Phase Equilibria for Lennard-Jones and Square-Well Fluids
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ABSTRACT

Both repulsive and attractive terms are necessary in the microscopic pair potential in order to observe macroscopic liquid and vapor phases. We explore the conditions for phase equilibria for particles interacting via Lennard-Jones and square-well pair potentials. A wide range of particle densities are simulated in the grand canonical Monte Carlo ensemble using the Wang-Landau method to develop a histogram flat for all particle numbers. We find that the critical temperature for a square-well fluid scales with the range of the attractive energy between particles. In particular, when the attractive range is half the width of the hard-shell diameter ($\lambda = 1.5$) the temperature-density phase envelope is similar to that for the Lennard-Jones fluid.

I. INTRODUCTION

Particles that do not interact only exhibit a single disordered phase. Particles that repel each other at close distances, but do not interact otherwise, additionally exhibit an ordered phase. In order to observe the three phases common to everyday experience, both repulsive and attractive forces between particles are necessary.

Both of these forces are present in the Lennard-Jones (LJ) pair potential

$$u_{LJ}(r) = 4\varepsilon\left[\left(\frac{r}{\sigma}\right)^{-12} - \left(\frac{r}{\sigma}\right)^{-6}\right] \qquad (1)$$

where r is the distance between particles, σ is the characteristic diameter of a LJ particle and ε is the strength of the interaction. The attractive term in the LJ potential follows the theoretically derived inverse-6th scaling with particle separation. The repulsive term was selected for computational efficiency, since it is the square of the attractive term. Both terms are short-range. In this paper we examine the relationship between the two fluid phases and the range of the attractive interaction.

However, when one attempts to vary the range of the attractive LJ potential, for example by increasing the power from -6 to -5, the strength of the interaction also changes. We, therefore, turn to the simplest model of a 2-phase fluid: the square-well (SQ) fluid. SQ particles interact via the pair potential

$$u_{SQ}(r) = \begin{cases} +\infty, & \text{if } r < \sigma \\ -\varepsilon, & \text{if } \sigma \leq r < \lambda\sigma \\ 0, & \text{if } r \geq \lambda\sigma \end{cases} \qquad (2)$$

where σ is the hard-sphere diameter of the particle, ε is the magnitude of the interaction, and λ scales the range of the attractive interaction.

Using Monte Carlo (MC) simulations, we find the conditions for equilibrium between the liquid and vapor phases of the SQ fluid for λ = 1.25, 1.5, 2.0. We compare these results to that for the LJ fluid.

II. METHODS

Simulations of the square-well fluid were performed using Monte Carlo moves in the grand canonical ensemble, holding the chemical potential μ, volume V and temperature T constant. Monte Carlo moves that displace, insert and delete particles were employed in a 2:1:1 ratio, respectively. The state conditions μVT were selected by considering the simulation algorithm used to sample a range of densities encompassing both liquid and vapor states.

Table 1. Conditions sampled by simulation.

Pair Potential	Temperature	N_{max}
Lennard-Jones	0.75	170
	0.80	170
	0.85	170
	0.90	170
	0.95	150
	1.00	150
	1.05	150
	1.10	150
Square-well, λ=1.25	0.66	180
	0.68	174
	0.70	170
	0.72	160
	0.74	150
	0.75	150
	0.76	130
	0.77	130
Square-well, λ=1.5	1.00	140
	1.05	140
	1.10	140
	1.15	120
	1.17	120
	1.19	120
	1.21	120
	1.22	120
Square-well, λ=2.0	2.40	140
	2.50	120
	2.60	120
	2.70	100
	2.75	100

We used the Wang-Landau method because it determines the free energy, A, with high accuracy for all N on a specified range N_{min} to N_{max}. To get good statistics, we want to bias the system in such a way that all N are equally probable; this is achieved by developing a bias equal to A. In the Wang-Landau method, we chose this bias to initially be zero, but after every MC move, the bias for the resulting value of N was decreased by an amount g, making it less likely for the system to return to that state without first visiting all other values of N. The modification factor g was initially set to 1 and was reduced by a factor of 2 when the sampled histogram of N was flat, such that the minimum bin height was 80% of the average bin height. We continued this algorithm until $g < 10^{-6}$.

The free energy is reweighted post-simulation to the coexistence chemical potential, so the ensemble can be simulated for any arbitrary μ. For convenience, we chose μ to be that of the ideal gas such that the excess chemical potential, $\mu_{ex} = \mu - \mu_{IG} = 0$.

The volume V directly determines the lowest density $\rho_{min} = 1 / V$ that the system can reach. The probability of ρ_{min} at coexistence should be significantly less

than the most probable density. However, in order to simulate liquid densities, a larger V requires a larger N_{max}, and thus longer simulation times are required. We found $V = 200\ \sigma^3$ to be a good trade-off between these competing interests.

