Density and Phase State of a Confined Nonpolar Fluid

Daniel F. Kienle and Tonya L. Kuhl[*]
Department of Chemical Engineering and Materials Science, University of California Davis, Davis, California 95616, USA

(Received 5 April 2016; published 14 July 2016)

Measurements of the mean refractive index of a spherelike nonpolar fluid, octamethytetracylclosiloxane (OMCTS), confined between mica sheets, demonstrate direct and conclusive experimental evidence of the absence of a first-order liquid-to-solid phase transition in the fluid when confined, which has been suggested to occur from previous experimental and simulation results. The results also show that the density remains constant throughout confinement, and that the fluid is incompressible. This, along with the observation of very large increases (many orders of magnitude) in viscosity during confinement from the literature, demonstrate that the molecular motion is limited by the confining wall and not the molecular packing. In addition, the recently developed refractive index profile correction method, which enables the structural perturbation inherent at a solid-liquid interface and that of a liquid in confinement to be determined independently, was used to show that there was no measurable excess or depleted mass of OMCTS near the mica surface in bulk films or confined films of only two molecular layers.

DOI: 10.1103/PhysRevLett.117.036101

A great amount of work has been devoted to developing an understanding of the behavior of confined fluids, which has proven itself to be a daunting task. In the literature, considerable disagreement and conflicting results still exist regarding this subject. Although it is generally agreed upon that a nonpolar fluid becomes more solidlike when confined to a thickness below 4–6 molecular layers [1–8], the molecular interpretation of this phase transition is an area of contention. Two competing theories based on differing experimental results dominate the literature. The experimental observation of first-order confinement-induced freezing is based on the onset of a static friction and a sudden, many-order-of-magnitude increase in viscosity when the fluid is confined to a particular separation distance [3–5,7,9,10]. Other experiments observed viscoelasticity in the fluid prior to the onset of a critical shear stress [1,11,12] and a continuous transition in the viscosity [2,13–18], leading to the conclusion that the fluid was approaching a glass transition. It has been suggested that the experimental results supporting either of these theories are fundamentally in agreement and that the conflicting models arise from differences in resolution and interpretation of the results [19]. Contamination from nanoparticles has also been suggested as a cause of discrepancies in the data [20–23], while some research indicates that the role of nanoparticles is unimportant [7,10]. This is perhaps why the subject remains controversial despite decades of research.

With a small system volume, Lennard-Jones spherelike molecular interactions, and near perfectly flat surfaces, the confinement of non-polar octamethytetracyclosiloxane (OMCTS) between molecularly smooth surfaces seems ideal for computer simulations, and countless studies have been performed. The majority of detailed molecular dynamics simulations have observed crystallization of nonpolar molecular fluids under increasing confinement to 4–6 molecular layers; these are summarized in a recent review [24]. However, there are several simulations which indicate that no phase transition occurs until a separation of only two molecular layers, if at all [25–28]. Consequently, simulation studies have not yet conclusively resolved the molecular behavior of confined fluids.

Experimentally, these conflicting theories are both based on shear force measurement between the confining surfaces, as opposed to measurements of the fluid structure properties directly, and a conclusive result may only come with direct mesurements of the fluid structure. Up to this point, no experimental technique has been capable of directly observing any first-order phase transition by structural measurements. The surface force apparatus (SFA) has been previously used to measure the fluid density (via refractive index) of cyclohexane, but the results are conflicting and difficult to interpret [21,29]. In one case the mica surfaces were likely contaminated with platinum particles [29]; when repeated with particle-free surfaces, the results showed unusual time-dependent onset of force oscillations with transitions starting as far out as 120 Å (30 molecular layers), a phenomenon that had not been observed in prior literature and has not been repeated since. X-ray reflectivity has also been used to determine the fluid density distribution in confinement. The results directly confirm the layered structure of the confined fluids, but could not indicate or refute a first-order phase transition [30,31].

Indeed, the structural and dynamic behavior of a molecularly thin film during confinement, and the effects of compression and tension on the structure are not well understood; this is primarily due to the inherent difficulty of directly measuring the fluid properties at such extremely small length scales. Using the SFA and the recently developed refractive index profile correction (RIPC) analysis [32], we were able to determine the effects of confinement on the refractive index and, thereby, the density of OMCTS. RIPC analysis sets this experiment apart from previous attempts to measure the refractive index of confined fluids because the method corrects the systematic error that is relevant in almost every experiment and allows for independent determination of the near-surface properties of bulk and nanoconfined fluids, which have been convoluted in previous measurements of this type [21,29]. As a result, we can simultaneously quantify any surface excess or depleted mass of OMCTS at a mica surface, any density changes (via refractive index) that occur when the fluid is confined to a nanoslit, and the corresponding interaction forces during confinement. Thus, we can observe changes in density that would occur with a phase transition.

