the average compressibility of fluid confined in the pore [63, 4, 132]. For representing our results it will be more convenient to use the reciprocal property: the isothermal bulk modulus

$$K_T = \beta_T^{-1} = -V \left( \frac{\partial P}{\partial V} \right)_{N,T},$$  \hspace{1cm} (3.3)

which is more applicable to the Gassmann equation.

We employ classical statistical mechanics in order to calculate the isothermal compressibility of the fluid. In order to predict the adsorption isotherms of the fluid in our porous system, we first utilize Monte Carlo simulations in the grand canonical $(\mu VT)$ ensemble[59, 133], where the chemical potential $\mu$ is set equal to the chemical potential of our bulk reservoir, and the system volume $V$ and temperature $T$ are held constant. In the grand canonical ensemble, the isothermal (bulk) modulus, can be expressed as a function of the fluctuation of the number of particles $N$ in the system:

$$K_T = \frac{k_B T \langle N \rangle^2}{V \langle \delta N^2 \rangle},$$  \hspace{1cm} (3.4)

where $k_B$ is the Boltzmann constant, and $\langle \delta N^2 \rangle$ is the variance of the number of particles in the system [57]. Although, strictly speaking, Equation (3.4) is valid for
bulk systems only, it has been employed for fluids in confinement, showing consistency with experiments [10, 131].

In addition to the grand canonical ensemble, in which the calculation of compressibility is straightforward, as seen from Equation (3.4), compressibility can also be calculated from molecular simulations in the canonical ensemble. The latter, unlike the grand canonical ensemble, can be realized using widespread MD algorithms. We utilize the canonical (NVT) ensemble – where the number of atoms $N$, the system volume $V$, and the temperature $T$ are held constant. Due to this fixed volume, the isothermal compressibility can be determined from the fluctuations of the internal virial [134]

$$\mathcal{W} = \frac{1}{3} \sum_i \sum_{j>i} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} = -\frac{1}{3} \sum_i \sum_{j>i} w(r_{ij}), \quad (3.5)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\mathbf{f}_{ij}$ is the force on particle $i$ due to $j$, and $w(r_{ij})$ is defined as

$$w(r_{ij}) = r_{ij} \frac{dv(r_{ij})}{dr_{ij}}, \quad (3.6)$$

where $v(r_{ij})$ is the interaction potential. Thus, the isothermal compressibility can be determined by

$$K_T = \frac{1}{V} \left( Nk_B T + \langle \mathcal{W} \rangle_{NVT} + \langle \mathcal{X} \rangle_{NVT} - \frac{\langle \delta \mathcal{W}^2 \rangle_{NVT}}{k_B T} \right), \quad (3.7)$$

where $\langle \delta \mathcal{W}^2 \rangle_{NVT}$ is the variance of the internal virial, and $\mathcal{X}$ is a hypervirial function defined as [134]

$$\mathcal{X} = \frac{1}{9} \sum_i \sum_{j>i} \mathbf{r}_{ij} \frac{dw(r_{ij})}{dr_{ij}}. \quad (3.8)$$

Prior to modeling confined methane, we performed grand canonical Monte Carlo (GCMC) simulations on bulk methane systems and calculated the compressibility. The bulk GCMC simulations were performed in the RASPA open-source software [135], using a simulation cell with dimensions $L_x = 42.72$ Å, $L_y = L_z = 49.32$ Å,
to be consistent with the simulation cell used in Reference [8]. Periodic boundary conditions were applied in the $x$, $y$, and $z$ directions of the cell. The methane molecule was represented using a united-atom LJ sphere as in Reference [136], the interaction potentials of which are described in Table 3.1. The simulation cell was filled with methane molecules to achieve the density of supercritical methane at temperatures between 298 K and 332 K and pressures between 1 and 10 MPa as in Reference [8]. Each simulation was run for $1 \times 10^6 \times N$ moves, where $N$ equals the number of methane molecules present in the system.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$\sigma$, nm</th>
<th>$\epsilon/k_B$, K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$ (UA methane)</td>
<td>0.373</td>
<td>148.0</td>
<td>[136]</td>
</tr>
<tr>
<td>C (EH methane)</td>
<td>0.331</td>
<td>0</td>
<td>[137]</td>
</tr>
<tr>
<td>H (EH methane)</td>
<td>0.331</td>
<td>15.3</td>
<td>[137]</td>
</tr>
<tr>
<td>C (Graphene)</td>
<td>0.34</td>
<td>28.0</td>
<td>[138]</td>
</tr>
</tbody>
</table>

Note: $\sigma$ represents the LJ diameter and $\epsilon$ represents the LJ energy scale. A cutoff distance $r_{\text{cut}}$ of 12 Å was used, and tail corrections were applied. The all-atom methane model describes the methane molecule as having interaction sites halfway along the C–H bonds, rather than on the individual atoms [137].

Because derivative thermodynamic properties such as the isothermal compressibility are more sensitive to the force-fields used in modeling than the main state properties (e.g., density) [139], we also studied a more rigorous all-atom methane model of Reference [137] called TraPPE-EH. TraPPE-EH methane models five distinct interaction sites for a single methane molecule, compared to a single interaction site used in the united-atom model of methane considered in Reference [8]. The bulk GCMC simulations were then repeated using this all-atom methane configuration, whose interaction potentials parameters are also given in Table 3.1.
Next, we performed MD simulations of bulk united-atom methane in the canonical ensemble using the LAMMPS open-source MD software [140]. We used an identical simulation cell as in our GCMC simulations. We applied a Nosé-Hoover thermostat with a damping parameter of 100 timesteps, where 1 timestep equals 1 fs. We then ran the bulk simulations for $2 \times 10^7$ timesteps.

For simulations of nanoconfined methane, we chose the same system as studied by Mosher et al. to represent geologically relevant conditions [8]. The porous system was composed of a graphene slit-pore, each wall of which consisted of 3 rigid graphene sheets arranged parallel to the $xy$-plane as in Figure 3.1. Because the intramolecular energy of the graphene sheets was not used in calculations, the carbon bonds, dihedrals, and impropers of the graphene were not considered. The dimensions of the simulation cell were $L_x = 42.72 \, \text{Å}$, $L_y = 49.32 \, \text{Å}$, and $L_z = 2.5 \times H_{\text{wall}} + H_{\text{pore}}$ where $H_{\text{wall}} = 6.70 \, \text{Å}$. The effective pore width is taken from Reference [8] as the center-to-center distances of the opposite pore wall carbon atoms minus the effective diameter of said carbon atoms (i.e., $H_{\text{pore,eff}} = H_{\text{pore}} - \sigma_{ss}$). The pore volume $V$ used for calculation of $K_T$ by Equations (3.4) and (3.7) is calculated based on this effective (internal) pore width $H_{\text{pore,eff}}$. The parameters for the interaction potential of carbon
atoms in the graphene sheets are detailed in Table 3.1. Lorentz-Berthelot mixing rules were used for the solid-fluid interactions.

Similarly to the bulk system, methane was simulated using both united-atom and all-atom configurations for the GCMC simulations. Each GCMC simulation was equilibrated for $1 \times 10^6 \times N$ moves, followed by a production run of $2 \times 10^6 \times N$ moves. For the more dense porous systems, the length of our simulations exceeded that of Mosher et al. by 200 - 700%, in order to achieve reliable normal distributions for fluctuating properties, which is necessary for calculation of derivative thermodynamic properties from the statistical mechanics relations [4, 10].

For the MD runs, only the united-atom methane model was used, as the all-atom model was too computationally expensive. Porous systems identical to those used in the GCMC runs were used for the MD simulations. The equilibrated atomistic configurations from the GCMC runs were used as starting points for the $NVT$ simulations. The canonical ensemble is convenient here because it requires that the number of particles be held constant, which can avoid sampling difficulties for compressibility calculations in the grand canonical ensemble [10]. Each MD simulation was run for $5 \times 10^6$ timesteps to equilibrate, followed by a production run of $2 \times 10^7$ timesteps, with a 1 fs timestep.

### 3.3 Results

In order to test our methods against the known case, we first calculated densities for bulk methane using GCMC and canonical ensemble MD simulations at $T = 298 \text{ K}$ and bulk reservoir pressures from 1 to 10 MPa. Figure 3.2 shows the bulk fluid densities for both united-atom and all-atom configurations of methane from our GCMC simulations. These results show good agreement with the bulk simulations from Reference [8] and with bulk fluid densities calculated from the Peng-Robinson equation of state following the convention of Reference [8], which is also used in
the RASPA software [9]. We then used the densities in Figure 3.2 to calculate the isothermal modulus of methane using Equations (3.4) and (3.7). Figure 3.3 shows the isothermal modulus of methane calculated for each of the points in Figure 3.2. Again, good agreement with the reference data is observed, which verifies the applicability of Equations (3.4) and (3.7).

![Figure 3.2](image-url)

**Figure 3.2** Methane density as a function of pressure: bulk simulation data for united-atom (○) and all-atom (×) methane GCMC simulations at 298 K compared to simulation data from Reference [8] (○). We also present united-atom canonical ensemble MD simulations data (△); for these simulations, the average bulk density from the GCMC simulations was used as an input, and the pressure was calculated. The dashed line represents bulk fluid densities calculated from the Peng-Robinson equation of state [9]. The error bars represent two standard deviations in the densities (for GCMC data) and pressures (for canonical ensemble MD data).
Figure 3.3  Isothermal modulus of bulk methane at 298 K as a function of pressure, calculated using united-atom GCMC (○), all-atom GCMC (×), and united-atom canonical ensemble MD (△). The dashed line represents the isothermal bulk moduli obtained using the Peng-Robinson equation of state [9].

The density of adsorbed supercritical fluid exceeds the bulk density of the same fluid at the same conditions. This excess is referred to as excess adsorption, and it is calculated by subtracting the bulk fluid density (calculated in Figure 3.2) from the total adsorbed fluid density. Figure 3.4 shows the excess adsorption isotherms for united-atom and all-atom methane models in pores with pore sizes $H_{\text{ext}}$ of 2, 3, 6, and 9 nm. The results of our simulations using both methane models show good agreement with the excess methane adsorption calculated in Reference [8].
Figure 3.4  GCMC simulations excess adsorbed density vs. bulk reservoir pressure for united-atom (♦) and all-atom methane (×) models at 298 K compared to simulation data from Reference [8]. Here excess adsorption is a measure of the amount of fluid in the pore due to adsorption versus the amount of bulk fluid present at the given conditions. The error bars represent 2 standard deviations in the excess fluid density.

