

Pressure of fluids and solids composed of particles interacting with a short-range repulsive potential

Siegfried Hess¹ and Martin Kröger^{1,2}

¹*Institut für Theoretische Physik, Technische Universität Berlin, PN 7-1, Hardenbergstrasse 36, D-10623 Berlin, Germany*

²*Polymer Physics, Department of Materials, ETH Zürich, ML H 18, CH-8092 Zürich, Switzerland*

(Received 15 October 1999)

A simple short range repulsive potential (SR), with an even smoother cut off than the Weeks-Chandler-Andersen (WCA)–Lennard–Jones potential, yields practically the same pressure, both in the fluid state and for the fcc solid, when the potential parameters are chosen such that the forces are the same at the distance where the two potential curves are equal to $k_B T$. The comparison of the pressure for the SR and the WCA systems is based on molecular dynamics computer simulations. The fluid branch of the equation of state is rather well described by a modified Carnahan-Starling expression.

PACS number(s): 47.10.+g, 62.10.+s, 64.10.+h, 66.20.+d

INTRODUCTION

A fluid composed of particles which interact via the 6-12 Lennard-Jones (LJ) potential cut off at its minimum (and shifted such that it vanishes at the cut off distance) was considered by Weeks, Chandler, and Andersen (WCA) [1] as a ‘hard-sphere-like’ reference system. This interaction with a purely repulsive force is frequently referred to as the WCA potential. In Ref. [1], effects of the attractive force in a fluid with the full LJ interaction potential were treated as a perturbation. Due to its short range of interaction and its smooth cut off, the WCA potential, taken as a model as such, is quite popular in equilibrium and nonequilibrium molecular dynamics (MD and NEMD) computer simulation studies. It is the purpose of this note to point out that a computationally still simpler short range repulsive potential (SR), with an even smoother cut off, yields practically the same pressure, both in the fluid state and in the fcc solid, provided that the forces are the same at the distance where the two potential curves are equal to $k_B T$. The comparison of the pressure for the SR and the WCA systems is based on MD computer simulations. The fluid branch of the equation of state is rather well described by a modified Carnahan-Starling (CS) expression [2,3].

I. THE POTENTIAL CURVES

The Lennard-Jones (LJ) potential, cut off in its minimum at r_{cut} and shifted such that it is zero at the cutoff distance r_{cut} , was used by Weeks, Chandler, and Anderson [1] as a purely repulsive reference potential. The WCA potential, for $r < r_{\text{cLJ}} = 2^{1/6} r_0 \approx 1.122 r_0$, is given by

$$\phi^{\text{WCA}}(r) = 4\Phi_0[(r/r_0)^{-12} - (r/r_0)^{-6}] + \Phi_0, \quad (1)$$

and $\phi_{\text{WCA}}(r) = 0$ for $r \geq r_{\text{cLJ}}$. The quantities Φ_0 and r_0 set the characteristic energy and length scales. A system composed of WCA particles possesses solid and fluid phases but no gas-liquid phase transition.

The SR potential, introduced in Ref. [4], is defined by

$$\phi^{\text{SR}}(r) = \Phi_0(9 - 8(r/r_0))^3, \quad r < r_{\text{csh}} = \frac{9}{8} r_0 = 1.125 r_0, \quad (2)$$

and $\phi^{\text{SR}}(r) = 0$ for $r \geq r_{\text{csh}}$. The potential parameters in Eq. (2) have been chosen such that, at $r = r_0$, the values of the potential functions and of their first derivatives are equal, viz., $\phi(r_0) = \Phi_0$ and $\phi'(r_0) = -24\Phi_0/r_0$, for both potentials. In the following, results for the pressure are presented for the temperature $T = \Phi_0/k_B$.