The muscovite mica substrates used in this experiment were cleaved to sheets with uniform thicknesses of 3–7 μm and cut with surgical scissors to avoid the possible influence of platinum particle contamination (which has been suggested to occur when the mica is cut with a superheated platinum wire) [33,34]. The mica was then silvered on the backside and glued onto cylindrical BaLF4 glass disks using refractive-index-matched EPON 1002F epoxy resin, resulting in cylinder radii ranging from 2 to 5 cm. The surfaces were rinsed with water and blown dry with nitrogen to remove any mica particles from the substrates. The disks were then mounted in a cross-cylinder orientation in a sealed SFA over P_2O_5. The SFA was purged with dry nitrogen and left for 30 min to allow the P_2O_5 to further dry the surfaces before the mica-mica contact measurement was taken. Then, without changing the position of the samples or any optics, the SFA was opened and several drops of 99.6%-pure OMCTS (used as received from Sarachem Labs and stored under dry nitrogen with desiccant) were placed between the surfaces. The SFA was again sealed and dried as before.

White light was passed normally through the samples to generate optical interference patterns with intensity peaks called fringes of equal chromatic order (FECO) [35]. Spectral images included the FECO and krypton calibration lines (the FECO and calibration lines were on separate portions of the spectral image) such that every data point could be calibrated independently. This is extremely important for sensitive refractive index measurements where minute thermal drift in the spectrometer can cause unphysical observations in the measured refractive index, especially at low separation distances. The FECO wavelengths were used with the multilayer matrix method [36] to determine uncorrected mica and OMCTS film properties. Using the recently developed RIPC method [32], the systematic error that exists in the refractive index-distance profile was corrected to determine accurate substrate properties and to quantify the optical thickness of any film or bulk density variations at the OMCTS-mica interface prior to, or induced by, confinement.

Force and refractive index-distance profiles were measured by driving the lower surface, which was mounted on a spring ($K = 260$ N/m) at constant step sizes from separation distances of around 3500 Å to contact, and determining the spring deflection, which was used to determine the force based on Hook's law. In total, 36 force-distance profiles from six independent sample sets were measured. Refractive index profiles and RIPC analysis were determined for 19 runs from three sample sets which were free of optical artifacts that can cause large error in refractive index and small error in separation distance (e.g., external interference from glue layer, particles in camera or spectrometer, large background, etc.). For each sample set, one profile was measured using a combination of mechanical drift and piezoelectric displacement of the top surface to drive the surfaces into contact, without any motor actuation. Prior to experiencing any forces, the samples approached one another at nearly constant speeds of between 2 and 3 Å/s, depending on the sample. Force data were also calculated for these runs based on the assumption that the rate of drift remained constant after the onset of the repulsive solvation forces.

The average force and position acquired for each layer transition across all 36 force runs is shown in Fig. 1(a). The results follow a similar trend and fall within the expected range of forces from the literature [10]. There was no consistent difference in the location or force of the layer transitions between the motor-driven experiments and the mechanical-drift-driven experiments; thus, hydrodynamic effects seem to have had little impact on the forces measured, and the rate of approach did not affect the measured refractive index or calculated density of the fluid.

Importantly, no distinct boundary layer or change in OMCTS density was observed at the mica surface or when confined. At all separations, the change in optical thickness of the fluid relative to bulk was ±0.1 Å, corresponding to an OMCTS surface excess of ± 0.2 mg/m^2 (calculated from the Lorentz-Lorenz equation). The uncertainty given is the standard deviation of all runs, and is acceptable for the RIPC method with random error [32]. This result demonstrates that any surface excess or depletion of OMCTS density near the surface is below detection.