Figure 3.5 shows the isothermal modulus of the confined methane configurations as a function of the bulk reservoir pressure and bulk reservoir chemical potential for 2 nm and 9 nm pores, calculated from the corresponding points in Figure 3.4, along with the bulk fluid modulus. Here the bulk chemical potential is equal to the molar Gibbs free energy for bulk methane calculated using the Peng-Robinson equation of state. For smaller pore sizes, the modulus of the fluid increases relative to the bulk fluid, yielding a stiffer fluid. However, as the pore size increases, the modulus of the confined fluid approaches the modulus of the bulk fluid. Of note here are the trends of each plot: while the modulus as a function of bulk reservoir pressure follows an approximately linear trend, the modulus as a function of chemical potential is nonlinear; this will be further discussed in the next Section.
Figure 3.5  GCMC and MD simulations $K_T$ as a function of bulk reservoir pressures (left) and bulk chemical potentials (right) for 2 nm and 9 nm pore sizes at 298 K. The calculations are based on Equations (3.4) and (3.7) applied to adsorption isotherms shown in Figure 3.4. For the GCMC simulations, the pores were filled to achieve a chemical potential so that $\mu_{\text{confined}} = \mu_{\text{bulk}}$. For the canonical ensemble MD simulations, the pore was initially packed with a number of molecules corresponding to the average bulk density of the corresponding GCMC simulation. The error bars here are calculated using the method described in Reference [4]. The solid pink line represents the $K_T$ of bulk methane.

In order to elucidate the behavior of the compressibility at other temperatures, we also ran simulations at 318 K and 332 K. Figure 3.6 shows the temperature dependence of the isothermal modulus of the confined united-atom methane configurations as a function of bulk reservoir pressure for 2 nm and 9 nm pores. As expected, Figure 3.6 demonstrates that the isothermal modulus decreases with increasing temperature. Of note also is the slope of the linear trend depends on temperature.
Figure 3.6 United-atom methane GCMC simulations $K_T$ as a function of bulk reservoir pressures for 2 nm and 9 nm pore sizes at 298 K, 318 K, and 332 K. The calculations are performed in the same manner as in Figure 3.5. The solid pink line represents the $K_T$ of bulk methane.

Figure 3.7 shows the isothermal modulus of the confined fluid versus the reciprocal pore size for bulk reservoir pressures of 1 MPa and 10 MPa. Although the isothermal modulus as a function of reciprocal pore size follows an approximately linear trend for low pressures, for higher pressures the trend is distinctly nonlinear. This difference has implications for analysis of CBM reservoirs, which are typically in supercritical conditions.
Discussion

We presented GCMC and canonical ensemble MD simulations of supercritical methane in carbon slit pores of various sizes, using both united-atom TraPPE-UA and all-atom TraPPE-EH methane models. While for some properties, such as boiling points and viscosities, TraPPE-UA model is known to give unsatisfactory predictions compared to TraPPE-EH [137], for our calculations here both methane models showed good agreement with each other. Note that the simpler united-atom model required about a quarter of the computational time than the all-atom model needed.

We calculated the adsorption isotherms from the GCMC simulations, and from these isotherms we calculated the isothermal (bulk) modulus of the confined fluid. Our aim in calculating the isothermal modulus is to determine the nanoconfinement effects since the elastic modulus of a fluid in nanopores contributes to the Gassmann equation, Equation (3.1), which determines the wave propagation in fluid saturated porous media. In order to verify our calculations with another approach, we also calculated the isothermal modulus from MD simulations in the canonical
ensemble. While for bulk systems, derivative thermodynamic properties calculated from fluctuations of different quantities in different ensembles should necessarily be the same [134], it is not obvious if this will hold for the confined systems. However, our calculation shows consistency between the isothermal compressibility calculated from fluctuations in canonical and grand canonical ensembles. This suggests that the physical meaning of those fluctuation properties remain well-justified.

According to Figure 3.5, the isothermal modulus is significantly increased by confinement, particularly for smaller pores, with an approximately 660% increase compared to bulk for 2 nm pores at 10 MPa and 298 K. However, for larger pores this confinement effect is greatly reduced: for the 9 nm pores at the same temperature and pressure, there is approximately a 63% increase in the isothermal modulus, which is still substantial. This difference with pore size occurs because, with an increase in pore width, a smaller fraction of the fluid is adsorbed onto the pore walls, decreasing the excess adsorption, and increasing the proportion of fluid that approaches bulk conditions (see Figure 3.8). An increase of the elastic modulus due to confinement has been theoretically predicted for simple subcritical fluids in silica pores by our group [84, 4, 58, 10, 131] and others [75, 132]. Moreover, for subcritical fluids, the trends similar to those shown in Figure 3.5 were reported experimentally based on ultrasound propagation data [1, 2, 45, 50].
Figure 3.8 A 9 nm slit pore filled with united-atom methane molecules at 298 K and 10 MPa. During adsorption, the methane fluid is attracted to the pore wall, and therefore densified. However, with larger pores, some fluid remains far enough from the walls so that it exists in a bulk-like phase between the adsorbed regions on opposite sides of the pore. The pictured adsorbed regions correspond to the cutoff distances of the innermost graphene layers, representing the maximum distance at which the methane molecules are attracted by the graphitic carbon atoms. The system was visualized using the iRaspa visualization package [7].

Previous simulations and experiments for subcritical fluids showed that the elastic modulus increases as a linear function of \( \log(p/p_0) \), where \( p_0 \) is the saturation pressure [58]. This dependence can be interpreted as the modulus being a linear function of chemical potential or solvation pressure \( P \) of the fluid in the pore. In contrast, Figure 3.5 shows that for supercritical methane, \( K_T \) is not a linear function of chemical potential, which indicates a significant departure from ideal-gas behavior.

Furthermore, another feature observed is that the modulus of subcritical methane in confinement differs from supercritical methane in confinement. It was previously shown that the moduli of confined argon and nitrogen at subcritical conditions change linearly as a function of the reciprocal pore size \( 1/H_{\text{ext}} \) [10, 131]. Here we find that at \( T = 298 \text{ K} \) and pressures \( p = 1 \text{ MPa} \) and \( 4 \text{ MPa} \) (below critical), as detailed in Figure 3.7, the moduli of methane also follow a linear trend with increasing reciprocal pore size, with \( R^2 \)-values of 0.997 and 0.994, respectively.
Table 3.2 Coefficients for the Linear Fit Lines of Figure 3.7

<table>
<thead>
<tr>
<th>$P$ (MPa)</th>
<th>Slope (nm $\times$ MPa)</th>
<th>Intercept (MPa)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.264</td>
<td>0.734</td>
<td>0.997</td>
</tr>
<tr>
<td>4</td>
<td>58.423</td>
<td>2.730</td>
<td>0.994</td>
</tr>
<tr>
<td>10</td>
<td>124.143</td>
<td>2.553</td>
<td>0.936</td>
</tr>
</tbody>
</table>

Note: The linear fit follows the form $K_T = \text{Slope}(\text{nm} \cdot \text{MPa})/H_{\text{pore}}(\text{nm}) + \text{Intercept}(\text{MPa})$.

However, for $P = 10$ MPa (above critical), as detailed in Figure 3.7, the modulus as a function of reciprocal pore size follows a distinctly nonlinear trend, with a much lower $R^2$-value of 0.936 for the linear fit. The equations for the linear fits are provided in Table 3.2.

We focused here exclusively on slit pores, without studying the effects of pore shape on the fluid compressibility. Our earlier work [10] explored the role of the pore geometry on compressibility of confined subcritical fluids and did not show any qualitative difference.

This linear dependence observed in subcritical cases, along with the dependence on $\log(p/p_0)$, was attributed to the Tait-Murnaghan equation [69]

$$K(P) = K_{\text{ref}} + \alpha(P - P_{\text{ref}}),$$  \hspace{1cm} (3.9)

where $K_{\text{ref}}$ is the modulus at some reference low pressure, $\alpha = \frac{dK}{dP}$. This equation gives the first term of the Taylor series expansion of $K$ as a function of pressure, which is a valid approximation at $P \ll K$. This strong inequality is fulfilled for subcritical fluid, where $K \sim 1$ GPa and $P \sim 10$ MPa [58], but not for supercritical methane where the considered pressure range is of the same order as the elastic modulus. For bulk solids or fluids this dependence could be described using higher order terms of the series [141, 142].
Another possible reason for not observing the known trends is also related to higher compressibility of supercritical fluid compared to liquid near its normal boiling point. For liquid at subcritical conditions the compressibility is low, thus molar volume does not appreciably change with pressure, and the Gibbs-Duhem equation at constant temperature \( N\,d\mu = V\,dP \) gives simply \( \mu \propto P \) [58]. For supercritical fluid the molar volume changes significantly, and the proportionality between the chemical potential and solvation pressure may vanish.\(^2\)

Although the Tait-Murnaghan Equation (3.9) for the modulus is not fulfilled here, the data in Figure 3.5 suggest that for supercritical methane there is a linear dependence between the modulus and the pressure. However, in this case the pressure is the bulk reservoir pressure \( p \) and not the solvation (pore) pressure \( P \). Similar to Equation (3.9), the dependence can be written as

\[
K(p) = K_{\text{ref}} + \alpha_H(p - p_{\text{ref}}),
\]

where \( \alpha_H \) is the slope relating the modulus with the external reservoir pressure. The left panel in Figure 3.9 shows the modulus as a function of reservoir pressure \( p \) for bulk methane, and methane in pores of widths 2 nm, 3 nm, 6 nm and 9 nm. The lines show the fit according to Equation (3.10). The right panel in this Figure shows the values of parameter \( \alpha \) obtained from this fit, as a function of reciprocal pore width. The dependence shown in Figure 3.9 should be considered as empirical correlation, which could be further used for estimating the pore size and pressure effects on the modulus of the fluid in Gassmann Equation (3.1). However, future theoretical work should be performed to get a relation between the slope \( \alpha_H \), pore size, and the other parameters of the system (such as solid-fluid interactions). It is more likely that

\(^2\)For example, the molar volume of subcritical methane at 123.15 K changes by approximately 3% between pressures of 1 bar and 10 MPa. However, for supercritical methane at 298 K, there is approximately a ten-fold decrease in the molar volume across the same pressure range.
analytical thermodynamic models for confined fluids, such as by Travalloni et al. [143, 144, 145] can help in developing these relations than molecular simulations. Those approaches are beyond the scope of the current paper, and will be addressed in future work.

![Figure 3.9](image)

**Figure 3.9** $K_T$ calculated from GCMC simulations as a function of bulk reservoir pressure for bulk methane and methane confined in 2 nm, 3 nm, 6 nm, and 9 nm pores, presented with linear fits calculated from Equation (3.10) (left); and $\alpha_H$ parameters from these fits as a function of reciprocal pore size (right). The $\alpha_H$ value at $H_p^{-1} = 0$ represents the value for bulk fluid.

