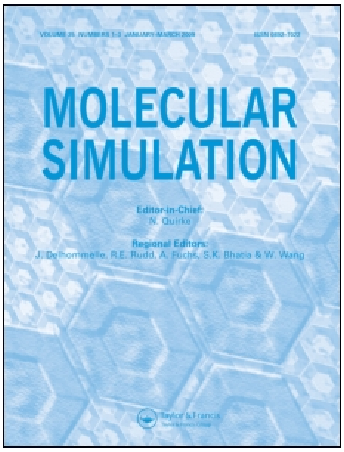

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Some physical properties of the Weeks-Chandler-Andersen fluid

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Some physical properties of the Weeks–Chandler–Andersen fluid

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Molecular dynamics (MD) simulations have been carried out of some properties of a Weeks–Chandler–Andersen (WCA) system in its fluid phase. Data for the potential energy components, mean square force, infinite frequency elastic moduli and Poissons ratio are presented as a function of density and temperature. The scaling behaviour of these quantities using reduced variables, such as an effective hard sphere diameter σ_{HS} was investigated. The infinite frequency Poisson's ratio ν_∞ was found to increase with packing fraction and temperature towards the incompressible fluid limit value of 1/3. Some success was achieved in scaling the mean square force, by the value of the force squared evaluated at σ_{HS}.

Keywords: LJ potential; WCA potential; Phase diagram; Thermomechanical properties; Molecular dynamics simulation

1. Introduction

The Weeks–Chandler–Anderson (WCA) potential is a popular pair potential,

$$\phi(r) = \begin{cases} 4\epsilon((\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6) + \epsilon, & r \leq 2^{1/6}\sigma \\ 0 & r > 2^{1/6}\sigma \end{cases} \quad (1)$$

.

This potential is the Lennard–Jones (LJ) potential, shifted upwards by ϵ and truncated at the LJ potential minimum of $2^{1/6}\sigma$. Although, the total potential is repulsive, it is composed of repulsive ("r") r^{-12} and attractive ("a") r^{-6} components. It was originally devised as a reference fluid in a perturbation treatment for the LJ fluid [1,2]. The LJ pair potential is decomposed into two parts, one entirely repulsive (the WCA potential) and the other entirely attractive. The WCA fluid has been examined in various dimensions [3,4]. The phase diagram of the WCA system is relatively simple, in that unlike the LJ potential it does not have a critical point and liquid–vapour co-existence region. The melting line of the WCA fluid has been determined [5], and its thermomechanical properties calculated by molecular dynamics (MD) simulations [6].

In this study, we consider various properties of the WCA fluid, including the potential energy, the mean square force, infinite frequency elastic moduli and Poisson's ratio. This study follows on from our recent MD simulation and theory of the generalised soft sphere potential, $\phi(r) = \epsilon(\sigma/r)^n$ where n is an adjustable parameter. This r^{-n} potential, like the WCA, is purely repulsive but exhibits a more convenient scaling of the static and dynamic properties [7]. For the soft sphere potential, there is a direct mapping between temperature and density, so that the complete equation of state can be computed from density dependent data carried out at a single temperature. In the WCA case, one cannot perform such a temperature-density interchange, although, one would expect that at high temperature ($k_{\mathrm{B}}T >> \epsilon$), the behavior of the WCA fluid should approach that of the soft sphere potential with the exponent $n = 12$.

2. Results and discussion

MD simulations were carried out with $N = 500$ particles in volume V for typically 70,000 time steps of $0.005/\sqrt{T}\sigma(m/\epsilon)^{1/2}$ where T is the "reduced" temperature or $k_{\mathrm{B}}T/\epsilon$, where k_{B} is Boltzmann's constant. All

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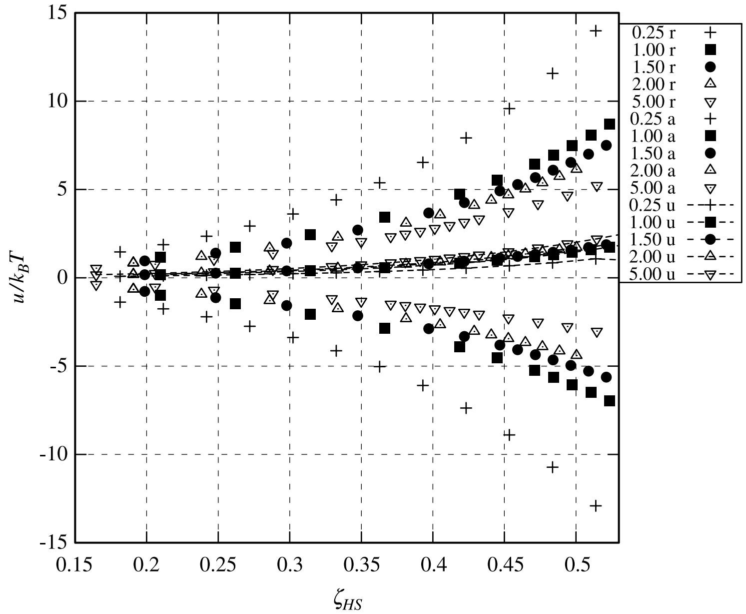

