

Thermodynamic properties of a two-dimensional square-well fluid

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Abstract. Analytic expressions for the thermodynamic properties of a classical two-dimensional square-well fluid and the first quantum correction to them are derived using the Barker-Henderson perturbation theory. Numerical results are reported. It is found that the quantum effect, which increases with increase of density, is largely determined by the hard-core and the attractive tail has a minor effect at high density.

Keywords. Helmholtz free energy; equation of state; internal energy; internal heat capacity; quantum effects.

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1. Introduction

In this paper, the influence of quantum effect on the thermodynamic properties of nearly classical two-dimensional (2-D) fluid of molecules interacting *via* the square-well (sw) potential is studied. Although ideally flat systems seldom occur, the adsorbed film can be reduced to a 2-D model by a Taylor series expansion, where the gas-substrate interaction is treated as a perturbation (Steele 1974). For most systems of physical interest, the 2-D approximation is a useful model even when the correction terms are neglected. This is evident from the experimental studies of the adsorption of krypton on graphite (Thomy and Duval 1970; Putnam and Fort 1975) and mobile adsorbed monolayers of helium (Bretz *et al* 1973), which indicate that the adsorbed molecules behave in many ways as a 2-D fluid. However the quantitative differences between the 2-D model and the adsorbed gas is presumably due to the interaction of the gas and the substrate. Thus the 2-D fluid is of interest because it is used as a model of the adsorbed film (Steele 1973; Dash 1975; Lado 1975) and as a starting point in a perturbational treatment of the effect of the gas-substrate interactions (Steele 1974). The sw model is the simplest potential model, which takes into account both the attractive and repulsive features of interactions. When this potential model is used, one can estimate the influence of the attractive tail on the quantum effects.

In the semiclassical limit (*i.e.* in the high temperature limit), the quantum effects are small and can be treated as a correction to the classical system. The usual way of studying the contribution of quantum corrections is to expand the physical property of interest in ascending power of Planck's constant \hbar . The first term is the classical value and the other terms give the contributions arising due to quantum effects. For hard-core system we use the Hemmer-Jancovici (Hemmer 1968; Jancovici 1969) method, in which the expansion is made in terms of modified Ursel function U_m^* .

In the quantum sw fluid, only dilute gas at high temperature has been studied (Sinha *et al* 1982). However, no work is available for a dense fluid.

The success of this approach is based on an understanding of the thermodynamic properties and radial distribution function (RDF) of the classical fluid. These properties can be calculated using the perturbation theory, where the repulsive part of the intermolecular potential is treated as the reference and the attractive part is considered as the perturbation. One such theory is given by Barker and Henderson (1967). They have used their perturbation theory to give an expression for the Helmholtz free energy of a classical sw fluid. This expression can be used even for a 2-D system.

The purpose of the present paper is two-fold. First we derive the analytic expressions for the thermodynamic properties of 2-D sw fluid. Second, we estimate the quantum effects on the thermodynamic properties of the dense fluid at high temperature. In §2 we discuss the basic theory to calculate the thermodynamic properties of the 2-D hard-core fluid in the semiclassical limit. Section 3 is devoted to study the thermodynamic properties of the classical 2-D sw fluid, using the perturbation theory. Section 4 considers the leading quantum correction.

2. Basic formalism

Consider a 2-D fluid, whose molecules interact *via* a sw plus hard-core potential

$$\begin{aligned} u(r) &= \infty, & r < \sigma \\ &= -\varepsilon, & \sigma < r < \xi\sigma \\ &= 0, & r > \xi\sigma, \end{aligned} \quad (1)$$

where σ is the hard-disc diameter, ε the well depth and ξ the potential cut-off. We divide the pair potential $u(r)$ as

$$u(r) = u_{\text{hd}}(r) + u_p(r), \quad (2)$$

where $u_{\text{hd}}(r)$ is the hard-disc potential treated as a reference potential and

$$\begin{aligned} u_p(r) &= -\varepsilon, & \sigma < r < \xi\sigma \\ &= 0, & r > \xi\sigma \end{aligned} \quad (3)$$

is the perturbation.