### 3.5 Conclusion

Various geological formations, including shales and coals, contain supercritical methane confined in nanopores. Although wave propagation can be used to assess the methane content, quantitative analysis of the wave propagation data requires knowledge of the elastic modulus of confined methane. Previous experimental and theoretical studies of confined fluids at subcritical conditions showed that the elastic modulus is affected by confinement, but no data for supercritical fluids have been reported. Here we performed Monte Carlo molecular simulations to calculate the elastic modulus of supercritical methane confined in model carbon nanopores. We used two different models for simulated methane molecules in our Monte Carlo
simulations. Additionally, we performed molecular dynamics simulations using one of the models; all simulation results showed consistency between methods. We showed that the effects of confinement on the elastic modulus of supercritical methane are similar to the effects on subcritical fluids: (1) the elastic modulus of confined fluid is higher than in bulk, (2) for a given pore size, the modulus monotonically increases with pressure, and (3) at a given pressure, the modulus monotonically increases with the reciprocal pore size. However, these effects appeared much more pronounced than for subcritical fluids, showing up to seven-fold increases of the modulus in 2 nm pores. These effects should be observable in laboratory ultrasonic experiments, similar to those performed on subcritical fluids. Therefore, we are hoping that our study will stimulate experimental investigation of elasticity of supercritical fluids in confinement.
CHAPTER 4
COMPRESSIBILITY OF SIMPLE FLUID IN CYLINDRICAL CONFINEMENT: MOLECULAR SIMULATION AND EQUATION OF STATE MODELING

4.1 Introduction

Materials that have pores with internal dimensions under 100 nm are known as nanoporous materials [12]. They have many applications in areas such as catalysis [13, 146], membrane separations [13, 147], heat exchange [14], nanofluidics [148], porous electrodes [14], carbon capture and storage [149, 150, 151], among others. Nanopores also occur naturally in various geological formations such as shales and coals [88, 152, 153, 154]. Many of the applications of nanoporous materials involve fluid phases confined in the pores. Confined fluids have properties that can differ significantly from the same fluid in the bulk such as density [17], diffusion [155, 156, 17], freezing temperature [157, 158], phase separation in mixtures [88], and phase behavior [159, 160, 154], and there are still large gaps in our fundamental understanding of the behaviors [161]. The differences in properties of fluids in confinement also arise in elastic properties, which have been observed extensively from experiments conducted on nanoporous glasses [1, 32, 2, 42, 45, 50]. Molecular modeling also confirms that one of the properties affected by confinement is the isothermal compressibility of the fluid [84, 4, 58, 5, 10, 131, 162]. Understanding the effects of confinement on the compressibility of fluid is important for interpreting the elastic wave propagation in fluid-saturated nanoporous media, such as hydrocarbon-bearing shales [26, 76]. Hence, there is a need for the ability to predict changes of compressibility of confined fluids.

In our recent research, we showed that the compressibility of simple fluids such as argon and nitrogen can be calculated from Monte Carlo molecular simulations in the grand canonical ensemble [4, 58, 10, 131], and these results compared well to
the experimental measurements performed on nitrogen [1] and argon [45] confined in nanoporous glass samples. However, even for the fluids with such simple molecular structures as argon confined in pores below 10 nm in size, the simulations can take up to several weeks of computation to obtain adequate statistical sampling of configurational space due to the deficiencies of GCMC for dense systems [133]. Moreover, while simulations of fluid confined in spherical pores provided high-quality data, simulations of argon at normal boiling point in cylindrical pores produced very noisy results for the compressibility [10]. These shortcomings necessitate an alternative method that is more useful to predict elastic properties for dense confined fluids.

Thermodynamic properties of bulk fluids can be readily calculated from various equations of state (EOS), varying from simple cubic [163, 9, 164, 165] to more advanced, based on statistical mechanics [166], or empirical relations involving more parameters [6, 167, 168]. But, the state of the fluids in the bulk can be very different from the state of the fluid confined in nanoporous materials, leading to differences in calculated properties when a bulk EOS is applied to the confined fluid. Therefore, an equation of state that can account for the effects of confinement would be of use to model fluid properties more efficiently than conducting experiments or simulations.

There have been several attempts to model effects of confinement using an EOS. Schoen and Diestler used perturbation theory to derive an EOS for fluids confined in slit pores [169]. They obtained the Helmholtz free energy expression for the confined fluid, from which evolved an equation identical in form to the van der Waals (vdW) EOS. This model was able to predict excess adsorption density of the fluid in the pore that qualitatively matched some molecular simulations, but was not able to predict critical temperature-depression on pore size and excess density depletion behavior near the critical point. These shortcomings likely stem from the assumption that local fluid density in the pore is constant over the pore space. Truskett et al. used the
approach of Schoen and Diestler and included hydrogen-bonding interactions [170]. Following the approaches of Schoen and Diestler as well as Truskett et al., Giaya and Thompson extended the EOS model to cylindrical pores [171].

Alternative approaches proposed recently include that of Zarrogoiechea and Kuz, which was to extend the vdW EOS to confined fluids based on classical thermodynamics and taking the pressure in the pore as tensors [172, 173]. These equations were able to predict phase transitions and a shift of the critical parameters in qualitative agreement with molecular simulations. Their model had limitations due to their considering the pore wall to be a hard wall with no fluid-wall attraction, which hinders its predictions of adsorption. Zhu et al. developed an equation of state based on thermodynamic arguments with consideration of interactions with a cylindrical pore surface [174]. Their model was shown to match well to experimental adsorption isotherms on MCM-41 silica nanopores between 2 and 5 nanometers in diameter. Travalloni et al. have taken a similar approach, by considering the interaction of fluid and cylindrical pore surface in developing the partition function, from which the pressure explicit EOS was analytically derived using thermodynamic relations. They have shown that adsorption behavior of fluids in nanoporous materials can be modeled using an EOS similar in for to van der Waals EOS [143, 175]. Travalloni et al. extended a generalized vdW theory to account for the wall-fluid interaction and showed that their simple model, with only two fitting parameters related to the wall-fluid interaction, can describe fluid adsorption behavior in nanopores. Their model allows directly solving the chemical equilibrium condition of chemical potential of the bulk fluid matching that of the adsorbed fluid $\mu_{\text{ads}} = \mu_{\text{bulk}}$ to determine the vapor-liquid equilibrium in the pore. Travalloni and coworkers also extended this method for other pore models and equations of state [144, 176, 145]. Their approach is also applicable to modeling the competitive adsorption of fluid mixtures, which showed good comparisons to experiments [143, 175, 144, 176, 145, 177].
Other approaches to EOS for confined fluids include the following. Alharthy and coworkers correlated the shift of the critical temperature and pressure due to confinement and used the new shifted critical properties in the Peng-Robinson equation to model phase equilibria in the pores, but their approach did not compare to experiments [178, 179]. Tan and Piri incorporated perturbed-chain statistical associating fluid theory (PC-SAFT) [180] to model the confined fluid via EOS [181, 182]. In addition to the robust PC-SAFT EOS, they included a term for the capillary pressure based on the Laplace equation that has been modified with an additional fitted parameter based on the wall-fluid interaction, which is taken as a function of pore size and temperature. Their model showed good comparison to experiments and simulations of confined fluids for phase equilibria and for shift of the critical points. Dong et al. extended the Peng-Robinson EOS for fluids confined in cylindrical nanopores [183]. Their method to calculate vapor-liquid equilibrium couples the effects of capillary pressure, adsorption, and shift of critical properties in an iterative procedure. They show that the adsorbed layer plays a significant role in the predictions of the vapor-liquid equilibrium, especially for the smallest pores, therefore the thickness of the adsorbed layer should not be neglected. Another approach taken by Yang et al. was to modify the Peng-Robinson EOS with a single new term relating to the fluid-wall interaction that accounts for the shift in critical temperature and pressure due to confinement [184]. They found less than 8% average error with their model tested against several molecular simulation and experimental data points. But, Yang et al. noted that their model is not accurate for micropores (pore size < 2 nm). Despite these developments of EOS for confined fluids, none of the aforementioned works focused on predictions of derivative thermodynamic properties of confined fluids, and isothermal compressibility in particular.

This research aims to assess the capability of an equation of state to model effects of confinement on elastic properties, showcasing an example of argon in silica
pores of various sizes. Since the modified vdW EOS developed by Travalloni et al. (TvdW EOS, for brevity) [143] has one of the simplest and the most transparent form, yet demonstrated impressive predictive capabilities for the adsorption isotherms, we chose to use it for our present study. We derived the analytical expression for the compressibility from the TvdW EOS. We compare the TvdW EOS predictions for compressibility to molecular simulations of argon confined in silica nanopores reported in our earlier work [10]. We also performed additional molecular simulations to explore the dependence of compressibility on the solid-fluid interaction parameters and compared them to the dependencies predicted by the TvdW EOS. The results of our comparison suggest that TvdW EOS predicts compressibility of simple fluids in confinement consistent with molecular simulations, and thus it can serve as a step towards quantitative description of wave propagation in fluid-saturated nanoporous media.

4.2 Methods

For calculation of elastic properties of confined fluids, we consider a simple model system: argon adsorbed in silica pores, which have been studied experimentally by Schappert et al. [3, 41, 42, 43, 45, 49, 50, 51] and using molecular modeling by us [84, 4, 185, 58, 10, 76]. Here, we consider cylindrical pore geometry.

4.2.1 Compressibility by Statistical Mechanics

We use molecular simulations data from our recent work [10], and performed additional simulations. We used the same method as in [10]; thus, we summarize the computational details only briefly. Both fluid-fluid (argon) and solid-fluid (argon-silica) interactions were modeled by Lennard-Jones (LJ) potentials. The LJ parameters and physical properties used in the simulations are summarized in Table 4.1. We conducted conventional grand canonical Monte Carlo (GCMC) simulations.
based on the Metropolis algorithm [95]. The adsorptive potentials between the fluid atoms and the pore wall were modeled by cylindrically integrated, site-averaged interaction potentials [97]. All simulations were performed using the Chainbuild code [186], modified for cylindrical pore geometry. [10]

Table 4.1 Parameters for the Fluid-fluid (ff) and Solid-fluid (sf) Interactions for the Argon-silica System

<table>
<thead>
<tr>
<th>Interaction</th>
<th>σ, nm</th>
<th>$\epsilon/k_B$, K</th>
<th>$\rho_s$, nm$^{-2}$</th>
<th>$r_{\text{cut}}$, \text{σ}_{\text{ff}}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-Ar</td>
<td>0.34</td>
<td>119.6</td>
<td>-</td>
<td>5</td>
<td>[98]</td>
</tr>
<tr>
<td>Silica-Ar</td>
<td>0.30</td>
<td>171.24</td>
<td>15.3</td>
<td>10</td>
<td>[99]</td>
</tr>
</tbody>
</table>

Note: \( \sigma \) is the LJ diameter, \( \epsilon \) is the LJ energy, \( \rho_s \) is the number density of solid LJ sites on the surface, and \( r_{\text{cut}} \) is the cut-off distance where interactions were truncated; no tail corrections were used.