Figure 1. The total energy per particle u ($u/k_{\mathrm{B}}T$) and the repulsive "r" ($u_{\mathrm{r}}/k_{\mathrm{B}}T$) and attractive "a" ($u_{\mathrm{a}}/k_{\mathrm{B}}T$) components plotted against effective hard sphere packing fraction, ζ_{HS} defined with σ_{HS} taken from the formula in equation (2). The $+\epsilon$ in the WCA interaction of equation (1) is added to the attractive component, u_{a}.

quantities quoted below and on the figures are in WCA reduced units, i.e. $\epsilon \equiv \sigma \equiv m = 1$ (m is the mass of the particle). The density of the fluid is usually written in terms of a packing or volume fraction, $\zeta = \pi N\sigma^3/6V$. The simulations were carried out at reduced temperatures in the range $0.25 - 5.0$, the same set as used in [5] and at densities up to and above the maximum fluid density at each temperature.

One of the main themes of this work is an attempt to collapse the computed quantities onto a single master curve in each case. In order to achieve this, we need to introduce a prescription for a state dependent characteristic lengthscale, which has had an extensive and rich history. Although, real molecules and the WCA particle are not hard spheres, the exercise of mapping their properties onto those of an "equivalent" hard sphere fluid has proved such a longstanding procedure in liquid state theory (e.g. see [8] Chapter 6). The requirement is to attribute an effective hard sphere diameter σ_{HS} to the real molecule. The WCA data can be rescaled by defining an effective hard sphere diameter σ_{HS}, which leads to an effective hard sphere packing fraction through

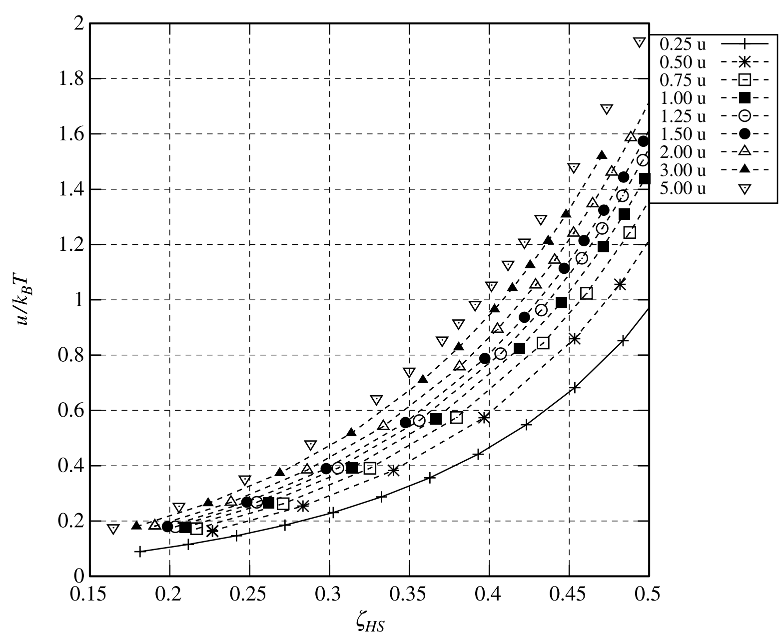

Figure 2. The total energy per particle u ($u/k_{\mathrm{B}}T$) plotted against effective hard sphere packing fraction, ζ_{HS} defined with σ_{HS} taken from the formula in equation(2).