In a quantitative comparison of analytic calculations with results obtained by MD simulations for the structure of a ferrofluid, an equivalent scaling was used to relate a r^{-12} soft sphere potential to a screened Coulomb interaction [5]. In numerical calculations and in the graph displayed here, all physical quantities are expressed in the standard LJ units of Refs. [6–9], e.g., lengths and energies are given in units of r_0 and Φ_0 . When no danger of confusion exists, the dimensionless variables will be denoted by the same symbols as the original quantities. Then the WCA and SR potentials read $\phi^{\text{WCA}}(r) = 4(r^{-12} - r^{-6}) + 1$, $r < r_{\text{cLJ}} = 2^{1/6}$, $\phi^{\text{WCA}}(r) = 0$ for $r \geq r_{\text{cLJ}}$, and $\phi^{\text{SR}}(r) = (9 - 8r)^3$, $r < r_{\text{csh}} = 1.125$, $\phi^{\text{SR}}(r) = 0$ for $r \geq r_{\text{csh}}$. Similarly, the number density $n = N/V$, where N and V are the number of particles and the volume of the system, and the temperature T are expressed in units of $n_{\text{ref}} = r_0^{-3}$ and $T_{\text{ref}} = \Phi_0/k_B$, respectively. The unit for the pressure is $p_{\text{ref}} = \Phi_0 r_0^{-3}$.

II. PRESSURE VERSUS DENSITY

A. Remarks on MD simulations

Simulations at the constant temperatures $T/T_{\text{ref}} = 1$ and constant number densities $n = N/V$ (NVT simulations) in the range $n/n_{\text{ref}} = 0.1, \dots, 1.2$ were performed for $N = 10^3 = 1000$ and $4 \times 8^3 = 2048$ particles, where the initial positions were simple cubic and face centered cubic (fcc) lattice sites. The equations of motion were integrated with the velocity Verlet algorithm with the time step $\delta t/t_{\text{ref}} = 0.002$. The LJ reference time is $t_{\text{ref}} = r_0(m/\Phi_0)^{(1/2)}$, and m is the mass of a particle. A cubic simulation box with volume V and periodic boundary conditions were used. The temperature was

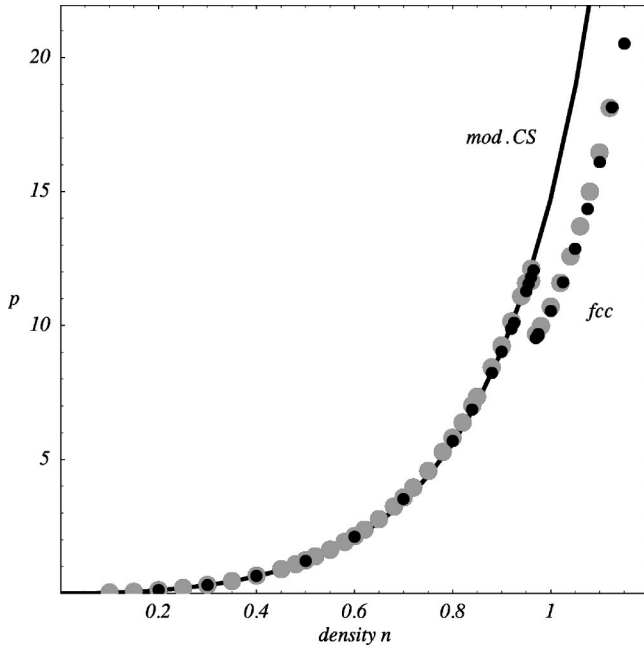


FIG. 1. The potential contribution to the pressure as function of the density, at the temperature $T/T_{\text{ref}}=1$. The large gray dots and the smaller black dots mark the results for the WCA and the SR interaction, respectively. The curve through the points on the left stems from a modified Carnahan-Starling equation of state, valid for the fluid phase. The points on the right pertain to the fcc solid. All physical quantities are in standard LJ units.

kept constant by rescaling the magnitude of the particle velocities which corresponds to the Gaussian constraint of constant kinetic energy. Typically, the system was aged for 10 000 or more time steps corresponding to 20 or more reduced time units before the data were extracted as time averages over 20 000 to 100 000 time steps corresponding to 40 to 200 time units. Aged states were also subjected to density changes. The NVT simulations were performed on various Silicon Graphics workstations. Due to a link list procedure [10] the computational time increases linearly with number of particles N when $N > 500$.