Simulations were performed with cylindrical pores, which is also the pore geometry on which the TvdW EOS is based. The pore size in the simulations refers to the external diameter \( d_{\text{ext}} \) which is taken as the center-to-center distance from one pore wall molecule to the molecule on the opposite side of the pore, following the convention in previous works [100, 4, 10]. The volume of the pore that is accessible to the fluid atoms \( V \) differs from the volume calculated using the external diameter of the pore. To calculate the internal diameter \( d_{\text{int}} \) we used the approach from References [92, 100] extended to cylindrical geometry [10]

\[
d_{\text{int}} \approx d_{\text{ext}} - 1.7168\sigma_{\text{sf}} + \sigma_{\text{ff}}. \tag{4.1}
\]

Each simulation was run for at least \( 5 \times 10^9 \) trial Monte Carlo moves. Each simulated data point was first equilibrated with at least \( 10^9 \) trial moves that were not considered in calculations. The Johnson et al. equation of state for LJ fluid was used to calculate the chemical potential at the vapor-liquid equilibrium [101]. The reduced chemical potential \( \mu^* = \mu/\epsilon_{\text{ff}} \) at saturation pressure of argon was calculated
as $\mu^* = -9.6$ at $T = 87.3$ K and $\mu^* = -11.6$ at $T = 119.6$ K. Considering the vapor at these conditions to be an ideal gas, we used

$$\mu = k_B T \ln(p/p_0) + \mu_0(T)$$

(4.2)

to calculate pressures at other values of chemical potential.

The isothermal compressibility $\beta_T$ is defined as

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

(4.3)

where $V$ is the volume of fluid, $P$ is the fluid pressure, and $T$ is the absolute temperature. The compressibility is also the reciprocal of the elastic modulus $K_T = \beta_T^{-1}$, which is the form predominately used in this work for convenience. The isothermal compressibility of the fluid can be calculated from fluctuations of the number of particles in the pore $N$ in the grand canonical ensemble through the following statistical mechanics relation [63]

$$\beta_T = \frac{V \langle \delta N^2 \rangle}{k_B T \langle N \rangle^2},$$

(4.4)

where $\langle N \rangle$ is the average number of particles, $\langle \delta N^2 \rangle$ is the variance of $N$, and $k_B$ is the Boltzmann constant. Although Equation (4.4) is rigorous only for homogeneous bulk systems, it can apply to a fluid confined in a nanopore, as long as the fluctuations are Gaussian [57, 4].

4.2.2 Equation of State Calculations

Travalloni et al. have extended vdW theory for modeling properties of fluids confined in cylindrical pores via an EOS [143, 175]. Their model assumed square-well interactions between fluid molecules and the wall-fluid interaction (Figure 4.1). They also showed that this framework can be used to describe adsorption of mixtures with good predictability. Here we use this model to calculate compressibility of adsorbed
Figure 4.1  The molecule-wall potential (red) as a function of molecule position (blue) along a cross section of the cylinder passing through its central axis. \( r_p \) is the pore radius, \( \sigma \) is the effective fluid molecular diameter, and \( \delta_p \) is the range of the attractive part of the interaction potential.

argon. We first summarize below the steps used to calculate adsorption equilibrium following Travalloni et al. [143].

The pressure \( P \) of a confined fluid can be obtained from the TvdW EOS as

\[
P = \frac{R_g T}{v - b_p} - \frac{a_p}{v^2} - \theta \frac{b_p}{v^2} \left( 1 - \frac{b_p}{v} \right)^{\theta - 1} (1 - F_{pr}) \left[ R_g T \left( 1 - \exp \left( -\frac{N_A \epsilon_p}{R_g T} \right) \right) - N_A \epsilon_p \right],
\]

and chemical potential \( \mu \) of the confined fluid is

\[
\mu = \mu_0 + R_g T \left[ \ln \left( \frac{N_A \lambda^3}{v - b_p} \right) + \left( \frac{b_p}{v - b_p} \right) \right] - \frac{2a_p}{v} - F_{pr} N_A \epsilon_p \\
\left( 1 - (\theta + 1) \frac{b_p}{v} \right) \left( 1 - \frac{b_p}{v} \right)^{\theta - 1} (1 - F_{pr}) \left[ R_g T \left( 1 - \exp \left( -\frac{N_A \epsilon_p}{R_g T} \right) \right) - N_A \epsilon_p \right],
\]

where \( v \) is the molar volume, \( T \) is the temperature, \( R_g \) is the gas constant, \( N_A \) is the Avogadro number, \( \epsilon_p \) is the energy parameter of the fluid-wall interaction, \( \mu_0 \) is the reference chemical potential, \( \lambda \) is the de Broglie wavelength, and \( a_p \) and \( b_p \) are
the vdW EOS parameters modified by confinement. The geometric function $F_{pr}$ is defined as

$$F_{pr} = \frac{(r_p - \sigma/2)^2 - (r_p - \sigma/2 - \delta_p)^2}{(r_p - \sigma/2)^2},$$

(4.7)

where $r_p$ is the pore radius, $\sigma$ is the effective diameter of the fluid molecule, $\delta_p$ is the fluid-wall interaction well width. In molecular modeling of fluids in pores, there is always some arbitrariness in what should be considered as the diameter of the pore for calculating pore volume [92, 100]. When considering argon in silica pores represented by the integrated LJ potential, the difference in these diameters for both spherical [4] and cylindrical [10] pores is 0.175 nm, which is based on the zero of solid-fluid interaction potential. When the solid-fluid interaction potential is represented by a square well, this approach is not as applicable. We chose a slightly different offset in order to better compare with the internal volume considered in the simulations. For calculating densities in pores using the EOS, a nominal value of 0.3 nm was subtracted from the $r_p$ defined for pores in EOS calculation. The parameter $F_{pr}$ is the fraction of confined fluid molecules in the square well region of the interaction with the pore wall for a randomly distributed fluid, whose physical meaning is transparent from Figure 4.1. The parameter $\theta$ modulates the effect of density on the fraction of molecules in the square-well region and is defined as

$$\theta = \frac{r_p}{\delta_p + \sigma/2},$$

(4.8)

As the pore size increases, $\theta$ increases, which makes the fluid behave more like a randomly packed fluid with a smaller overall contribution coming from the fluid-wall interaction. The $\sigma$ is calculated to be consistent with the vdW model as

$$\sigma = \sqrt[3]{1.15798 \frac{b}{N_A}},$$

(4.9)
where $b$ is the volume parameter of the original vdW EOS. The modified vdW parameters $a_p$ and $b_p$ are taken as

$$a_p = a \left(1 - \frac{2}{5} \frac{\sigma}{r_p}\right), \quad (4.10)$$

where $a$ is the attraction parameter of the vdW EOS for bulk fluids, and

$$b_p = \frac{N_A}{\rho_{\text{max}}}, \quad (4.11)$$

where the $\rho_{\text{max}}$ is the molecular density of the packed fluid, which has a dependence on pore size. Travalloni et al. used the following empirical expression fit to data from Reference [187] of packing of hard spheres in cylindrical pores

$$\rho_{\text{max}} \sigma^3 = \frac{6}{\pi} \left(1 - c_1 - c_2 \exp \left(c_3 \left[\frac{1}{2} - \frac{r_p}{\sigma}\right]\right) + c_4 \exp \left(c_5 \left[\frac{1}{2} - \frac{r_p}{\sigma}\right]\right)\right), \quad (4.12)$$

where $c_1 = 0.393684$, $c_2 = 0.250942$, $c_3 = 0.620861$, $c_4 = 0.311601$, and $c_5 = 4.01377$. These set of equations comprise the TvdW EOS, which enables calculating fluid adsorption. In order to calculate adsorption properties at certain bulk conditions using this model, one must relate the properties of the bulk fluid to the confined fluid.

When conducting an adsorption calculation, firstly, the bulk pressure $P_{\text{bulk}}$, temperature $T$, pore radius $r_p$, and interaction parameters $a$, $b$, $\epsilon_p$, and $\delta_p$ are specified. The condition of adsorption equilibrium of the confined fluid requires equal chemical potentials of the adsorbed and bulk phases

$$\mu_{\text{ads}} = \mu_{\text{bulk}}. \quad (4.13)$$

From the solution of Equation (4.13), one can obtain the density of the adsorbed phase $\rho_{\text{ads}}$. However, it is possible to obtain multiple solutions, so care must be taken to determine the real solution. The conditions we modeled had 1 or 3 solutions.
depending on the pore size, temperature, $\epsilon_p$, and $\delta_p$ used. Here we follow the steps for calculating the adsorption equilibrium outlined in Reference [143].

The vdW parameters ($a$ and $b$) of the bulk fluid were calculated using the generalized formulas of the vdW EOS model from the critical temperature and critical volume, following the convention of Travalloni et al. [143, 175]. The relative pressures $p/p_0$ in the EOS calculations are relative to the bulk saturation vapor pressure calculated from the modified vdW EOS, which differ significantly from the experimental values as the vdW model itself is not very accurate. Initially, the fluid-wall interaction parameters $\epsilon_p$ and $\delta_p$ were fit to the isothermal adsorption data from our GCMC simulations at a single pore size and temperature. Parameter optimization was performed using the differential evolution method [188] with a least-squares objective function. We chose to use differential evolution because it has been found to be superior to other numerical optimization techniques [189, 190] and also showed better performance in our preliminary tests compared to some other optimization methods. The parameters obtained from fitting to a single adsorption isotherm at a single temperature did not translate well to other pore sizes and temperatures. So, instead we used the values of $\epsilon_p/k_B = 1700$ K and $\delta_p/\sigma = 0.35$, which showed reasonable agreement to adsorption isotherms for the point of capillary condensation across pore sizes and temperatures.