The density change corresponding to the transition of a fluid of Lennard-Jones spheres in a random close-packed configuration to a crystal of Lennard-Jones spheres in hexagonal close pack (i.e. a first-order phase transition) is well above resolution at the separation distance where a phase transition has been suggested to occur (30–60 Å). At these separation distances, the experimental setup had a refractive index resolution of better than ±0.012, which translates to an OMCTS density resolution of $\pm 0.03\rho_{\mathrm{bulk}}$; thus, a first-order phase transition which will increase density by $\sim 0.14\rho_{\mathrm{bulk}}$ would be easily detected. (The refractive index resolution of ±0.012 was calculated using the method for determining random error based on uncertainty in peak fitting parameters as described in Ref. [32]. The value is dependent on the sample properties and FECO image quality, and we have reported the highest error between all samples used in this study).

Figure 1(b) shows the mean refractive index and corresponding density-distance profiles for 19 runs from three samples. As can be seen, the refractive index and density of the fluid remains within resolution of the bulk liquid value throughout confinement, and never approaches the estimated or measured density of crystalline OMCTS [38]. The simplicity of these results is actually quite interesting. While the body of experimental work surrounding confined liquids has at least agreed that there is some type of confinement-induced transition to solidlike behavior, the refractive index reported here demonstrates that there is in fact no measurable density change of the confined liquid at all. That is not to say that the film is behaving as a bulk liquid, but it does not show any discrete or continuous average density changes that would be indicative of a phase transition.

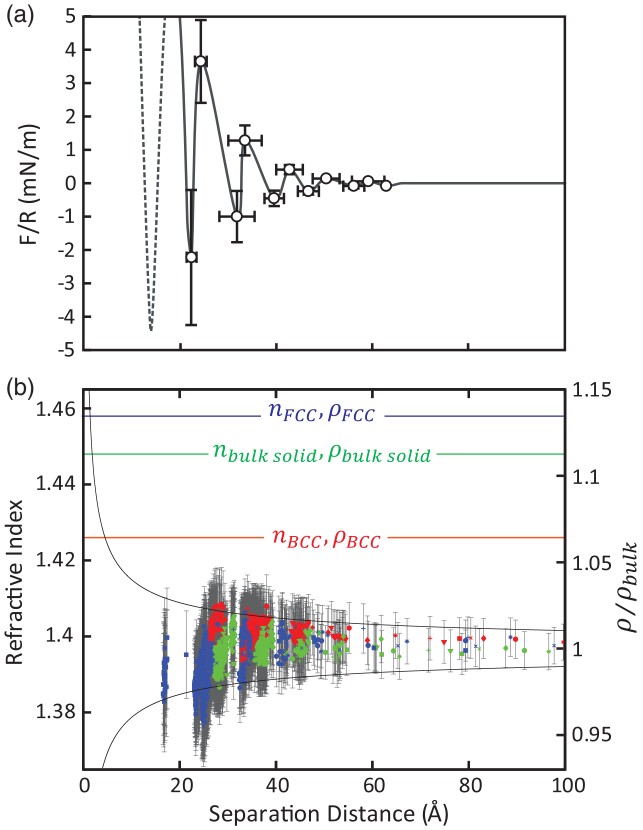

FIG. 1. (a) Average force and separation distance where layer transitions occurred for all measured force runs. The black line is an illustration of what the full force profile would look like based on the measured forces, and the dashed line is an extrapolation not based on any force measurements. (b) The mean refractive index and normalized density (calculated from the Lorentz-Lorenz equation) of the OMCTS film during confinement is plotted against the separation distance between the surfaces. The different colors represent different samples and the different symbols represent different runs. The error bars are system dependent and were determine using Monte-Carlo-type error analysis as described previously [37]. The two black lines represent a confidence interval about the bulk properties, where data between these lines show no measureable difference from the bulk fluid properties. The red, blue, and green horizontal lines are the expected densities and refractive indices of a crystal of Lennard-Jones spheres with body-center-cubic (bcc) and face-center-cubic (fcc) lattice structures and the density of crystalline OMCTS, respectively [38].

Although these results appear to be incongruent with many previous experiments, recall that the evidence indicating a phase change is based on force measurements alone, and that these are the first reliable measurements of OMCTS force and density profiles. In the following paragraphs, we will discuss the implication of these results with regard to previous experimental findings.

Considering only normal force measurements, the absence of solidification in a confined liquid should not be surprising. The average layer transition step size measured was 8.3 ± 1 Å, which is consistent with previous findings [2,4,10,14,39]. This transition step size is consistently larger than expected for the removal of a single layer of a close-packed crystalline solid. An oscillatory force profile is expected for a fluid with density fluctuations near a surface based on simple qualitative description using chemical potential (contact value theorem) or van der Waals interactions [40], although these do not quantitatively agree with the observed lack of density change during the compression. The consistent observation that only single molecular layers may be squeezed out during a layer transition, and that the squeeze-out front propagates in a fluidlike manner, is likewise expected for a layered fluid [41]. This would be very surprising behavior for any type of solid that should undergo a brittle or ductile failure. As OMCTS films behave elastically in that the force-distance curve between each step is reversible, a brittle failure would be expected if the film were solid.

