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Equilibrium properties of a semiclassical fluid with square-well plus hard core potential

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Abstract. A cluster expansion theory, in which the quantum hard sphere system is taken as a reference system and the attractive interactions as a perturbation, is applied to calculate the equilibrium properties of the square-well fluid in the semiclassical limit. The radial distribution function and direct correlation function are obtained using the exponential approximation. The isothermal compressibility is also evaluated.

Keywords. Equilibrium properties; radial distribution function; direct correlation function; compressibility; cluster expansion theory.

1. Introduction

The square-well potential is, perhaps, the simplest potential function which takes into account both the attractive and repulsive features of intermolecular interactions although it is unrealistic in certain aspects. In the semiclassical limit, the quantum effects are small and can be treated as a correction to the classical behaviour. The contribution of the quantum corrections is usually calculated by using the Wigner-Kirkwood method (Wigner 1932; Kirkwood 1933) for the analytic potential and by using Hemmer-Jancovici method (Hemmer 1968; Jancovici 1969a, b) for the non-analytic potential.

Many authors (Mohling 1963; Nilson 1969; Edward 1970; Gibson 1970; D'Arruda and Hill 1970; Sinha and Singh 1977; Singh and Sinha 1978a) investigated the effect of quantum mechanics on the equilibrium properties of a fluid interacting via square-well plus hard-core potential. But most of these attempts were confined to the virial coefficients. In the case of a dense fluid, very little information is available. Recently Singh and Sinha (1979) have calculated the quantum corrections to the thermodynamic properties of a dense fluid with square-well plus hard-core potential.

Singh and Sinha (1978b) have also developed a method for calculating the equilibrium properties of a semiclassical fluid, using the quantum hard sphere as a reference system and the attractive interaction as a perturbation. This approach is based on the assumption that, for a dense fluid, the quantum effects are largely determined by the repulsion due to the hard core and the attractive interactions play a minor role. The effect of perturbation is expressed in terms of the 'renormalised potential'. The exponential approximation for correlation functions may provide an accurate theory for semi-classical fluids.

In this paper, we adopt this method to investigate the correlation functions and isothermal compressibility of a semiclassical fluid, whose molecules interact via square-well plus hard-core potential. We calculate the radial distribution function (RDF), direct correlation function (DCF) and isothermal compressibility. However, the exchange effect is not considered in this paper.

2. Correlation functions

We consider a fluid in the semiclassical limit, whose molecules interact via the square-well (SW) plus hard-core potential, defined by

$$\begin{aligned} u(r) &= \infty \qquad r < d, \\ &= -\epsilon \qquad d < r < \eta d, \\ &= 0 \qquad r > \eta d, \end{aligned} \tag{1}$$

where d is the hard sphere diameter, ϵ the depth of the well and η the width of the well. We may write the potential in the form

$$u(r) = u_{\rm hs}(r) + u_p(r), \tag{2}$$

where $u_{\rm hs}(r)$ is the hard sphere (reference) potential and

$$\begin{aligned} u_p(r) &= -\epsilon \qquad d < r < \eta d, \\ &= 0 \qquad r > \eta d, \end{aligned} \tag{3}$$

is the perturbation. The effect of perturbation is expressed in terms of the 'renormalised potential' $\mathscr{C}(r)$ defined by (Singh and Sinha 1978a)

$$\mathscr{C}(r) = \frac{1}{(2\pi)^3 \rho^2} \int d\mathbf{k} \exp(i\mathbf{k}\cdot\mathbf{r}) \left[\frac{P(\mathbf{k})}{1 - P(\mathbf{k})}\right] F_{\rm hs}(\mathbf{k}), \tag{4}$$

where $P(\mathbf{k}) = F_{\rm hs}(\mathbf{k})\, \phi(\mathbf{k}) \cdot \phi(\bar{k})$ and $F_{\rm hs}(\bar{k})$ are the Fourier transforms of $\phi(r)$ $[\equiv -\beta u_p(r)]$ and $F_{\rm hs}(r)$ [$F_{\rm hs}(r)$ is the reference hypervertex function].