In order to calculate the isothermal elastic modulus of the confined fluid, we first derived the expression for the isothermal elastic modulus from the TvdW EOS from Equation (4.3)

\[
K_T \equiv -v \left( \frac{\partial P}{\partial v} \right)_T = \frac{v R_g T}{(v - b_p)^2} \\
+ \frac{2}{v^2} \left( -b_p (1 - F_{pr}) \theta \left[ R_g T \left( 1 - \exp \left( -\frac{N_A \epsilon_p}{R_g T} \right) \right) - N_A \epsilon_p \right] \left( 1 - \frac{b_p}{v} \right)^{\theta-1} - a_p \right) \\
+ \frac{b_p^2}{v^3} (1 - F_{pr}) (\theta - 1) \theta \left[ R_g T \left( 1 - \exp \left( -\frac{N_A \epsilon_p}{R_g T} \right) \right) - N_A \epsilon_p \right] \left( 1 - \frac{b_p}{v} \right)^{\theta-2}. \tag{4.14}
\]
Thus, for each bulk pressure, the molar volume obtained from the solution of Equation (4.13) can be used in Equation (4.14) to obtain the elastic modulus of the confined fluid.

The type of materials, solid and fluid, used during adsorption is related to their interaction strength. In order to understand what the behavior could be for the EOS model when modeling other materials with different interaction strengths, we varied the solid-fluid interaction parameters in the EOS calculations, as well as in our simulations for comparison. In the simulations, we varied $\epsilon_{sf}$ and proceeded with the same GCMC simulation methods mentioned above. Analogously, in the EOS calculations we varied $\epsilon_p$ and performed the calculations mentioned above to obtain the adsorption isotherms and modulus behaviors.

### 4.3 Results

Adsorption isotherms were obtained from GCMC simulations of argon confined in cylindrical silica nanopores of various pore diameters at 87.3 and 119.6 K. The TvdW EOS has two adjustable parameters, $\epsilon_p$ and $\delta_p$, related to the solid-fluid interaction strength and range respectively. Using the adsorption isotherms obtained from GCMC simulation at 119.6 K, we estimated the $\epsilon_p$ and $\delta_p$ by ensuring the point of capillary condensation – transition from vapor to liquid density – of the EOS approximately matches the simulations for the various pore sizes and temperatures. Adsorption isotherms and the corresponding EOS curves are plotted in Figure 4.2. The EOS shows a reasonable match to the saturated density for each of the pore sizes used in simulations. The density of the fluid prior to capillary condensation differs for the two methods. The simulations show a more gradual increase in fluid density compared to the EOS calculations. It is possible that this lower density of the TvdW model could be attributed to the relatively short-range approximated interaction via
square-well potential not accounting for longer range attractions compared to the Lennard-Jones fluid model used in simulations.

Using Equation (4.4), we calculated the isothermal elastic modulus $K_T$ of the confined argon from the molecular simulation data based on the fluctuation of the number of particles in the pore. Equation (4.14) was used to calculate the isothermal modulus of confined argon from TvdW EOS at the same relative pressures as the adsorption isotherms. The comparison of simulations and EOS calculations of the modulus are shown in Figure 4.3. Both methods show a similar trend on the filled pores: logarithmic-like dependence of the modulus on pressure. At both temperatures, the modulus predicted from the EOS calculations shows to be slightly higher than for the simulations, especially at larger pore sizes.

![Figure 4.2](image_url)  
**Figure 4.2** Adsorption isotherms at 119.6 (left) and 87.3 K (right) comparing GCMC simulation (circles) from Reference [10] and TvdW EOS calculation (lines) of fluid density $\rho$ as a function of relative pressure.
Figure 4.3  Isothermal modulus $K_T$ at 119.6 K (left) and 87.3 K (right) comparing GCMC simulation (circles) from Reference [10] and TvdW EOS calculation (lines) as a function of relative pressure.

In order to show how the pore size affects the elastic properties of the fluid, we plotted the isothermal modulus of the confined fluid at saturation pressure versus reciprocal pore size for both simulations and EOS calculations in Figure 4.4. We see that for the fluid saturated pores, there is a nearly linear increase of modulus with increase of reciprocal pore size for both simulations and EOS calculations. The calculations based on TvdW EOS show deviation from this linearity at pore sizes below ca. 3 nm. Figure 4.5 shows the fluid density corresponding to the moduli showed in Figure 4.4. Change in trend for the modulus correlates to the change in trend for the density predicted by TvdW EOS.
Figure 4.4  Isothermal elastic modulus $K_T$ of confined liquid argon at saturation as a function of the reciprocal of the confining pore size, predicted by molecular simulations from Reference [10] and TvdW EOS.

Figure 4.5  Density $\rho$ of confined liquid argon at saturation as a function of the reciprocal of the confining pore size, predicted by molecular simulations from Reference [10] and TvdW EOS.

Many fluids and solids have different affinities to one another: confinement could be solvophilic if solid-fluid interactions are strong, or solvophobic, if they are
weak. It is useful to know the behavior of the elastic properties for materials whose interactions differ from the combination presented here: silica-argon. In order to elucidate how other wall-fluid material combinations could behave, we varied the parameters associated with the strength of interaction in both the simulations and the EOS calculations. We conducted GCMC molecular simulations of argon in 4 nm pores with the $\epsilon_{SF}$ parameter (shown in Table 4.1) in the simulations multiplied by 1/2, 1, and 2 with respect to the value for argon-silica from Reference [99]. The plots of the isotherms obtained by varying $\epsilon_{SF}$ are shown in Figure 4.6. The figure shows that the point of capillary condensation is shifted to lower pressures when the interaction is higher. The density is also larger for higher interaction strength. The isothermal moduli obtained from simulations with varied $\epsilon_{SF}$ are shown in Figure 4.7. The simulations show that the stronger the interaction, the larger the elastic modulus of the fluid, and the lower the pressure of capillary condensation. But, at the lower temperatures, the higher interaction plot displays noisier behavior in elastic modulus, which is due to the poorer sampling of GCMC for very dense systems [133].

Similarly with the EOS model, we show how the variation of $\epsilon_p$ changes adsorption isotherm and the elastic properties. We multiplied the $\epsilon_p$ used before, $\epsilon_p/k_B = 1700$ K, by factors of 1/2, 2/3, 1, 3/2, and 2. In Figure 4.6, the adsorption isotherms reveal that a stronger wall-fluid interaction parameter $\epsilon_p$ leads to pore-filling at lower pressures, and higher densities at each pressure compared to cases of weak wall-fluid interactions. The higher $\epsilon_p$ also makes the fluid stiffer, which can be seen by the increased fluid elastic modulus at higher $\epsilon_p$ in Figure 4.7.
Figure 4.6  Adsorption isotherms at 119.6 (left) and 87.3 K (right) showing how varying the fluid-wall interaction parameters for the GCMC simulations ($\epsilon_{sf}$) and TvdW EOS ($\epsilon_p$) in the 4 nm pore affects adsorbed density. Lines are calculations from the EOS and points are from the GCMC simulations.

Figure 4.7  Isothermal modulus at 119.6 (left) and 87.3 K (right) of confined the fluid showing how varying the fluid-wall interaction parameters for the GCMC simulations ($\epsilon_{sf}$) and TvdW EOS ($\epsilon_p$) in the 4 nm pore affects elastic properties. Lines are calculations from EOS and points are from GCMC simulations.

We also investigated how the elastic properties at saturation depend on the strength of the wall-fluid interaction and how they behave with respect to pore size. One of the questions to answer is if the nearly linear relationship of the isothermal modulus with reciprocal pore size, as reported in recent works [4, 10], always holds. In Figure 4.8 we plotted the EOS calculations of the isothermal modulus of the confined fluid versus reciprocal pore size for $\epsilon_p/k_B$ values between 200 and 3700 K.
Although the simulations showed a nearly linear trend, the TvdW EOS calculations can show a non-monotonic increase with reciprocal pore size, depending on the wall-fluid interaction. We see that for moderate interaction strengths displays a linear behavior and the maximum modulus is at the smallest pore size. However, for higher interaction strengths, there is a maximum in the isothermal modulus that is in between the largest and smallest pore sizes. Also, for very low interaction strengths, there can be a minimum that occurs in the modulus, as is seen from the $\epsilon_p/k_B = 700$ K curve.

**Figure 4.8** Confined fluid isothermal modulus at 119.6 (left) and 87.3 K (right) as a function of reciprocal pore size with varying fluid-wall interaction strength as predicted via the TvdW EOS.

### 4.4 Discussion

GCMC molecular simulations can be used to calculate the elastic properties of confined fluids, but this technique has some difficulties. The sampling in the simulations can become very inefficient as the fluid becomes denser, which can require longer simulations and/or produce noisy data as shown in Figure 4.7. Moreover, the simulations become computationally expensive when the pore is larger than about 10 nm, making GCMC simulations to calculate elastic properties in these larger pores practically unfeasible. In contrast, calculations of elastic properties from an
EOS enables overcoming many of the disadvantages that are faced with molecular simulations.

The original van der Waals EOS is a simple two-parameter EOS that can describe the transition of fluids from gas to liquid, but it is not capable of quantitative predictions even for most bulk fluids. Therefore, the TvdW EOS for confined fluids, based on the van der Waals EOS is also limited to qualitative predictions. Importantly, the TvdW EOS is purely physics-based equation with the transparent of each of the terms. Predictions for derivative thermodynamic properties (such as compressibility) from an EOS are challenging even for bulk fluids [191, 192]. Despite multiple versions of equations of state for confined fluids, they have been rarely used for predicting derivative thermodynamic properties of confined fluids, and to our knowledge have never been used for calculation of isothermal compressibility (or elastic modulus). Thus the obtained qualitative agreement between the predictions of isothermal compressibility from the TvdW EOS and from the molecular simulations a significant step forward.

The degree to which an adsorbate wets the wall is influenced by the how the solid-fluid interaction differs from the fluid-fluid interaction, and this can change the qualitative nature of confinement effects [193]. In order to probe how other combinations of materials are predicted to behave, we modified the fluid-wall interaction strengths in both the simulations and EOS calculations. Both the resulting simulations and the EOS calculations showed the expected trends that higher fluid-wall interaction strengths leads to capillary condensation at lower pressures and a larger fluid elastic modulus. Lower interaction strengths lead to capillary condensation at higher pressures, or sometimes no condensation at the lowest interaction strengths.
The dependence of modulus of confined fluid on vapor pressure showed the same trend if calculated using the EOS as in GCMC simulations:

\[ K_T \propto \log(p/p_0). \]  (4.15)

The dependencies of moduli on the pore size, predicted by the EOS and GCMC, are also quite close, yet one can see the difference. In GCMC molecular simulations, there is an approximately linear trend seen of the isothermal elastic modulus increasing linearly with reciprocal pore size; however, the calculations from EOS showed that this dependence is non-linear for many cases and that the degree of linearity depends on the wall-fluid interaction strength. The EOS calculations showed that depending on the interaction strength \( \epsilon_p \), the modulus could display peaks, valleys, or nearly straight lines. For example, the plot of isothermal modulus in Figure 4.8 when \( \epsilon_p = 3700 \) K has a peak corresponding to about 2.5 nm pore size (0.4 nm\(^{-1}\) reciprocal pore size).