An interesting property of these fluids is the high compressibility of the film prior to undergoing each layer transition. The average compression for all steps for our system is 1.4 ± 0.8 Å, which would correspond to a resolvable density change if the fluid were compressible and the mass in the cavity did not change with the decreasing volume. This effect would manifest as an increase in the refractive index between each step that exceeds the measured refractive indices beyond error bars for almost every data point in Fig. 1(b). Thus, the film is actually incompressible and some mass must be redistributed laterally during the compression between steps.

When reduced to 2–3 molecular layers, there does appear to be systematic deviation from the bulk refractive index, decreasing as compression is increased. Although these trends are only just resolvable and should not be considered quantitatively, the trend is consistently observed. At such confinement, molecular motion is extremely hindered, and the squeeze-out mechanism is likely different than for thicker films. A possible explanation of the observed decrease in refractive index is that the layers dilate as the molecules interpenetrate and spread to move past one another. It may be that such an effect is only observed at this level of confinement because a layer transition would occur before this effect could be observed in thicker films.

In a bulk liquid, an increase in the viscosity would be expected to coincide with an increase in density. Interpretation of the increased viscosity previously observed in confined fluids is less clear. Our density measurements demonstrate that the density of OMCTS does not change under conditions where the viscosity has been observed to increase by many orders of magnitude. Several recent simulation experiments have demonstrated that an increase in the viscosity and a decrease in the diffusivity of a fluid can occur during confinement without corresponding density changes or phase transitions [25–27]. Given that the density and temperature are constant, the reduction in diffusivity can be considered as solely a result of confinement. As the number of molecular layers decreases and the system becomes more two-dimensional, the configurational entropy and diffusivity of the film decrease while the viscosity increases. Although the experimental observation of a viscosity change that is not accompanied by a temperature or density change is very unusual, the direct relationship between entropy and the kinetic properties of a bulk or confined fluid is not a new concept [42–44]. Thus, it is reasonable to conclude that the viscosity increase that accompanies confinement is a result of decreasing entropy and not molecular packing, and that confined OMCTS is approaching a jammed state.

As a confined fluid that may not be in equilibrium, the possible structure of the film will be complexly related to the structures and interactions of both the fluid and the mica surface. A large array of nonbulklike phase behaviors have been observed and previously reviewed for various confined systems [45]. The measurements presented here may not be able to distinguish between a liquid and possible phase states that exist only in confined films. For example, an amorphous glass or a highly defective crystalline solid may have densities that do not deviate far from the bulk liquid. Likewise, heterogeneous states such as local freezing of the surface or central layers [45], which have been reported from experimental observations, or crystal bridging [46,47], which has been predicted by molecular dynamics simulation of confined dodecane, may also be relatively close to bulk liquid density. The simulations observing crystal bridging support full transition to a tetratic crystalline phase at separation distances below six molecular layers and, in this way, contrast with our measurements. Nonetheless, the results illustrate that nonequilibrium phase behavior exclusive to confined films may be expected for mica-confined OMCTS, and such states cannot be ruled out based on our measurements alone.

In summary, direct measurements of the refractive index of confined OMCTS have conclusively demonstrated that there is no confinement-induced first-order phase transition in OMCTS. The film is also found to be incompressible, where small changes in the confined volume during compression must lead to lateral displacement of the molecules in the film as evidenced by a constant density during the compression between steps. These results are most consistent with the conclusion that the fluid is approaching a glass transition, where confinement is restricting motion as opposed to being the result of increased molecular packing as is the case for supercooled fluids. Whether or not it is appropriate to consider this system to be supercooled is less clear. Previous experimental observations—which suggested that a crystalline state can be achieved at the same temperature under specific experimental circumstances (circumstances possibly related to better control over surface orientation or chemistry, approach rate, or solvent purity)—would suggest that the confined fluid measured here is in a metastable state.

Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund for support of this research.

---

[*] Corresponding author.
tlkuhl@ucdavis.edu

[1] G. Carson, H. W. Hu, and S. Granick, Molecular tribology of fluid lubrication: Shear thinning, Tribol. Trans. **35**, 405 (1992).

