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Temperature of Maximum Density (TMD) Line in the Gaussian Core Model Liquid

1. Introduction

The occurence of isobaric density maxima, or negative thermal expansion coefficients, has been observed in several substances and computer models [1]. Liquid water with its density maximum at 4°C and atmospheric pressure is the most prominent example. As has been demonstrated by a number of computer simulation studies and thermodynamic calculations, the locus of density maxima in the p,T–phase diagram, the so called TMD (temperature of maximum density) line, strongly influences the phase behaviour.

There are two major scenarios, that are of special relevance for the properties of supercooled water [2]. In the first one, a negatively sloped TMD–line intersects the liquid spinodal in the negative pressure region and thus causes the spinodal to retrace towards positive pressures. On supercooling, the liquid approaches this limit of stability, leading to increasing fluctuations, as observed in water. In a second scenario, the negatively sloped TMD line at high pressures develops a temperature maximum and becomes positively sloped under high tensions, thus avoiding an intersection with the liquid spinodal. In this case, the increasing fluctuations in supercooled water are explained by the occurence of a second, metastable critical point, which is the endpoint of a first order liquid–liquid transition line [3]. This intriguing scenario has far reaching consequences for the understanding of the liquid and amorphous state.

The simplest model in classical statistical mechanics, that exhibits a density maximum is the Gaussian core model (GCM). Recently, Stillinger and Stillinger [1] concluded from analytic and simulation calculations the existence of a simply–connected region of negative thermal expansion. We present results of a simulation study to obtain the equation of state (EOS) for the GCM in a large range of pressure, temperature and density and determine the exact location of the TMD line.

2. The Model

We study a fluid of structureless point particles, interacting via a repelling Gaussian pair potential

$$\phi(r_{ij}) = \phi_0 \exp\left[-(r_{ij}/l)^2\right].$$

r_{ij} is the distance between two particles i and j, and ϕ_0 and l are the height and width, respectively, of the interaction profile. In a series of molecular dynamics simulation runs the classical equations of motion are integrated for systems of $N = 512$ particles with periodic boundary conditions. ϕ_0, l and $\sqrt{ml^2/\phi_0}$ are used as units of energy, length and time (m is the mass of the particles). This leads to further reduced units $T' = k_BT/\phi_0$, $\rho' = Nl^3/L_B^3$ and $p' = pl^3/\phi_0$ for temperature, density and pressure (k_B is Boltzmanns constant, L_B the edge length of the periodic box). Our simulation series covers isochores of density $\rho' = 0.4$ to 1.2 in a temperature range from $T' = 0.001$ to 0.035. The density was varied in steps of $\Delta\rho' = 0.1$. Each isochore started with a thermalisation run of 20.000 time steps ($\Delta t' = 0.05$) at $T' = 0.035$. Then the system was cooled down stepwise along the isochore with 5.000 timesteps of thermalisation and a production period of 10.000 timesteps at each temperature.

3. Results

In Fig. 1a the dimensionless pressure is shown as a function of the reduced temperature for all isochores. Each curve exhibits a pronounced pressure minimum (marked by a triangle), which corresponds to a density maximum at constant pressure. The pressure axis in Fig. 1a is discontinuous, as the isochores cover an extremely large pressure range. In Fig. 1c a continuous pressure axis is used. In this representation the minima can not be seen, but their location is indicated by small circles and connected by the corresponding TMD line. In Fig. 1d a 3D representation is given. To clarify the structure of the EOS surface near the minimum, a scaled pressure $p'_{scal} = (p' - p'_{min})\,scal + p'_{min}$ with $scal = 300$ is used. From these figures it becomes clear that the Gaussian core model exhibits a behaviour similar to water. In close agreement to the estimates of Stillinger and Stillinger [1], at a density of $\rho' = 0.7$ and a temperature of $T' = 0.018$ the TMD line changes the sign of its slope. In water this behaviour is related to the possible

occurence of a second critical point, as discussed in the introduction. It is rather amazing that such a simple interaction model without directed interactions as produced by the hydrogen-bonds in water can lead to several waterlike properties [1]. Additionally, the potential energy per particle ϕ'/N is given in Fig 1b, but here, no pecularities are observed. Further studies along such lines should therefore be done.

