Particle size and phase equilibria in classical logarithmic fluid

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Abstract. An interparticle interaction potential has been recently proposed in studies of condensate-like systems described by logarithmically nonlinear equations, such as the superfluid helium-4 and Korteweg-type melts. It has the shape of a Gaussian multiplied by a linear function and can switch between the attraction and repulsion regimes as the distance varies. We consider a classical fluid model with a discretized version of this potential in Monte Carlo molecular simulations in the Gibbs ensemble. We demonstrate a two-phase system consisting of a dense “liquid” phase in coexistence with a significantly less dense “vapour” phase. For computations, the particle size term in the potential was varied to determine its effect on both the phase envelope and the critical point of the system. It is found that the logarithm of the dimensionless critical temperature decreases in a sigmoid fashion with increasing particle size, while the critical density may be directly proportional to the particle size.

1. Introduction

Wave equations with logarithmic nonlinearity find fruitful applications in different branches of physics - from nuclear physics and condensed-matter theory to particle physics, theory of physical vacuum and quantum gravity. Such a diversity can be explained by the fact that the logarithmic nonlinearity occurs as a leading-order approximation if many-body interaction potentials predominate kinetic energies [1]. Examples of such systems include not only low-temperature quantum Bose liquids [2, 3, 4, 5, 6, 7, 8, 9, 10], but also Korteweg-type materials, in which capillarity and surface tension play a substantial role [11, 12, 13, 14]. In the corresponding models, liquid-solid or liquid-gas phase transitions occur, which makes them useful for describing flows in presence of surface and interface effects.

One of theory’s predictions are large-scale periodical inhomogeneities of density, caused by the existence of multiple Gaussian-shaped solitary wave solutions for an underlying logarithmic wave equation in the vicinity of a liquid-solid phase transition. Their occurrence indicates that they can become independent dynamical objects therefore new degrees of freedom. In ref. [4], an interparticle potential was proposed which effectively describes a leading order of interactions between fluid elements (parcels) with a Gaussian-like density profile:

$$U(r) = \frac{U_0}{a}(r - r_0) \exp\left(-\frac{r^2}{a^2}\right),$$

(1)
where \( r \) is an inter-particle separation, Gaussian width \( a \) and central potential \( U_0 = -aU(0)/r_0 \approx -1.34U(0) \) are free parameters of the model. Here the value
\[
r_0 = a \left( \frac{1}{2} + \frac{1}{e\sqrt{\pi}} \text{erf}(1) \right) \approx 0.75 a,
\]
refers to a point where the potential (1) changes its sign. In this context, \( r_0 \) is the critical value, which determines the inter-particle (or inter-parcel) separation at which the potential switches between attraction and repulsion regimes.

In this paper, we shall use this potential for a classical fluid model, referred to as the classical logarithmic fluid hereafter, and study statistical mechanical properties thereof. We shall employ Monte Carlo simulations to examine various general features of this type of fluid, such as phase equilibria and fluid structure.

2. Methods and results

Previously, Monte Carlo simulations were used to study a model fluid with a logarithmic pair potential [16], and it was confirmed that predictions [17] regarding the calculation of the internal energy using standard statistical mechanics were acceptable. The influence of the size term in the potential (which will be described in more details below) on the pure species phase equilibria is discussed, including the effect of this term on the critical point (the point at which the lighter and denser phase become indistinguishable).

The inter-particle two-body potential (1) is implemented by means of a tabulated potential, with its value computed at 1000 discrete points over the range \( 0 \leq r \leq 1.85 \text{ nm} \). A cubic spline was used to interpolate between tabulated values. A cut-off radius of 1 nm was employed in all simulations for use in periodic boundary conditions, following the minimum-image convention [18].

Monte Carlo (MC) simulations were performed in the isochoric-isothermal Gibbs ensemble [19, 20] for systems consisting of 522 particles distributed across two phases using the Metropolis scheme [21] and MCCCS Towhee software [23]. Simulations were performed for \( 52.2 \times 10^6 \) Monte Carlo moves to achieve equilibrium, after which an additional \( 52.2 \times 10^6 \) Monte Carlo moves were run to generate results. The following Monte Carlo moves were considered (with their relative occurrences in parentheses): volume exchange [22] (0.5 %), particle exchange between phases (39.5 %), particle exchange within a phase (30.0 %), and particle translation (30.0 %).