The pressure $P = nk_B T + p^{\text{pot}}$ is the sum of the “kinetic” or “ideal gas” contribution $nk_B T$ and the “potential” contribution p^{pot} . The latter quantity is computed according to

$$V p^{\text{pot}} = \frac{1}{3} \left\langle \sum_i \mathbf{r}^i \cdot \mathbf{F}^i \right\rangle = \frac{1}{3} \left\langle \sum_{i < j} \mathbf{r}^{ij} \cdot \mathbf{F}^{ij} \right\rangle. \quad (3)$$

The bracket indicates a time average. Here $\mathbf{F}^i = \sum_{j \neq i} \mathbf{F}^{ij}$ is the force acting on particle i , $\mathbf{F}^{ij} = \mathbf{F}(\mathbf{r}^{ij})$ is the force exerted on particle i from particle j , $\mathbf{r}^{ij} = \mathbf{r}^i - \mathbf{r}^j$, and $\mathbf{F}(\mathbf{r}) = -\partial\phi(\mathbf{r})/\partial\mathbf{r}$. The symbol $\sum_{i < j}$ means a double summation over pairs of particles.

B. Pressure of the SR and WCA systems

For the WCA system, the pressure as function of the density has previously been reported [3]. In Fig. 1, the potential contributions to the pressure are displayed as functions of the density n , the temperature being $T/T_{\text{ref}}=1$. These WCA data are shown as large gray dots, the small black dots mark the corresponding results for the SR potential. Data points in the

fluid (left) and the fcc solid (right) are presented. In simulations where the particles are initially located on fcc lattice sites, both the SR and WCA systems stay in the fcc crystalline state for densities $n/n_{\text{ref}} \geq 0.97$, and the crystal melts when $n/n_{\text{ref}} \leq 0.96$. Starting the simulations with the particles on the highly instable simple cubic lattice sites, a fluid, or at higher densities, at least amorphous state can be “supercooled,” or rather “overcompressed,” to densities above $n/n_{\text{ref}}=1.0$.

The pressure at the temperature chosen for the systems containing particles which interact with the WCA and the SR potentials, respectively, is practical equal, for all densities studied, both in the fluid state and in the fcc solid.

The liquid-solid phase coexistence has been analyzed in Ref. [3] for the WCA system by simulations with constant pressure (NPT). For the SR system a rather similar phase behavior is expected. The pressure curve shown in the graph for the fluid branch is based on a modified CS equation of state to be discussed next.

C. Equation of state

A modification of the CS equation of state for hard spheres to particles with softer repulsive interaction has been suggested and tested successfully in Ref. [3]. The equation of state involves the second virial coefficient $B_2 = B_2(T)$ and an effective volume v_{eff} , to be defined below, which also depends on the temperature. The potential contribution to the pressure of the fluid is

$$p^{\text{pot}} = nk_B T \left(\frac{nB_2}{(1 - nv_{\text{eff}})^2} + 2 \frac{(nv_{\text{eff}})^2}{(1 - nv_{\text{eff}})^3} \right). \quad (4)$$

For spherical particles, the second virial coefficient is computed according to

$$B_2(T) = 2\pi \int_0^\infty \{1 - \exp[-\phi(r)/k_B T]\} r^2 dr. \quad (5)$$

The effective volume $v_{\text{eff}}(T)$, is given by

$$v_{\text{eff}}(T) = (\pi/6) d_{\text{eff}}^3, \quad (6)$$

with the effective diameter $d_{\text{eff}} = d_{\text{eff}}(T)$ determined by the distance where the binary interaction potential is equal to the temperature

$$\phi(d_{\text{eff}}) = k_B T. \quad (7)$$

At $T = T_{\text{ref}}$, one has $d_{\text{ref}} = r_0$ and consequently $v_{\text{eff}} = (\pi/6) r_0^3 \approx 0.5236 r_0^3$ both for the WCA and the SR interaction. The virial coefficients differ slightly, viz. one has, at the temperature considered, $B_2/r_0^3 = 2.1900, 2.2047$ for the SR and WCA cases, respectively. The curve shown corresponds to the SR case, on the scale of the figure, it agrees with the WCA curve.

At the temperature $T = 0.5T_{\text{ref}}$, one has $v_{\text{eff}}/r_0^3 = 0.5652, 0.5667$ and $B_2/r_0^3 = 2.338, 2.357$, for the SR and WCA interactions, respectively. At the temperature $T = 2T_{\text{ref}}$, the corresponding values are $v_{\text{eff}}/r_0^3 = 0.4742, 0.4766$ and $B_2/r_0^3 = 2.014, 2.036$. The differences of these values for the SR and WCA cases are rather

small. Thus also for these temperatures in the vicinity of $T = T_{\text{ref}}$, the modified CS equation of state practically yields the same pressure for the two potentials compared here.