The exponential approximation for the RDF $g(r)$ is given by

$$g_{\rm exp}(r) = g_{\rm hs}(r) \exp \mathscr{C}(r), \tag{5}$$

where $g_{\rm hs}(r)$ is the RDF of the quantum hard sphere fluid. The 'exp' approximation for the DCF $\mathscr{C}(r)$ is

$$\mathscr{C}_{\rm exp}(r) = \mathscr{C}_{\rm hs}(r) + \phi(r) - \mathscr{C}(r) + g_{\rm hs}(r)\,[\exp \mathscr{C}(r) - 1], \tag{6}$$

where $\mathscr{C}_{\rm hs}(r)$ is the DCF of the quantum hard sphere fluid.

The values of the RDF for the SW fluid with $\eta=1{\cdot}50$ obtained under 'exp' approximation, are given in figure 1 for $\pi^*=0{\cdot}593$ at $\rho^*(\equiv\rho d^3)=0{\cdot}30$, $T^*(\equiv kT/\epsilon)=1{\cdot}40$. Here $\pi^*=h/d\sqrt{m\epsilon}$ is the quantum mechanical parameter and for neon $\pi^*=0{\cdot}593$. The values of the quantum hard sphere RDF, which is obtained by using the 'exp' approximation given by Sinha and Singh (1977), are also shown in the figure. On comparison, we find that the effect of the attractive perturbation on the RDF is substantial, which decreases with the increase of r. In the neighbourhood of two points at $r=d$, and ηd, the effect is more pronounced and makes a significant change in the RDF of the fluid.

The values of the DCF, calculated in the 'exp' approximation, are plotted in figure 2 for $\pi^*=0{\cdot}593$ at $\rho^*=0{\cdot}30$, $T^*=1{\cdot}40$. The quantum hard sphere DCF,

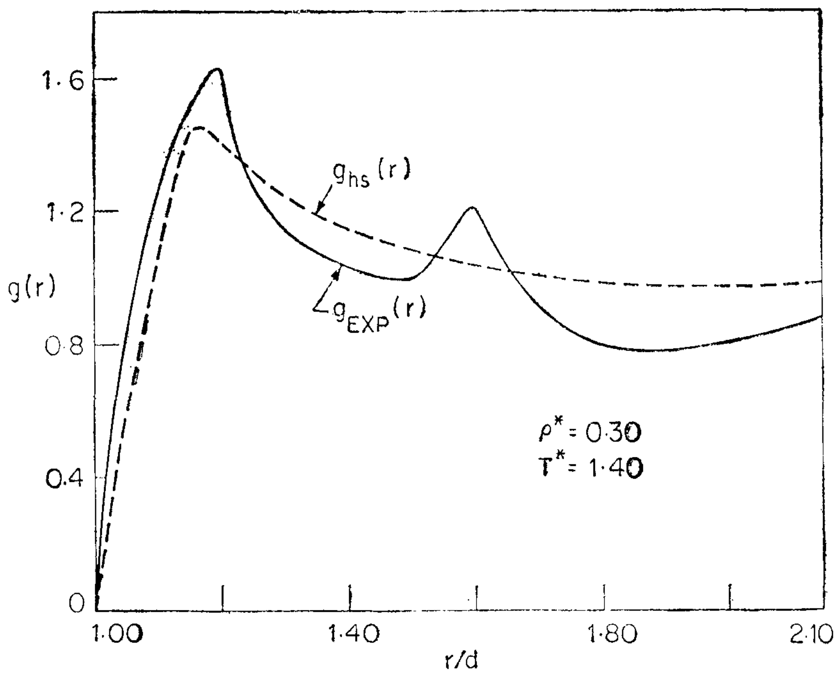

Figure 1. Radial distribution function for a square-well fluid with $\eta=1{\cdot}50$ in the semiclassical limit at $\rho^*=0{\cdot}30$, $T^*=1{\cdot}40$ and $\pi^*=0{\cdot}593$.