[2] A. L. Demirel and S. Granick, Glasslike Transition of a Confined Simple Fluid, Phys. Rev. Lett. **77**, 2261 (1996).

[3] M. L. Gee, P. M. Mcguiggan, J. N. Israelachvili, and A. M. Homola, Liquid to solid-like transitions of molecularly thin-films under shear, J. Chem. Phys. **93**, 1895 (1990).

[4] J. Klein and E. Kumacheva, Confinement-induced phase-transitions in simple liquids, Science **269**, 816 (1995).

[5] J. Klein and E. Kumacheva, Simple liquids confined to molecularly thin layers. I. Confinement-induced liquid-to-solid phase transitions, J. Chem. Phys. **108**, 6996 (1998).

[6] E. Kumacheva and J. Klein, Simple liquids confined to molecularly thin layers. II. Shear and frictional behavior of solidified films, J. Chem. Phys. **108**, 7010 (1998).

[7] S. Perkin, L. Chai, N. Kampf, U. Raviv, W. Briscoe, I. Dunlop, S. Titmuss, M. Seo, E. Kumacheva, and J. Klein, Forces between mica surfaces, prepared in different ways, across aqueous and nonaqueous liquids confined to molecularly thin films, Langmuir **22**, 6142 (2006).

[8] J. Vanalsten and S. Granick, The origin of static friction in ultrathin liquid-films, Langmuir **6**, 876 (1990).

[9] M. Mizukami, K. Kusakabe, and K. Kurihara, Shear resonance measurement on structuring of liquids confined between mica surfaces, Surf. Colloid Sci. **128**, 105 (2004).