We find that peak occurrence corresponds to a change in the density behavior of the confined fluid. As the pore size decreases from the bulk case, the confined fluid molar volume starts decreasing until eventually (at about 2.5 nm for \( \epsilon_p = 3700 \) K curve) the expression \( v - b_p \) becomes nearly constant as the pore size decreases further. This changes the behavior of the first term in the expression for pressure in Equation (4.5), which begins to decrease as pore size decreases. This change in behavior is then amplified and reflected in the first term of the Equation (4.14), which comes from the derivative with respect to molar volume of the first term of pressure in Equation (4.5).

These behaviors of peaks and in the elastic modulus of confined fluid has yet to be seen for simulations in the whole range of pore sizes and wall-fluid interactions. The deviation from the linear trend in EOS starts around pore size of 2.5 nm. This is the pore size around which the GCMC method starts to fail to predict the modulus [10]. Moreover, the modulus predicted by GCMC can be rather noisy due to how
difficult proper sampling is as noted in Reference [10]. Therefore, it is possible that this trend exists, but cannot be appreciably measured in GCMC simulations.

Fluids confined in nanopores have inhomogeneous structure (see density profiles in Figure 7 of Dobrzanski et al. [10]). Therefore, many of the properties of confined fluids become inhomogeneous, including the compressibility or elastic moduli. Molecular simulation or classical density functional theory (cDFT) can provide information on local elastic moduli [74, 79, 194, 75]. However, here we do not consider the local moduli, and focus exclusively on moduli of the pore fluid as a whole, which can be predicted by an EOS or probed by acoustic experiments. It is worth noting that a recent work showed that the average of the local moduli of confined liquid argon calculated using cDFT matches the elastic moduli calculated from the GCMC simulations using Equation (4.4) [132].

Although the agreement between the predictions for the elastic modulus from molecular simulation and from EOS is only qualitative, it is still an important milestone. The lack of quantitative agreement is not unexpected; the primary reason for the deviation may be the difference of fluid-fluid and solid-fluid interaction potentials. Perhaps temperature and/or pore-size-dependent square-well parameters would also improve the quantitative matching [195]. While our simulations use LJ potentials, conventional for argon-argon and argon-silica interactions, the TvdW EOS is based on the a square-well potential. The next steps towards connecting molecular simulation with EOS would be the following: first, to compare the TvdW EOS with simulation data for the square-well fluid and second, to derive the equation for elastic modulus for more advanced EOS for confined fluids, such as those based on Peng-Robinson EOS [144, 176, 145, 177]. We expect that the latter could provide quantitative agreement with LJ fluid. However, we will leave those steps for subsequent research.
4.5 Conclusion

Fluids confined in nanoporous materials exhibit thermodynamic properties that differ from the same fluid in bulk. Recent experiments and molecular simulations suggested that isothermal compressibility is among these properties. The compressibility determines the elastic response of a fluid to mechanical impact, and in particular, the speed of acoustic wave propagation through it. Knowledge of the compressibility of confined fluids is needed for understanding the elastic wave propagation in fluid-saturated nanoporous media, such as hydrocarbon-bearing shales.

In our earlier works we calculated the elastic properties of confined fluids using molecular simulations. However, it required computationally expensive calculations for each system and pore size. Therefore, there is a demand for a more straightforward model that can predict the elastic properties of confined fluids as a function of the external pressure and confining pore size. Such models can be based on an equation of state (EOS) for a confined system. Here we explore a possibility for a generalized van der Waals EOS [143] to predict the compressibility of liquid argon confined in silica pores, and verified these predictions by grand canonical Monte Carlo simulations. Additionally, we vary the solid-fluid interaction parameters in both the EOS and in molecular simulations to represent solids other than silica and see how the elastic moduli (or compressibility) depend on the other properties of confining pores related to the interaction strength. We showed reasonable agreement between the isothermal compressibility calculated based on molecular simulations and based on the EOS. Although this agreement is only qualitative, to our knowledge it is the first work which predicts compressibility of confined fluid based on an EOS. Future research should focus on use of more advanced EOS, as well as experimental verification of the theoretical models.
5.1 Introduction

One of the ways to determine the amount of a particular fluid or solid in a porous material is to use an effective medium theory (EMT). One of the most popular theories, the Gassmann equation, is known to have some difficulties when being applied to analyze nanoporous samples [26, 50]. Such theories utilize the different elastic properties of the constituent materials and their relative proportions in the sample to determine the effective elastic properties, which determined the speed of sound through the sample. But, for nanoporous materials, the properties of both the solid and fluid can differ from the same materials in bulk. For fluids, confinement is known to modify the elastic properties [4, 10]. For the solid, the elastic properties are known to depend highly on the grains and thermal history of the sample [196]. Which currently makes determining the constituent contribution to the elastic modulus nearly impossible to measure experimentally. Therefore, there is need in understanding how exactly the constituents are modified for nanoporous systems to be able to apply an EMT.

Gor and Gurevich showed that by applying some reasonable assumptions, one can apply Gassman equation for nanoporous samples [26]. But, their method is still based on some unverifiable quantities (i.e. the elastic modulus of the solid part of the porous material, heat capacity ratio). Schappert and Pelster attempted a similar calculation with their own EMT [50]. They used the EMT to predict the elastic modulus of the confined fluid. Their result matched simulations fairly well, but they had to apply a constant smudge factor to account for the assumed weakening of the solid elastic modulus in the nanoporous material.
These studies have provided valuable input in terms of understanding the implications of using an EMT for nanoporous materials. But, they are not conclusive in their own regards, and definitely leave gaps in our understanding. Hence, the goal of this research is to fill in some of the gaps in our understanding, in particular, to use molecular simulation to model each of the components of the Gassmann equation and see how the elastic properties calculated compare to the Gassmann equation.

5.2 Methods
The components of a fluid-filled porous material and their relative proportion regulate the effective elastic moduli of the composite material following the Gassmann equation

\[ K = K_0 + \phi \frac{1 - K_0}{K_s} \left( 1 - \phi \right) K_f + \left( 1 - \phi \right) K_s - K_0 K_s^2, \]  

where \( K \) is the effective elastic modulus of the composite material, \( K_0 \) is the modulus of the empty porous sample, \( K_s \) is the modulus of the solid, \( K_f \) is the modulus of the fluid, and \( \phi \) is the porosity. This works for macroporous systems, but there is uncertainty in its application for nanoporous materials. Here we test this equation using molecular simulation.

Using molecular simulation, we can model the individual components of the composite fluid-saturated porous material and calculate the elastic moduli of the individual species, as well as of the composite. We can then combine the component elastic properties in the Gassmann equation to give us the elastic modulus of the composite. The bulk moduli of bulk solid, dry porous solid, and fluid saturated solid are calculated from the elastic constants obtained from the small perturbations of the sample dimensions during molecular dynamics (MD) simulations in \( NVT \) ensemble. The modulus of the fluid is obtained from GCMC simulations similarly to Chapter 2, except that in Chapter 2 an integrated potential was used to represent the solid, while here the solid is given with all-atom details.
5.2.1 Force-field

The force-field we used for the solid silica structure was from Sundararaman et al. [197] known as the SHIK-1 potential. We chose this force-field because of 2 main reasons:
1 – it has a simple two-body form, which should make calculations more efficient and
2 – it has shown to be quite accurate in calculating elastic properties compared to other similar potentials. The functional form of the SHIK-1 potential is given by

\[ U(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} + \frac{D_{ij}}{r_{ij}^{24}}, \]  

(5.2)

where \( r_{ij} \) is the distance between atoms of type \( i \) and \( j \), \( e \) is the elementary charge, and \( D_{ij} \) is a repulsive term included to avoid divergence of the potential at tiny distances \( r_{ij} \). The silica solid interaction parameters used in modeling solid-solid interactions is given in Table 5.1.

<table>
<thead>
<tr>
<th>Interaction i-j</th>
<th>( A_{ij} ) (eV)</th>
<th>( B_{ij} ) (Å(^{-1}))</th>
<th>( C_{ij} ) (eV Å(^6))</th>
<th>( D_{ij} ) (eV Å(^{24}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Si</td>
<td>2797.9</td>
<td>4.407</td>
<td>0.0</td>
<td>3423204</td>
</tr>
<tr>
<td>O-O</td>
<td>1120.5</td>
<td>2.893</td>
<td>26.1</td>
<td>16800</td>
</tr>
<tr>
<td>Si-O</td>
<td>23107.8</td>
<td>5.098</td>
<td>139.7</td>
<td>66.0</td>
</tr>
</tbody>
</table>

Note: The charge of the silicon atom is defined as \( q_{Si} = 1.7755e \).

Source: [197].

For the interactions involving argon, we used the Lennard-Jones (LJ) force-field from Vujic and Lyubartsev [198]. We chose this force-field because it was found to well model argon adsorption in silica zeolites and the force-field includes both interactions between argon and silicon atoms as well as between argon and oxygen atoms, which may be useful for modeling interactions between argon and the flexible silica framework. The table of LJ interaction parameters used is given in Table 5.2.
Lorentz-Berthelot combining rules were used to between the LJ interactions for the solid-fluid pairs given in Equation (5.3)

\[ \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad \epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}. \]  

(5.3)

<table>
<thead>
<tr>
<th>Atom Type</th>
<th>( \sigma ) (\AA)</th>
<th>( \epsilon/k_B ) (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>2.97</td>
<td>31.98</td>
<td>[198]</td>
</tr>
<tr>
<td>O</td>
<td>3.011</td>
<td>52.0</td>
<td>[198]</td>
</tr>
<tr>
<td>Ar</td>
<td>3.40</td>
<td>119.6</td>
<td>[98]</td>
</tr>
</tbody>
</table>

Note: \( \sigma \) is the LJ diameter, \( \epsilon \) is the LJ energy, and \( r_{cut} = 17 \) \AA{} is the cut-off distance where interactions were truncated.

