Pramāṇa – J. Phys., Vol. 35, No. 6, December 1990, pp. 533–555. © Printed in India.

Quantum corrections to thermodynamics of polar hard sphere fluids

BALRAM RAI*, NAGENDRA PRASAD and SURESH K SINHA

Department of Physics, L S College, Bihar Univerity, Muzaffarpur 842 001, India
Permanent address: Department of Physics, M S S G College, (Bihar University), Areraj 845 411, East Champaran, India

MS received 28 February 1989; revised 2 July 1990

Abstract. The quantum corrections to the thermodynamic properties of polar hard sphere fluids and fluid mixtures are estimated taking into account the influence of dipole and quadrupole moments. Expressions are given for the second virial coefficient, free energy and pressure and results are given for different values of μ^* and θ^*. The first order quantum correction arises due to the translational contribution only. The quantum effect increases with density, μ^* and θ^*. Numerical results are also estimated for binary mixtures of (i) hard spheres and dipole hard spheres and (ii) hard spheres and quadrupole hard spheres. The 'excess' free energy for dipole hard sphere binary mixture is also reported. It is found that the 'excess' quantum effect depends on the concentration and the particle diameter ratio and increases with increase of μ^* and θ^*.

Keywords. Polar hard sphere fluid; dipole moments; quadrupole moments; semiclassial fluid; quantum corrections; free energy; equation of state.

PACS No. 61·25

1. Introduction

This paper estimates the quantum corrections to the thermodynamic properties of simple polar fluid and fluid mixtures. The simplest model for such fluids is hard spheres with imbedded point dipoles and point quadrupoles. The pair potential for such a system is given by

$$u_{\alpha\gamma}(x_1, x_2) = u_{\alpha\gamma}^{\mathrm{HS}}(r_{12}) + u_{\alpha\gamma}^{a}(x_1, x_2), \tag{1}$$

where $u_{\alpha\gamma}^{\mathrm{HS}}(r_{12})$ is the hard sphere potential and $u_{\alpha\gamma}^{a}(x_1, x_2)$ is the angle dependent part of the pair potential. In (1) the vector $x_i \equiv (\bar{r}_i, \omega_i)$ represents both the position of the centre of mass and orientation of the ith molecule. For polar fluids we take

$$u_{\alpha\gamma}^{a} = u_{\alpha\gamma}^{dd} + u_{\alpha\gamma}^{dq} + u_{\alpha\gamma}^{qq}, \tag{2}$$

where $u_{\alpha\gamma}^{dd}$ is the interaction between the permanent dipole moment of molecules of species α and γ, $u_{\alpha\gamma}^{dq}$ is the interaction between the dipole moment in one molecule and the quadrupole moment in other molecule and $u_{\alpha\gamma}^{qq}$ is the interaction between the quadrupole moments of the molecules. They are expressed as

$$u_{\alpha\gamma}^{dd} = \frac{\mu_\alpha \mu_\gamma}{r^3}[\sin\theta_\alpha \sin\theta_\gamma \cos\phi_{\alpha\gamma} - 2\cos\theta_\alpha \cos\theta_\gamma], \tag{3}$$