III. FURTHER COMPARISON BETWEEN THE SR AND WCA SYSTEMS

To provide a feeling for physical quantities which are practically equal for the SR and WCA potentials, and for others where somewhat larger differences are expected, numerical values are mentioned next. These quantities are computed at the temperature is $T/T_{\text{ref}}=1$ and at the density $n/n_{\text{ref}}=0.84$, which corresponds to the triple point density of the LJ system. The potential contributions to the energy per particle and to the pressure are $e^{\text{pot}}/\Phi_0=0.97, 0.96$, $p^{\text{pot}}/p_{\text{ref}}=6.9, 7.0$ ($p_{\text{ref}}=r_0^{-3}\Phi_0$) for the SR and WCA cases, respectively. Here the differences are less than 2%. The values of the high frequency shear modulus, computed according to the Born-Green expression [11–13], $G/p_{\text{ref}}=22.9, 25.8$, differ by somewhat more than 10 percent for the SR and WCA potentials. Similar differences are found for the viscosity, evaluated by nonequilibrium molecular dynamics (NEMD) computer simulations, viz. $\eta/\eta_{\text{ref}}=2.2, 2.5$, with $\eta_{\text{ref}}=p_{\text{ref}}t_{\text{ref}}$, $t_{\text{ref}}=r_0(m/\Phi_0)^{1/2}$. The Max-

well relaxation time $\tau=\eta/G$ is approximately $0.1t_{\text{ref}}$, in both cases.

IV. CONCLUDING REMARKS

At the temperature $T=T_{\text{ref}}=\Phi_0/k_B$, and for temperatures close to it, the simple SR potential leads to practically the same pressure, as function of the density, as the WCA-Lennard-Jones potential. The SR potential has no singularity at $r=0$, and it has a smoother cutoff, compared with the WCA interaction. Not only the force, but also its first derivative vanishes at the cut off distance. This point can be advantageous in MD and NEMD computer simulations. The analytic form of the SR potential makes it well suited as the repulsive part of the interaction of atoms in metals, or of colloidal particles in solutions, in the spirit of embedded-atom models [14,15].

ACKNOWLEDGMENTS

This work has been performed under the auspices of the Sonderforschungsbereich 448 Mesoskopisch strukturierte Verbundsysteme. We thank Bill Hoover and Harald Posch for urging us to publish the results presented here.

-
- [1] J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.* **54**, 5237 (1971).
 - [2] F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**, 635 (1969).
 - [3] S. Hess, M. Kröger, and H. Voigt, *Physica A* **250**, 58 (1998).
 - [4] S. Hess, in *Computational Physics*, edited by K. H. Hoffmann and M. Schreiber (Springer, Berlin, 1996) pp. 268–293.
 - [5] S. Hess, J. B. Hayter, and R. Pynn, *Mol. Phys.* **53**, 1527 (1984).
 - [6] W. G. Hoover, *Molecular Dynamics* (Springer, Berlin, 1986); *Computational Statistical Mechanics* (Elsevier, Amsterdam, 1991); *Physica A* **194**, 450 (1993).
 - [7] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
 - [8] D. J. Evans and G. P. Morris, *Statistical Mechanics of Non-equilibrium Liquids* (Academic Press, London, 1990).
 - [9] R. Haberlandt, S. Fritzsche, G. Peinel, and K. Heinzinger, *Molekular-Dynamik* (Vieweg, Braunschweig, 1995).
 - [10] G. S. Grest, B. Dünweg, and K. Kremer, *Comput. Phys. Commun.* **55**, 269 (1989).
 - [11] M. Born, *J. Chem. Phys.* **7**, 591 (1939); *Proc. Cambridge Philos. Soc.* **36**, 160 (1940); H. S. Green, *The Molecular Theory of Fluids* (North-Holland, Amsterdam, 1952); M. S. Green, *J. Chem. Phys.* **22**, 398 (1954).
 - [12] R. Zwanzig and R. D. Mountain, *J. Chem. Phys.* **43**, 4464 (1965).
 - [13] S. Hess, M. Kröger, and W. G. Hoover, *Physica A* **239**, 449 (1997).
 - [14] M. S. Daw and M. I. Baskes, *Phys. Rev. B* **29**, 6443 (1984).
 - [15] W. G. Hoover and S. Hess, *Physica A* **267**, 98 (1999).