MC molecular simulation essentially generated a set of configurations sampled from the desired ensemble, with each configuration in sequence being used to generate the next one thereby forming a Markov chain. The simulation proceeds as follows: Firstly, a trial configuration \( m \) is generated and its energy computed, then this trial configuration is compared to the original configuration \( n \), and if it possesses a lower energy it is accepted, while if it does not, then it has a chance to be accepted \( P_{mn} \):
\[
P_{mn} = \min \left[ 1, \frac{p_n}{p_m} \right],
\]
wherein \( p \) represents the probability of each configuration.

For the Monte Carlo simulations, phase equilibrium was studied by initializing one phase as the dense phase (with 520 particles) and the other as a lighter one (with 2 particles). The parameter \( r_0 \) was varied, and a set of temperature and phase density values was generated for each value of \( r_0 \). In each case, a critical point may naturally form at which the two phases are indistinguishable in terms of density. Configurations were sampled every 5000 Monte Carlo steps during the course of the production stage in order to generate data.

Results of the two-phase MC simulations are shown in Figure 1, which shows a shift towards higher densities for both phases as the value of the parameter \( r_0 \) is increased. In all cases,
there was a critical point at which the two phases became indistinguishable for a specific temperature value. This critical point shifted towards lower temperatures as the value of $r_0$ increased. Previous work on systems of collapsing hard disks with a repulsive inter-particle interaction coupled with a square well potential [24] can provide a useful comparison to describe the behaviour observed here. In the low density region of the phase diagram for hard disks, increasing the width of the repulsive step produced a qualitatively similar effect to decreasing the size term of the pair potential used in the present study, in terms of shifting the phase envelope from high density and low temperature towards low density and high temperature.

In terms of the effect of particle size on the two phases in the system, the ratio of the liquid density to the vapour density decreased monotonically increases as the particle size increased. Hence, it can be concluded that the particle size term influences the lighter (vapour) phase more than the dense (liquid) phase on account of fewer aggregate interactions due to greater spatial dispersion between particles coupled with the relatively short range of the interparticle attractions.

The locus of the critical point is presented in Figure 2, illustrating the effect that the particle size term $r_0$ has on both the temperature and density at criticality. While the dimensionless density increased seemingly in proportion with $r_0$, this did not hold when the density was considered in dimensional terms in which case the critical density was constant at about 2.5 g/cm$^3$ in all cases. The critical temperature was strongly influenced by the particle size, as evidenced by its rapid decrease with increasing $r_0$ (in logarithmic terms, the curve takes the general shape of a sigmoid function).

**Figure 1.** Phase diagram of the classical logarithmic fluid, generated by two-phase MC simulations, where $r^* = r_0/r_{\text{ref}}$ and $r_{\text{ref}} = 0.346$ nm.
Figure 2. The locus of the critical point as the particle size term $r_0$ is increased.

3. Conclusion
Monte Carlo simulations were used to investigate the phase behaviour of the classical logarithmic fluid (1), while varying both the temperature and the size term in the interparticle potential. The pair potential for this fluid differs from the commonly used Lennard-Jones potential for classical fluids in that it allows, in principle, complete particle overlap as the short-range repulsive energy is finite.

It was demonstrated that there is a monotonic relationship between the size term and both the critical density and the critical temperature of the fluid. In this context, criticality refers to the point $(T, \rho)$ at which the lighter and denser phases of the fluid become indistinguishable, a condition that is expected from a classical fluid. For the fluid in this study, the critical density increased as the particle size term increased, while the critical temperature decreased. It was also observed that the density ratio between the two phases was related to particle size, with this parameter having a greater effect on the density of the lighter (vapour) phase, probably due to fewer aggregate interactions coupled with greater spatial dispersion and the lack of long-range attractions using the pair potential under consideration.

Comparison was made with systems of collapsing disks for which qualitatively similar behaviours were observed. Specifically, the width of a repulsive interparticle interaction was found to influence the phase diagram in an inverse manner to the effect of the of the size term in the present work.

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