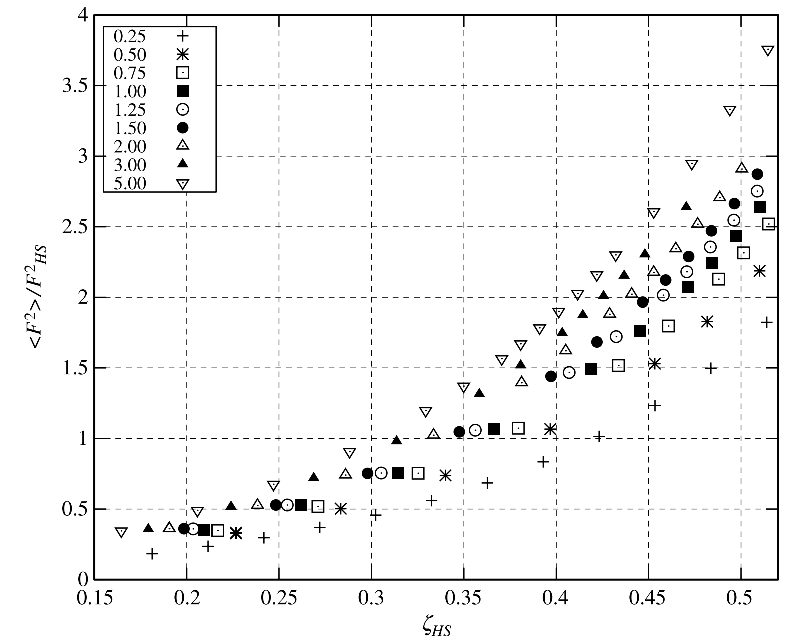

Figure 3. The mean square force per particle $< F^2 > /F^2_{\mathrm{HS}}$ plotted against effective hard sphere packing fraction, ζ_{HS} defined with σ_{HS} taken from the formula in equation (2). The mean square force is normalized by the square of a characteristic force, $F_{\mathrm{HS}} = (\mathrm{d}\phi(r)/\mathrm{d}r)_{r=\sigma_{\mathrm{HS}}}$.

$\zeta_{\mathrm{HS}} \equiv \pi N \sigma^3_{\mathrm{HS}}/6V$. A number of presciptions for σ_{HS} exist in the literature (e.g. see [6] and references therein) which involve, for example, integrating the Boltzmann factor of the potential. Unfortunately, for WCA (indeed for most commonly used potentials) these do no lead to simple analytic expressions for the usual potential forms. An alternative scheme is to simply use the distance at which the WCA potential equals the thermal energy $k_{\mathrm{B}}T$ (or a factor times the thermal energy), which leads to a simple analytic expression for σ_{HS}. This criterion for σ_{HS} has also been used by Hess *et al.* [6]. In reduced units, this requires us to solve the quadratic equation, $T = 4X^2 - 4X + 1$ for X, where (in reduced units) $X = r^{-6}$. Then, substitution of X for r gives,

$$\sigma_{\mathrm{HS}} = \frac{2^{1/6}}{(1+\sqrt{T})^{1/6}}, \tag{2}$$

on setting $r \equiv \sigma_{\mathrm{HS}}$. The formula in equation (2) indicates that the effective hard sphere diameter decreases with increasing temperature. This prescription is a specific example of a more general formula derived by Ben-Amotz

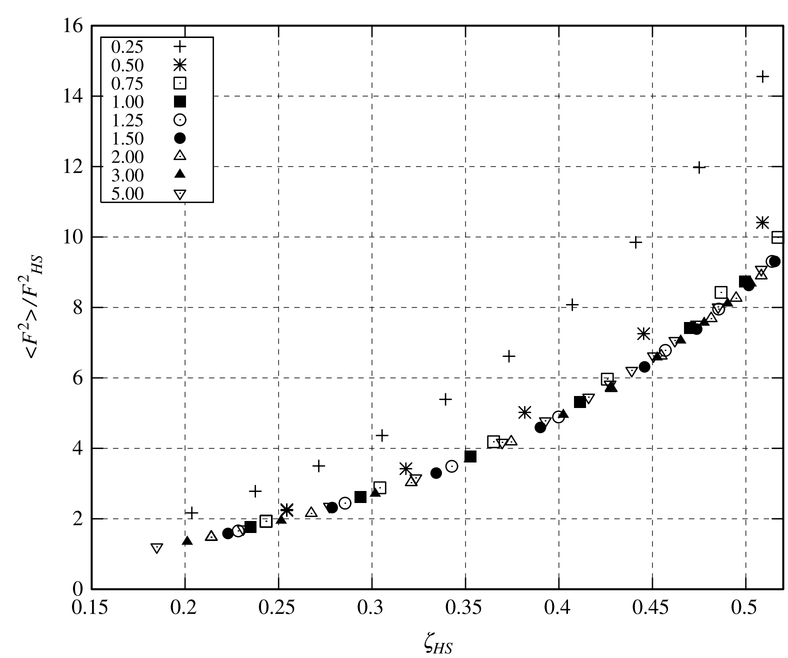

Figure 4. As for figure 3, except that the empirical formula given in equation (4) is used to define σ_{HS}.