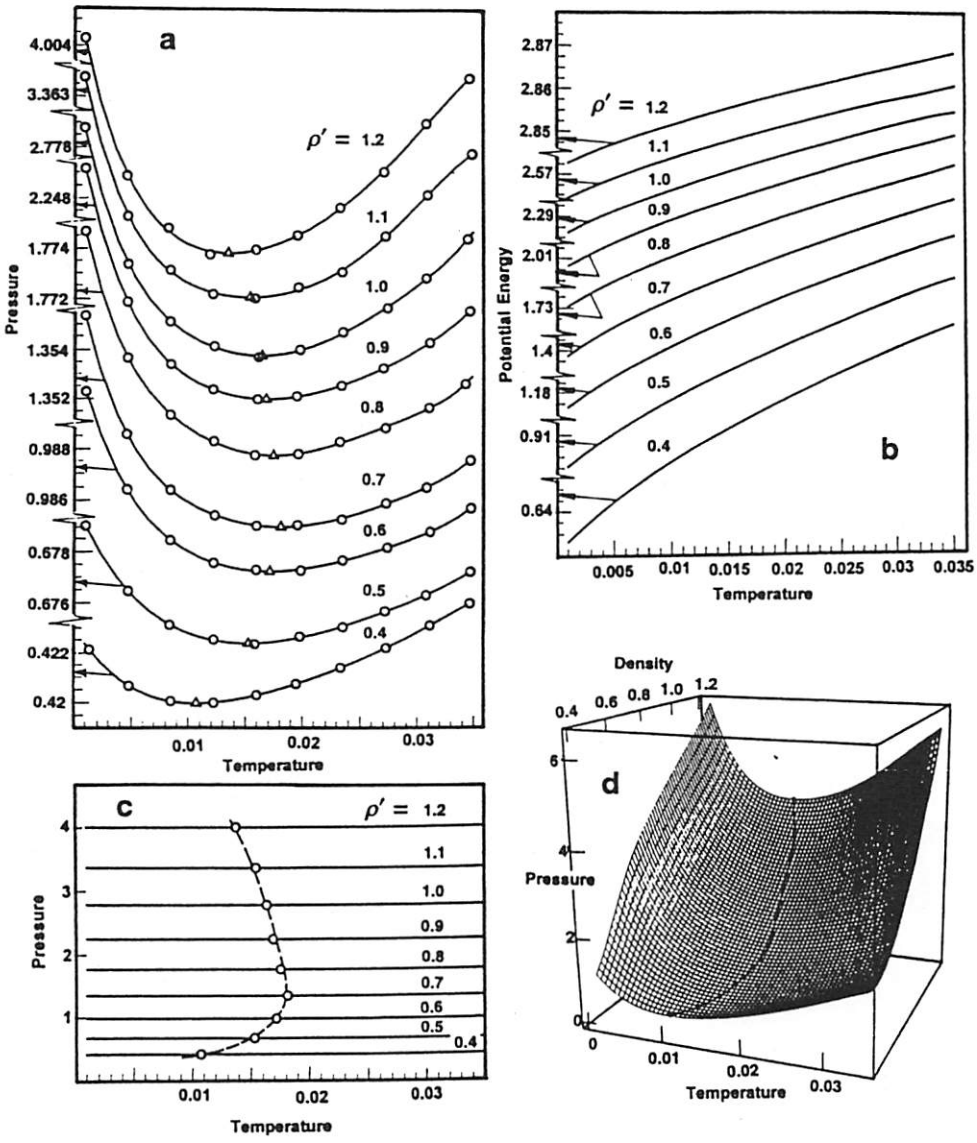

Figure 1: EOS of the Gaussian core model. *a*: isochoric pressure dependence (minima are marked by triangles, pressure axis is discontinuous); *b*: potential energy per particle; *c*: course of the TMD line (broken line) in the p,T–plane; *d*: 3D representation of the EOS (units: see text).

4. References

1 Stillinger, F.H., Stillinger, D.K.: Negative thermal expansion in the Gaussian core model; Physica **A 244** (1997), 358–369

2 Debenedetti, P.G.: Metastable Liquids — Concepts and Principles; Princeton University Press 1996

3 Mishima, O., Stanley, H.E.: The relationship between liquid, supercooled and glassy water; Nature **396** (1998), 329–335

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