### 5.2.2 Generating Initial Structures

To create the amorphous structure of solid silica, we first started by generating \( \beta \)-cristobalite cubic structure consisting 17496 atoms. To prepare the amorphous solid silica structure, we followed the melt-quench steps of Sundararaman et al. [197]. We set initial Gaussian velocity profiles for each system corresponding to 4000 K. The system was equilibrated at that temperature for 1 ns in \( NVT \) ensemble (constant number of atoms, volume, and temperature). As a check to ensure an amorphous structure, we examined the radial distribution functions (RDFs) between the types of atoms to ensure it was no longer crystalline and matched the high temperature RDFs of Sundararaman et al. [197]. The liquid-like structure was then quenched to 300 K at a cooling rate of about 1 K/ps in \( NPT \) ensemble (constant number of atoms, pressure, and temperature). The system was then equilibrated at 300 K for 100 ps in \( NPT \) ensemble, resulting in a nearly cubic solid about 6.2 \AA{} long on each
side resulting in a density of 2.38 g/cm$^3$. This structure were subsequently used to create the nanoporous silica samples.

![Image of silica structures](image)

**Figure 5.1** From left to right starting from top row: 12 Å thick slices of equilibrated 17496 atom solid non-porous silica structure, followed by the diameter $d = 20, 24, 30, 40,$ and $50$ Å spherical porous structures. Visuals made using Ovito software [11].

The pores were generated by replicating the solid systems creating 5 more copies of each and deleting all atoms within radial distances of 10, 12, 15, 20, and 25 Å from the centers of the silica structures. In order to ensure neutral charge, some additional atoms nearest to the center were deleted if necessary to balance the charge. Slices of 12 Å thickness through the center of the structures is shown in Figure 5.1.

After some atoms were deleted to create the porous structures, the remaining atoms had their velocities reassigned to a Gaussian profile at 87.3 K. The systems were then equilibrated in $NVT$ ensemble for 200 ps. The configurations of the equilibrated systems are shown in Figure 5.1.
Figure 5.2  From left to right starting from top row: 12 Å thick slices of equilibrated 17496 atom solid non-porous silica structure, followed by the diameter $d = 20, 24, 30, 40,$ and $50$ Å spherical porous structures filled with liquid argon fluid. Visuals made using Ovito software [11].

5.2.3 Calculating Elastic Constants

The elastic properties of the materials were calculated by first calculating the stresses of the system in its unperturbed state, then performing deformations by a factor of 1% of the dimensions of the system (i.e. $L_x$) and calculating the changes to the stresses, following the direct method for elastic constant calculation [199, 200]. The averages of the stresses were calculated from 100 samples over 200 ps of the $NVT$ simulation, following a 200 ps equilibration after deforming. Elastic constants following Voigt notation (i.e., $c_{xx}$) are obtained from the change in the pressure tensor $p_{xx1} - p_{xx0}$ in response to a deformation such as

$$c_{xx} = -\frac{(p_{xx1} - p_{xx0})L_{x0}}{L_{x1} - L_{x0}}.$$  \hspace{1cm} (5.4)
The equivalent elastic constants are averaged together. The bulk elastic modulus comes from \((c_{11} + 2c_{12})/3\) and the shear is \(c_{44}\).

The porous structures were then used to conduct GCMC simulation to model the adsorption of argon onto the silica structures. The simulations were conducted at the normal boiling point of argon, 87.3 K and gas reservoir pressure was set to 1 atm. We calculated the bulk isothermal elastic modulus of the fluid using from the fluctuation of the number of fluid particles \(N\) in the pore

\[
K_f = \frac{k_B T \langle N \rangle^2}{V \langle \delta N^2 \rangle}, \tag{5.5}
\]

where \(\langle \delta N^2 \rangle\) is the variance of \(N\), \(V\) is the pore volume, and \(k_B\) is the Boltzmann constant. Equation (5.5) can be applied to a small system provided the fluctuations are normally distributed [57, 4].

From the GCMC simulations, we obtained the average number of fluid particles in the pores \(\langle N \rangle\). For each of the porous structures, we inserted the corresponding number of fluid atoms into the pores from the average obtained in the GCMC simulations. The configurations were minimized to prevent overlaps, and then relaxed in \(NVT\) MD simulation for 200 ps. The plots 12 Å slices through the center of systems filled with argon fluid after \(NVT\) relaxation are shown in Figure 5.2. Then, similar to the elastic calculations performed on the empty porous samples, we calculated the elastic properties after small deformations of the filled pore samples using LAMMPS [140]. This gave us the effective modulus of the composite \(K\).

Then, from our simulations we had all of the parameters of the Gassmann Equation (5.1). The parameters obtained from our simulations allow us to compare the predictions of the effective modulus from simulation to the effective modulus obtained from the Gassmann analysis.
Figure 5.3 Bulk elastic modulus of the confined argon fluid in the all-atom pore (this work) and using an integrated potential to model the pore (data from Dobrzanski et al. [10]) calculated using Equation 5.5.

5.3 Results

We first show the calculation of the elastic modulus of the confined fluid using GCMC and compare it to the model used in Chapter 2 and in Dobrzanski et al. [10]. It is important relating the different models for the pores, all-atom representation versus integrated potential. We see a very good match in the calculated moduli, indicating that the current all-atom pore is appropriate for modeling the elastic properties of the confined argon.

We calculated the modulus of the non-porous solid silica to obtain $K_s = 49.04$. We then calculated the elastic properties of the amorphous silica porous structures with pore diameters of 24, 30, 40, and 50 Å. The graphics of these figures from a 12 Å slice through the center of the structure is shown in Figure 5.1. Before considering fluid-saturated media, it is worth looking at the properties of the porous solid itself, in particular its dependence on porosity.

Gibson and Ashby studied cellular solids and their elastic properties [201, 202]. They note that the most important feature of the cellular solids is the relative density
(reciprocal of porosity). They found that the dependence of the elastic properties on porosity is well described by the following relation

$$X_0 = X_s (1 - \phi)^2,$$  

(5.6)

where $X$ is an elastic property such as the Young’s, bulk, or shear modulus and $\phi$ is the porosity. The subscripts 0 and s represent the porous sample and nonporous solid from which the porous sample is derived respectively. Although the cellular solids they envisioned have a porosity typically above 0.7, it has shown to be useful for materials even with lower porosity, including nanoporous materials [203, 18]. Here, we calculate the elastic properties of our nanoporous silica systems and plotted them vs porosity in Figure 5.4. We compared our calculated elastic properties of the porous samples to the Gibson-Ashby prediction in Figure 5.4. The moduli obtained from simulations is in excellent agreement to the Gibson-Ashby Equation (5.6) for both the bulk and shear moduli for the porosities examined.

![Figure 5.4](image_url)

**Figure 5.4** Bulk and shear moduli vs porosity for the silica solid and porous systems obtained from MD simulations and comparison to the Gibson-Ashby formalism Equation (5.6).
Figure 5.5  Bulk modulus of the empty porous sample $K_0$ along with the effective moduli $K$ of the fluid-filled solid calculated from direct MD simulations of the filled pores and from the Gassmann Equation (5.1) calculations based on the constituent properties as a function of pore size and porosity. Both follow a similar trend and show that the elastic modulus of the porous silica is increased by the confined argon.

We calculated the elastic properties of the solid parts in Figure 5.5. We see the solid sample (corresponding to 0 diameter pore size) has a modulus of 49.04 GPa. The empty pore moduli $K_0$ decrease negligibly for the 20 Å diameter pore, but then trends much lower for the larger pore sizes. The results of the Gassmann analysis and MD simulations of the composite are also shown. The empty pore moduli $K_0$ is slightly lower compared to the moduli of the filled composite fluid-filled porous structures calculated by both methods. The moduli of the Gassmann analysis is shown to be lower than the moduli from the MD simulations.

We calculated the change of the modulus of the porous structure due to the fluid adsorption in Figure 5.6. We see the first point at 0 is the same, due to not being any pore nor fluid. The 20 Å diameter pore shows to be nearly zero for both methods, Gassmann equation and MD simulation. But at larger pore sizes, the discrepancy can be seen between the two methods. The Gassman equation method shows a
Figure 5.6  The difference of the elastic modulus of the composite sample and the modulus of the empty porous sample calculated by Gassmann equation and MD simulation.

moderately increasing difference of $K - K_0$, whereas MD simulation shows a much more scattered increasing behavior. This can mainly be explained by the fluid.

In order to understand the discrepancy of the moduli calculated by MD and Gassmann equation, we also rearranged the Gassmann equation to solve for the fluid modulus $K_f$ and used the composite moduli $K$ from our MD simulation as an input to the rearranged Gassmann equation. We plot the modulus of the fluid calculated from the GCMC simulations and the rearranged Gassmann equation in Figure 5.7. We can see that GCMC predicts that the fluid modulus is very modestly lowered as the pore size increases, whereas for the Gassmann calculation, the moduli behaves much more erratically and no trend can be extracted.

5.4 Discussion

We find that the Gassmann equation, when supplied the constituent property values obtained from molecular simulations, predicts fairly well the effective elastic modulus of the composite nanoporous sample as from simulation, although there are some shortcomings of the comparison. In particular, the elastic properties of the
nanoconfined fluid calculated by GCMC can have somewhat scattered, noisy data especially for smaller pore sizes below about $d = 25$ Å [10]. This makes a quantitative comparison between simulation and Gassmann difficult.

It is interesting to compare our calculated elastic properties to some experimental values for a similar system. Indeed, such a comparison would not be an ideal. Reason being, the solid silica and nanoporous systems we model are constructed with virtually no defects or imperfections compared to real systems. Additionally, the pore is a perfect sphere created artificially without any necks or connections to other pores. So including a nearly perfect spherical pore would also not be a true comparison to experiment, and would likely further overestimate the elastic properties obtained from simulation. Nevertheless, such a comparison can show a qualitative behavior and inform future studies.

For EMT analysis, quartz glass is often used as a proxy for the solid part of Vycor glass, which is a silica nanoporous material [3, 50]. The experimental bulk and shear moduli of base Vycor (essentially quartz) are 35.65 and 27.9 GPa respectively [204, 3, 50]. Comparing to the respective moduli obtained from simulation, 49.04 and
31.70 GPa, we indeed see that the simulations predict higher bulk and shear moduli for the silica solid. However, quartz is a crystalline material and it is uncertain how the crystallinity and other properties are modified from the physical and chemical process of creating the analogous nanoporous material. The analogous material is therefore not squarely analogous. It is possible that the modulus of the solid part of Vycor glass is also lower compared to quartz, as has been shown elsewhere [26, 50]. So, our simulations can still be much more reasonable than the comparison to quartz glass shows. Furthermore, from the comparison of simulation and experiment, there is potential to include a factor in the Gassmann analysis related to the imperfections and defects to better predict the experimental values of the elastic properties from trends observed in simulations.