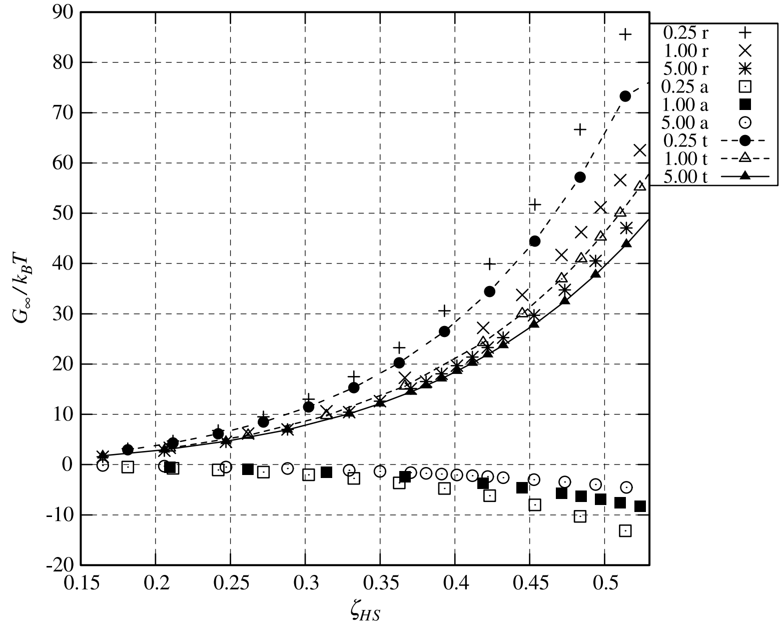

Figure 5. The infinite frequency shear rigidity modulus normalized by the temperature, $G_\infty/k_\mathrm{B}T$. The contribution from the attractive (r^{-6}) part of the potential (denoted by "a") is the lowest set of data points. The contribution from the repulsive part of the potential (r^{-12}) (denoted by "r") is the highest set of data points. The total quantity made up of the kinetic, attractive and repulsive potential parts (denoted by "t") forms the lines and points, where the formula in equation (6) was used. The moduli are plotted against effective hard sphere packing fraction, ζ_HS defined with σ_HS taken from the formula in equation (2). The reduced temperatures and the component indicators are given in the caption.

and Herschback [9],

$$\sigma_\mathrm{HS} = \frac{\alpha_0}{(1+\sqrt{T/T_0})^{1/6}}, \qquad (3)$$

where α_0 and T_0 are variables that could be density dependent [9,10].

In figure 1, the potential energy per particle divided by $k_\mathrm{B}T$, $u/k_\mathrm{B}T$ and the repulsive ($u_\mathrm{r}/k_\mathrm{B}T$) and attractive components ($u_\mathrm{a}/k_\mathrm{B}T$) of the WCA potential energy are presented, plotted against ζ_HS derived from equation (2). It can be seen that both components are important at all temperatures (even though the total potential energy is always positive). Figure 2 shows the total potential energy per particle only. There is no obvious way of scaling $< u >$ as at σ_HS the equation (2) energy per particle is always $k_\mathrm{B}T$ (this fact was used in deriving the formula in equation (2)).

Figure 3 shows the mean square force per particle plotted against effective hard sphere packing fraction, ζ_HS defined with σ_HS from the formula in equation (2). The force is normalised by the value derived from the pair potential, evaluated at $r=\sigma_\mathrm{HS}$. It can be seen that the scaling is not good. However, it can be improved if the definition of σ_HS is modified empirically to,

$$\sigma_\mathrm{HS} = \frac{2^{2/9}}{(1+\sqrt{T})^{1/6}}, \qquad (4)$$

as can be seen in figure 4. The difference between the definitions of σ_HS in equations (2) and (4) is in the coefficient $2^{1/6}$ being replaced by $2^{2/9}$. These two definitions still fall within the general definition of σ_HS of Ben-Amotz and Herschback [9] given in the formula of equation (3). Using equation (4), convergence of the data onto a single line is reasonable, at least for $T>1$.