The range of temperatures T was chosen to be near but below the critical temperature for each fluid. Corresponding values of N_{max} are shown in Table 1.

For soft-core potentials, such as LJ, the system is relatively insensitive to the chosen N_{max}. Although dense configurations often have core overlap, and thus in an unbiased simulation would be sampled only rarely, using the Wang-Landau method any configuration with a finite energy can be accessed once enough bias has been built up. For square-well fluids, however, the potential energy of overlapping particles is infinite. No amount of sampling of other configurations will ever drive the system to access configurations with core overlap. Thus simulations with a poorly chosen N_{max} for the square-well fluid may never finish.

III. RESULTS & DISCUSSION

The coexistence curves for the LJ and square-well fluids with $\lambda = 1.25, 1.5, 2.0$ are shown in Figure 1. The value of λ significantly elevates or depresses the critical temperature of the square-well fluid. The critical temperature of SQ for $\lambda = 1.5$ is on the order of LJ. However, for $\lambda = 2.0$ the critical temperature is more than doubled or for $\lambda = 1.25$ the critical temperature is about 2/3 the $\lambda = 1.5$ value.
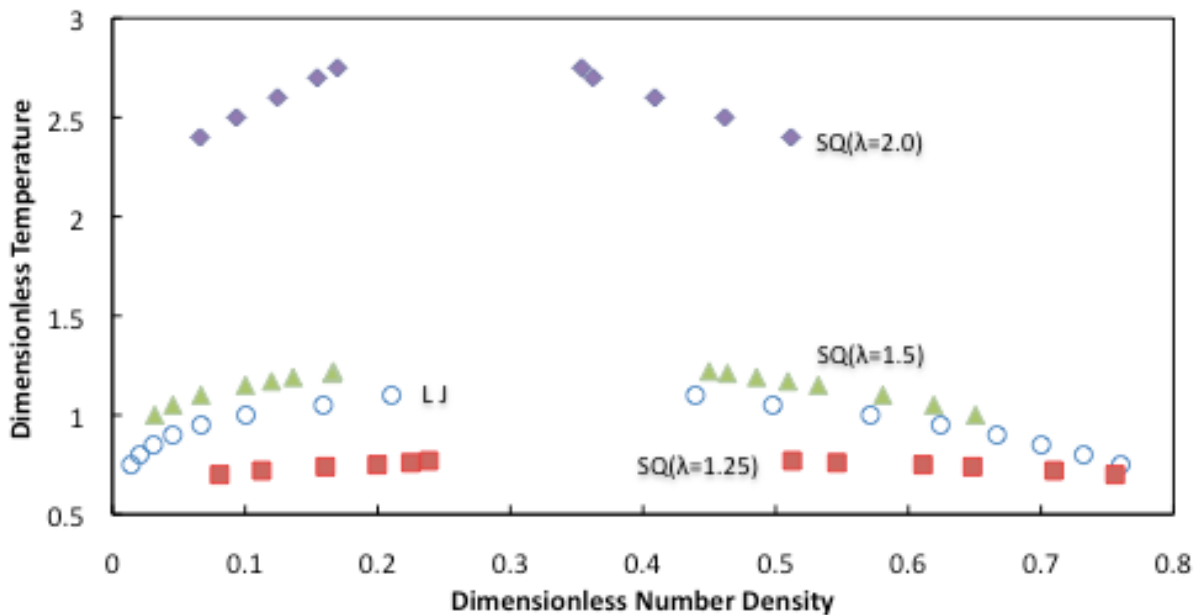

Figure 1. Temperature-density phase diagrams for the Lennard-Jones (LJ) and square-well (SQ) fluids showing the equilibrium vapor and liquid densities at temperatures approaching the critical temperature. The parameter λ scales the range of the attractive interaction. Density errors were calculated from multiple runs and are not shown since they were < 0.02.

From these results, we could expect in the limit that $\lambda \rightarrow 1$, we recover the hard sphere fluid, which does not exhibit a disordered-disordered phase transition. Additionally, it would be interesting to see the liquid-vapor coexistence curves in the context of the full phase diagram, including both liquid-solid and vapor-solid equilibrium conditions.

As mentioned above, low temperature simulations of square-well fluids were highly sensitive to the chosen N_{max}. In fact, the two lowest temperature simulations at T=0.66 and T=0.68 did not finish within the time frame of this project. With this limitation in mind, we also simulated a modified square-well fluid in which the hard core of the pair potential was replaced by the LJ inverse-12th term. While this modified square-well fluid did not exhibit the same sensitivity to N_{max}, however, the phase diagram was significantly altered. Specifically, the critical temperature of the modified square-well temperature was greater than for its unmodified counterpart. Alternatively, a more stiff repulsive term could be used to modify the square well potential or biased insertion moves that exhibit increased acceptance at high densities could be developed.