We calculated the elastic modulus of the confined fluid from all-atom GCMC simulation and ensured that it matched previous modelling techniques in figure 5.3, which showed that our new method was consistent with previous simulations. We also used the Gassmann equation to extract the elastic modulus of the nanoconfined fluid $K_f$ from constituent properties of the solid $K_s$, empty pore $K_0$, and filled pore $K$ obtained from the MD simulation. We compared this Gassmann prediction to the modulus calculated from GCMC in Figure 5.7. We find that the elastic properties of the nanoconfined argon are significantly increased compared to the experimental bulk value of argon at these conditions, 0.47 GPa [6], although the fluid modulus calculated through Gassmann analysis shows a very noisy behavior. This can explain the relatively large discrepancy in the Figure 5.6. The fluid moduli play a much greater role in the change in the elastic modulus of filling $K - K_0$ calculated in MD as opposed calculated using the Gassmann equation. Gassmann equation predicts that the fluid modulus has a smaller effect on increasing the effective modulus of the system, whereas the MD calculation on the fluid filled sample shows that the fluid has a much more pronounced effect. The elastic modulus of argon fluid is relatively
small compared to a silica solid. This results in a modest increase in the $K - K_0$. If one were to use a stiffer fluid, such as mercury, we might expect a more significant effect. Mercury is also useful to model since it is often used in mercury porosimetry experiments on porous materials, thus giving potential useful insights into application of the technique to nanoporous materials. Such tasks will be reserved for future works.

Also, investigating further the behavior of the elastic modulus of the empty porous sample $K_0$ in Figure 5.5, we can see a relatively large dip at a pore diameter of 24 Å. This is not necessarily a true drop, but can be explained with the randomness involved in creating the pore. After equilibration, some pores had a noticeably less spherical shape compared to the others. This can be seen in the slices of pores in Figure 5.1. We can see a rather large indents in the left sides of the pores, allowing fluid to intrude into the solid. Such imperfections is likely to cause such a decrease in the modulus of the porous structure, and can be an explanation of the dramatic peak in the difference plot of $K - K_0$ in Figure 5.6 at 24 Å. Averaging the elastic constants over 3 to 5 replicate simulations of these systems for each of the pore sizes would be able to smooth out the noise, but such a task would be reserved for future works.

5.5 Conclusions

We performed molecular simulations to develop the constituent properties needed for Gassmann analysis. We calculated the elastic moduli of the porous silica samples and compared them to a Gibson-Ashby relation. We find that both the elastic bulk and shear moduli can be well describe by Gibson-Ashby relations. We tested the Gassmann analysis applicability in predicting the elastic modulus of the fluid-filled nanoporous system to the calculation obtained from molecular simulation. The effective elastic modulus obtained from molecular simulation was slightly higher than that obtained from the Gassmann analysis. We find that the difference in
the calculated elastic moduli of fluid-filled samples to the empty porous sample was smaller for the Gassmann analysis. Both methods predicted nearly no increase in elastic moduli of the empty porous structure until the pore size was greater than 20 Å in diameter. The Gassmann analysis showed a relatively steady increase in effective elastic modulus as the pore diameter increased, whereas the simulations showed a noisier and larger increase with pore size. The difference in behavior can be attributed to the role of the fluid modulus in the calculations: the Gassmann analysis shows that the fluid effect on the effective modulus of the fluid-filled sample is smaller than the direct calculation via molecular simulation.

We have shown that the Gassmann equation can be used to qualitatively predict the elastic properties of nanoporous systems. For a more quantitative conclusion, we would need to perform additional and longer simulations. The modulus calculated by Gassmann thus far have shown to be slightly below what simulations predict, but follow the trends. Future works will help develop this further, in particular, smoothing the noisy data and using stiffer fluids to enhance the role of the fluid in the Gassmann analysis.
This dissertation has tackled the understanding of the elastic properties of confined fluids from multiple methods: grand canonical Monte Carlo simulation, molecular dynamics simulation, and equation of state models for confined fluids. Through the strategic implementations of these techniques, a robust understanding of the various confinement effects and modeling challenges have been addressed.

In Chapter 1, we outlined the state of the research on the topic of ultrasonic measurements of elastic properties of confined fluids. In particular, there is very little experimental data available on the confined fluid elastic properties. This is due to the small number of experimental set-ups that can accurately make such measurements. Beyond the experiments, there have been several studies based in theory which have calculated the changes of the elastic properties of the fluid due to confinement in nanoporous materials. The modeling literature span over Monte Carlo methods, DFT, and MD. We gave a brief overview of these studies, and outlined some potential research paths, which were addressed in later chapters.

In Chapter 2, we addressed the issue of how the elastic properties of the confined fluid depend on the shape of the pore. We use GCMC molecular simulation to model the fluid adsorption in the pores and uses two different techniques to calculate the compressibility of the confined fluid: 1 – statistical mechanics based on the fluctuation of the number of particles in the pore; and 2 – macroscopic thermodynamic relations. We showed that the two pore shapes, sphere and cylinder, produce similar relationships of the compressibility with pressure and with pore size. The statistical mechanical relations used to calculate compressibility require that the fluctuations are normally distributed, which, as we have shown, may not always be the case.
for modeling fluids in nanoporous materials, especially for GCMC simulations on the smallest pores at low temperatures. However, the macroscopic technique is not restricted by the type of distribution and we showed that it matches well to the statistical mechanics calculation route. We showed that the elastic modulus of the fluid is significantly higher when it is confined in nanopores compared to in bulk and the is true for both geometries, but slightly greater for the spherical pores. Also, the modulus of the fluid had a logarithmic increase with respect to pressure. But, there are challenges in modeling the adsorption in the smallest nanopores, where the GCMC simulations fail to produce normal distributions of the fluctuation of particles. These results leave various uncertainties that could be addressed in later works, such as how to improve sampling in the smallest nanopores (under 2 nm). Improvements in sampling can also help for other systems such as modeling more complex fluids such as hydrocarbon chain molecules and water. Such a task would be even more challenging for GCMC simulations due to the improbability of insertions in dense fluids. Future research could employ some enhanced sampling techniques such as continuous fractional component Monte Carlo [205, 206]. These techniques can improve sampling configurational space by allowing for partial insertions, whereas classical GCMC simulations involve inserting the entire molecule into the fluid. Such techniques have the potential to improve our understanding of the elastic properties of complex fluids in confinement.

In Chapter 3, we shifted our focus from modeling systems that are typically only tested in laboratory settings (argon confined in silica), and modeled a system more relevant for geophysics (supercritical methane confined in carbon nanopores). Methane confined in coals and shales is typically in the supercritical state. However, no experimental data has shown how confinement effects the elastic properties of supercritical methane. Therefore, we modeled supercritical methane confined in carbon nanopores. Because of the novelty of such a task, we used two different
techniques to reinforce the validity of the results. We performed GCMC and MD simulations to calculate the elastic modulus of the confined supercritical methane. Both methods were consistent with each other. We found the effects on the elastic modulus of the supercritical methane resulted in: 1 – a higher modulus compared to bulk; 2 – a monotonic increase of the modulus with increased pressure; and 3 – a nearly linear dependence of the modulus with reciprocal pore size, which becomes less linear at pressures higher than about 10 MPa. We also compared the confinement effects on supercritical fluid to subcritical fluid and found the effects on the elastic modulus to be much greater on the supercritical fluids. These results can be useful for understanding wave propagation in coals and shales. Hopefully, this will stimulate some experimental investigations on the elastic properties of supercritical methane in confinement, which could have significant impact on geological research.

In Chapter 4, we investigated whether or not the confinement effects on fluid compressibility can be seen from an EOS. We used the EOS of Travalloni et al., which takes the form similar to the van der Waals EOS and has only two fitting parameters related to the solid-fluid interaction [143]. We derived the analytical expression for the elastic modulus and showed that this relatively simple equation can be used to predict fairly well the elastic modulus of the confined fluid across various pore sizes and temperatures using the same two fitting parameters. Of course, these results were only qualitative, which can be largely attributed to the simplicity of the EOS. Moreover, the EOS is based on approximating the interactions between the particles and with the pore-wall using square-well potential, whereas the simulations we used had Lennard-Jones potential interactions. In the future, a more fair comparison with simulations would be using the same interaction potentials, such as conducting molecular simulations using the square-well interaction potentials. Such comparisons would be beneficial for connecting molecular simulations to EOS models, which could potentially result in a large saving of computational time due to how
computationally expensive simulations are. Another improvement would be utilizing a more advanced EOS, such as an EOS based on the Peng-Robinson equation [144]. Such improvements may lead to better elastic property calculations due to it being more accurate for modeling most fluids. Moreover, a Peng-Robinson formulation allows for better modeling derivative properties with respect to temperature, such as the heat capacity and thermal expansion coefficient, which are not available within the van der Waals EOS formulation. One of the big questions related to nanoporous materials that has not been answered is how the heat capacity ratio is affected by confinement. This ratio is needed to connect isothermal compressibility typically obtained from molecular simulations to the adiabatic compressibility obtained from ultrasonic experiments.

In Chapter 5, we examined how an effective medium theory known as the Gassmann equation can be applied to nanoporous systems from a molecular simulations perspective. The Gassmann equation relates the effective elastic properties of the fluid-saturated porous medium to the elastic properties of its constituents: the nonporous solid part, the empty porous solid, and the fluid, in their relative proportions. We find that the predictions of the elastic modulus of the fluid-saturated sample obtained from the molecular simulations matches fairly well to the Gassmann equation predictions, however the values obtained from the Gassmann equation are slightly lower. However, more and longer simulations would be needed to provide results which are less noisy and to have error-bars in the estimates. We also found that the increase of the modulus of the porous solid is only slightly increased when it is saturated with argon. But, argon has a much lower modulus compared to silica. This leaves the question on the role of the fluid in the Gassmann analysis, in particular, how stiffer fluids would effect the overall modulus of the composite. Future works could look deeper into the role of the fluid in the Gassmann analysis, in particular, fluids such as mercury have a much larger elastic moduli than argon.
The shear modulus of fluids is typically assumed to be zero, however this has not been proven for fluids confined in nanopores. It is important to understand the shear modulus because many effective medium theories utilize this assumption. We believe modeling stiffer fluids such as mercury can produce more significant influence on the porous solid, and would also be relevant for experimental techniques on nanoporous materials such as mercury porosimetry. Moreover, modeling more solid and fluid combinations in parallel to experimental investigations can give more results for comparisons, which would lead to better models and better effective medium theories by understanding quantitatively the role each constituent plays in nanoporous systems.
REFERENCES


[204] Data sheet for Base Vycor 7913; Corning, Inc., (Corning, NY).