We now consider the mechanical properties of the WCA fluid. The infinite frequency elastic shear modulus, G_∞ for pair-wise additive interactions can be written as follows [11],

$$G_\infty = \rho k_\mathrm{B}T + \frac{2\pi\rho^2}{15}\int_0^\infty \mathrm{d}rg\,(r)\frac{\mathrm{d}}{\mathrm{d}r}(r^4\phi'), \qquad (5)$$

where $g(r)$ is the radial distribution function and $\phi' \equiv \mathrm{d}\phi/\mathrm{d}r$. $\rho = N/V$ is the number density for N particles in volume V. In a MD or Monte Carlo (MC) simulation, G_∞ can be computed from equation (5) rewritten as a sum over pair interactions,

$$G_\infty = \rho k_\mathrm{B}T + \frac{1}{15V}< \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} r_{ij}^{-2}\frac{\mathrm{d}}{\mathrm{d}r_{ij}}(r_{ij}^4\phi_{ij}') > . \qquad (6)$$

where r_{ij} and ϕ_{ij} are the separation and pair potential between particles i and j, respectively. $< \cdots >$ stands for a simulation time or ensemble average. Similarly, for the infinite frequency bulk or compressional modulus, K_∞, [11],

$$K_\infty = \frac{5\rho k_\mathrm{B}T}{3} + \frac{2\pi\rho^2}{9}\int_0^\infty \mathrm{d}rg\,(r)r^3(r\phi'' - 2\phi'), \qquad (7)$$

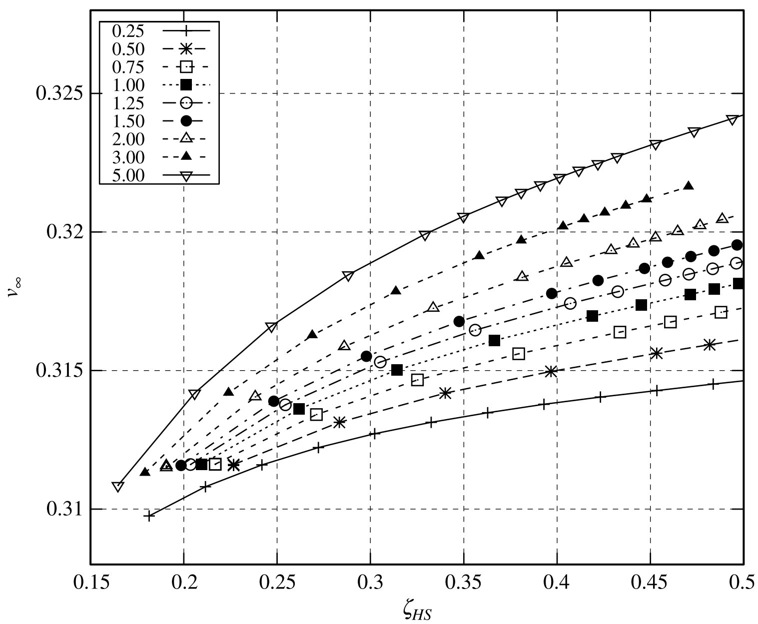

Figure 6. The infinite frequency Poisson's ratio for the WCA fluid along the isotherms. The formula in equation (9) was used. The $\zeta_{\rm HS}$ are defined with $\sigma_{\rm HS}$ taken from the formula in equation (2). The temperatures are given in the key.

where, $\phi'' = (\mathrm{d}/\mathrm{d}r)\phi'$, which in terms of pair interactions is,

$$K_\infty = \frac{5\rho k_{\rm B}T}{3} + \frac{1}{9V} < \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} r_{ij}(r_{ij}\phi''_{ij} - 2\phi'_{ij}) > . \quad (8)$$

At liquid-like densities, the kinetic contributions to G_∞ and K_∞ are relatively small compared with the ϕ-dependent terms.

Figure 5 shows the packing fraction dependence of G_∞ along the isotherms considered. The total G_∞, and its repulsive and attractive components are also shown in the figure. The repulsive component can be seen to dominate the total. Because of the complex nature of the formulas for this quantity, given in equation (5), one would not expect any simple scaling of the data. The corresponding plot for K_∞ is qualitatively similar, although, the magnitude of each term is larger. The (infinite frequency) Poisson's ratio, ν_∞ can be obtained from the computed G_∞ and K_∞ using the formula [12],

$$\nu_\infty = \frac{3K_\infty - 2G_\infty}{6K_\infty + 2G_\infty} \quad (9)$$

which is plotted as a function of the equivalent hard sphere packing fraction in figure 6. The ν_∞ increase with packing fraction and temperature towards the incompressible fluid limit of $\nu = 1/3$. Note that Poisson's ratio, like the compressibility factor, Z is a dimensionless quantity and therefore cannot be scaled by any function of $\sigma_{\rm HS}$.

In this report, we have explored the density and temperature dependence of some of the less well studied properties of the WCA fluid. We have illustrated how these properties vary with temperature and density. We have also made some attempts to scale the various data sets onto master curves using an effective hard sphere diameter treatment. These quantities we find are, however, rather difficult to collapse onto master curves, presumably because of the relatively complicated functional form of the potential.

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