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Positivity of pressure in the canonical Gibbs ensemble

© Ikhtier H. Umirzakov
Laboratory for Simulation. Institute of Thermal Physics, SB RAS. Lavrent'ev Pr., 1. Novosibirsk, 630090. Russia. Phone: +7 (383) 354-20-17. E-mail: tepliza@academ.org

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Abstract

It is proved within the framework of the classical canonical Gibbs ensemble *(N,V,T) = const* that the equilibrium pressure is non-negative for any potential independent of density. It is shown that: 1) the pressure can be negative in a macroscopic system if the interaction potential depends on the density; 2) the pressure is non-negative if the density-dependent interaction potential does not include attraction; 3) the pressure can be negative only if the potential depends on the density and it is not fully repulsive.

Physical consistency criterion (inequality) obtained for exact and approximate solutions of the equations for the pair correlation function.

It is shown that if we assume that Van der Waals equation of state obtained for a system of particles interacting via the potential energy independent of density, than there is a triple point in this system at which the temperature and pressure are not equal to zero. Formula was obtained for estimating the temperature and density of the liquid at the triple point.

It is shown that the equation of state of hard spheres with interaction energy described by Katz potential is not exact, its theoretical derivation contains a hidden error, and this equation must be supplemented by condition of positivity of the pressure at finite temperature and density.