[10] J. Israelachvili, N. Maeda, and M. Akbulut, Comment on reassessment of solidification in fluids confined between mica sheets, Langmuir **22**, 2397 (2006).
[11] S. Granick, Motions and relaxations of confined liquids, Science **253**, 1374 (1991).
[12] H. W. Hu, G. A. Carson, and S. Granick, Relaxation-Time of Confined Liquids under Shear, Phys. Rev. Lett. **66**, 2758 (1991).
[13] A. L. Demirel and S. Granick, Relaxations in molecularly thin liquid films, J. Phys. Condens. Matter **8**, 9537 (1996).
[14] L. Bureau, Nonlinear Rheology of a Nanoconfined Simple Fluid, Phys. Rev. Lett. **104**, 218302 (2010).
[15] A. Maali, T. Cohen-Bouhacina, G. Couturier, and J. P. Aime, Oscillatory Dissipation of a Simple Confined Liquid, Phys. Rev. Lett. **96**, 086105 (2006).
[16] S. J. O'Shea and M. E. Welland, Atomic force microscopy at solid-liquid interfaces, Langmuir **14**, 4186 (1998).
[17] G. B. Kaggwa, J. I. Kilpatrick, J. E. Sader, and S. P. Jarvis, Artifact-free dynamic atomic force microscopy reveals monotonic dissipation for a simple confined liquid, Appl. Phys. Lett. **93**, 011909 (2008).
[18] L. Bureau and A. Arvengas, Drainage of a nanoconfined simple fluid: Rate effects on squeeze-out dynamics, Phys. Rev. E **78**, 061501 (2008).
[19] A. L. Demirel and S. Granick, Origins of solidification when a simple molecular fluid is confined between two plates, J. Chem. Phys. **115**, 1498 (2001).
[20] Z. Q. Lin and S. Granick, Platinum nanoparticles at mica surfaces, Langmuir **19**, 7061 (2003).
[21] M. Heuberger and M. Zach, Nanofluidics: Structural forces, density anomalies, and the pivotal role of nanoparticles, Langmuir **19**, 1943 (2003).
[22] Y. Zhu and S. Granick, Reassessment of solidification in fluids confined between mica sheets, Langmuir **19**, 8148 (2003).
[23] S. Granick, Y. X. Zhu, Z. Q. Lin, S. C. Bae, J. S. Wong, and J. Turner, Reply to comment on reassessment of solidification in fluids confined between mica sheets, Langmuir **22**, 2399 (2006).
[24] P. T. Cummings, H. Docherty, C. R. Iacovella, and J. K. Singh, Phase transitions in nanoconfined fluids: The evidence from simulation and theory, AIChE J. **56**, 842 (2010).
[25] A. Das and J. Chakrabarti, Dimensional crossover in fluids under nanometer-scale confinement, Phys. Rev. E **85**, 050601 (2012).
[26] H. Matsubara, F. Pichierri, and K. Kurihara, Mechanism of Diffusion Slowdown in Confined Liquids, Phys. Rev. Lett. **109**, 197801 (2012).
[27] S. A. Somers and H. T. Davis, Microscopic dynamics of fluids confined between smooth and atomically structured solid-surfaces, J. Chem. Phys. **96**, 5389 (1992).
[28] R. G. Xu and Y. S. Leng, Solvation force simulations in atomic force microscopy, J. Chem. Phys. **140**, 214702 (2014).
[29] M. Heuberger, M. Zach, and N. D. Spencer, Density fluctuations under confinement: When is a fluid not a fluid?, Science **292**, 905 (2001).
[30] O. H. Seeck, H. Kim, D. R. Lee, D. Shu, I. D. Kaendler, J. K. Basu, and S. K. Sinha, Observation of thickness quantization in liquid films confined to molecular dimension, Europhys. Lett. **60**, 376 (2002).
[31] E. Perret, K. Nygard, D. K. Satapathy, T. E. Balmer, O. Bunk, M. Heuberger, and J. F. van der Veen, Molecular liquid under nanometre confinement: density profiles underlying oscillatory forces, J. Phys. Condens. Matter **22**, 235102 (2010).
[32] D. F. Kienle and T. L. Kuhl, Analyzing refractive index profiles of confined fluids by interferometry, Anal. Chem. **86**, 11860 (2014).
[33] M. M. Kohonen, F. C. Meldrum, and H. K. Christenson, Particles on melt-cut mica sheets are platinum, Langmuir **19**, 975 (2003).
[34] S. Ohnishi, M. Hato, K. Tamada, and H. K. Christenson, Presence of particles on melt-cut mica sheets, Langmuir **15**, 3312 (1999).
[35] J. N. Israelachvili, Thin-film studies using multiple-beam interferometry, J. Colloid Interface Sci. **44**, 259 (1973).
[36] M. Born and E. Wolf, *Principles of Optics*, 6th ed. (Pergamon, Oxford, 1980), pp. 58–60.
[37] D. Kienle, J. de Souza, E. Watkins, and T. Kuhl, Thickness and refractive index of DPPC and DPPE monolayers by multiple-beam interferometry, Anal. Bioanal. Chem. **406**, 4725 (2014).
[38] M. J. Hunter, J. F. Hyde, E. L. Warrick, and H. J. Fletcher, Organo-silicon polymers–the cyclic dimethyl siloxanes, J. Am. Chem. Soc. **68**, 667 (1946).
[39] R. G. Horn and J. N. Israelachvili, Direct measurement of structural forces between 2 surfaces in a non-polar liquid, J. Chem. Phys. **75**, 1400 (1981).
[40] J. N. Israelachvili, *Intermolecular and Surface Forces*, 3rd ed. (Academic Press, San Diego, CA, 2011), p. 184.
[41] B. N. J. Persson and E. Tosatti, Layering transition in confined molecular thin-films: Nucleation and growth, Phys. Rev. B **50**, 5590 (1994).
[42] Y. Rosenfeld, Relation between transport-coefficients and internal entropy of simple systems, Phys. Rev. A **15**, 2545 (1977).
[43] J. Mittal, J. R. Errington, and T. M. Truskett, Relationships between self-diffusivity, packing fraction, and excess entropy in simple bulk and confined fluids, J. Phys. Chem. B **111**, 10054 (2007).
[44] G. Adam and J. H. Gibbs, On temperature dependence of cooperative relaxation properties in glass-forming liquids, J. Chem. Phys. **43**, 139 (1965).
[45] C. Alba-Simionesco, B. Coasne, G. Dosseh, G. Dudziak, K. E. Gubbins, R. Radhakrishnan, and M. Sliwinska-Bartkowiak, Effects of confinement on freezing and melting, J. Phys. Condens. Matter **18**, R15 (2006).
[46] A. Jabbarzadeh, P. Harrowell, and R. I. Tanner, Crystal bridges, tetratic order, and elusive equilibria: The role of structure in lubrication films, J. Phys. Chem. B **111**, 11354 (2007).
[47] A. Jabbarzadeh, P. Harrowell, and R. I. Tanner, Crystal Bridge Formation Marks the Transition to Rigidity in a Thin Lubrication Film, Phys. Rev. Lett. **96**, 206102 (2006).