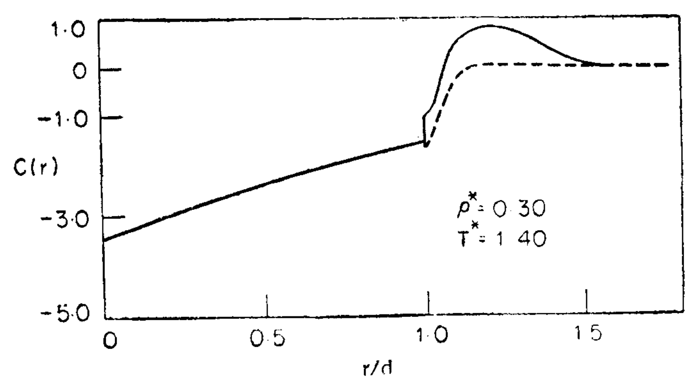

Figure 2. Direct correlation function for a square-well fluid with $\eta=1{\cdot}50$ in the semiclassical limit at $\rho^*=0{\cdot}30$, $T^*=1{\cdot}40$ and $\pi^*=0{\cdot}593$.

obtained under the ' exp ' approximation, are also given for comparison. Since $\phi(r)$ and $\mathscr{C}(r)$ are zero for $r \leqslant d$, the DCF inside the hard-core remains unaffected due to the attractive perturbation. In the region $r \geqslant d$, the effect of perturbation on the DCF is substantial.

3. Isothermal compressibility

In this section, we use the expression for the DCF [equation (6)] to evaluate the isothermal compressibility of a SW fluid in the semiclassical limit, which is given by

$$\rho K/\beta=[1-4\pi\rho \int_0^\infty \mathscr{C}(r)r^2dr]^{-1}, \tag{7}$$

where $K = \bar{\rho}^1 (\partial\rho/\partial P)_T$,

is known as isothermal compressibility and $\mathscr{C}(r)$ is the direct correlation function.

Substituting (6) in (7), we get an expression for the compressibility equation, which may be called the ' exp ' approximation,

$$K_{\exp} = K_{\mathrm{hs}}\left[1+\frac{\rho K_{\mathrm{hs}}}{\beta}(A_1+A_2)\right]^{-1}, \tag{8}$$

where $$A_1 = -4\pi\rho \int_d^{\eta d} \phi(r)r^2\,dr = \frac{4\pi}{3}\frac{\rho d^3}{T^*}(\eta^3-1), \tag{9}$$

$$A_2 = -4\pi\rho \int_d^\infty [g_{\mathrm{hs}}(r)-1]\,\mathscr{C}(r)r^2\,dr$$

$$-4\pi\rho \int_d^\infty g_{\mathrm{hs}}(r)\,[\exp \mathscr{C}(r)-1-\mathscr{C}(r)]\,r^2\,dr, \tag{10}$$

and $$\rho K_{\mathrm{hs}}/\beta = \left[1-4\pi\rho \int_0^\infty \mathscr{C}_{\mathrm{hs}}(r)\,r^2\,dr\right]^{-1}. \tag{11}$$

Here K_{hs} is the isothermal compressibility of the quantum hard sphere fluid (Sinha 1978).

The values of the isothermal compressibility given in table 1, show that the effect of the attractive tail is appreciable at all densities.

Table 1. Values of the isothermal compressibility for a SW fluid with $\eta=1{\cdot}50$ in the semiclassical limit under the exponential approximation for $\pi^*=0{\cdot}593$

ρ^*	T^*	$\frac{\rho K_{\mathrm{hs}}}{\beta}$	$\frac{\rho K_{\exp}}{\beta}$	$\frac{K_{\exp}}{K_{\mathrm{hs}}}$
0·30	1·40	0·2611	0·1783	0·6829
0·60	1·40	0·0997	0·0707	0·7091

4. Conclusion

The correlation function of the square well fluid in the semiclassical limit has been evaluated using the method given by Singh and Sinha (1978b). The DCF values have been used to evaluate the isothermal compressibility. The results show that the effect of attractive tail on the correlation functions and isothermal compressibility of the SW fluid is substantial at density $\rho d^3 = 0{\cdot}3$. At a low density, the attractive forces may have a significant effect on the structural and thermodynamic properties of a fluid. However, at a higher density, the effect of attractive tail is not expected to be significant.

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