At moderately high temperatures (semiclassical limit), where the deviation from the classical behaviour is small, the Slater sum W_N can be written as (Hemmer 1968; Jancovici 1969)

$$W_N = W_N^c W_N^m, \quad (4)$$

where

$$W_N^c(1, 2, \dots, N) = \exp\left[-\beta \sum_{i < j} u(i, j)\right] \quad (5)$$

$$\beta = (kT)^{-1}.$$

Here W_N^c is the Boltzmann factor and W_N^m is a function which measures the deviation from the classical behaviour. It is well known (Hemmer 1968; Jancovici 1969) that

$$\begin{aligned} W_N^m(1, 2, \dots, N) &= 1 + \sum_{i < j} U_2^m(i, j) + \sum_{i < j < k} U_3^m(i, j, k) \\ &+ \dots, \end{aligned} \quad (6)$$

where U_l^m is the l -particle 'modified' Ursell function. The two-particle 'modified' Ursell function $U_2^m(r)$ is expressed as (Sinha and Singh 1981; Sinha *et al* 1982)

$$\begin{aligned} U_2^m(r) &= -\exp\left[-\frac{2\pi}{(\lambda/\sigma)^2}(r/\sigma-1)^2\right] + 0(\lambda^2) \\ &= -\frac{(\lambda/\sigma)}{2\sqrt{2}}\delta(r/\sigma-1) + 0((\lambda/\sigma)^2), \end{aligned} \quad (7)$$

where λ is the thermal wavelength and δ is the Dirac δ -function.

The first order quantum correction to the thermodynamic properties of the hard-core fluid is obtained from these terms which are linear in U_2^m . For the second order quantum correction, one has to consider terms involving U_2^m , U_3^m and $U_2^m U_2^m$, and so on. At high temperature, where quantum correction terms are small, one can consider only the first order quantum correction term, neglecting the higher order terms. Then the expression for the Helmholtz free energy correct to the first order quantum correction is given by

$$\frac{\beta A}{N} = \frac{\beta A^c}{N} - \frac{1}{2}\rho \int g^c(r) U_2^m(r) d\vec{r}, \quad (8)$$

where A^c and $g^c(r)$ are respectively the free energy and radial distribution function (RDF) of the classical 2-D system. In the canonical ensemble, the RDF $g^c(1, 2)$ is defined as

$$\rho^2 g^c(1, 2) = N(N-1) \frac{\int \dots \int W_N^c(1, 2, \dots, N) \prod_{i=3}^N d\vec{r}_i}{\int \dots \int W_N^c(1, 2, \dots, N) \prod_{i=1}^N d\vec{r}_i} \quad (9)$$

Here ρ is the number density.

The first quantum correction to the Helmholtz free energy of the 2-D hard-core fluid is obtained, using (7) in (8). Thus

$$\beta A/N = (\beta A^c/N) + A_1, \quad (10)$$

where

$$A_1 = \frac{\pi}{2\sqrt{2}}(\rho\sigma^2)g^c(\sigma)(\lambda/\sigma). \quad (11)$$

For pressure, we find

$$\beta P/\rho = (\beta P^c/\rho) + P_1 \quad (12)$$

with

$$P_1 = \frac{\pi}{2\sqrt{2}}(\rho\sigma^2)\frac{\partial}{\partial(\rho\sigma^2)}[(\rho\sigma^2)g^c(\sigma)](\lambda/\sigma). \quad (13)$$

Other thermodynamic properties of the 2-D hard-core fluid can be obtained, using (10). Equation (10) is a high temperature approximation which is valid for a whole range of density provided (λ/σ) is small so that the contribution of $0((\lambda/\sigma)^2)$ can be neglected.

3. Thermodynamic properties of classical sw fluid

Barker and Henderson (1967) have used their perturbation theory to obtain an expression for the Helmholtz free energy of the classical sw fluid. We use the Barker-Henderson approach to calculate the Helmholtz free energy of a 2-D fluid. Thus we expand the Helmholtz free energy A^c of the system as a Taylor series about the hard-disc value A_{hd}^c as

$$\frac{A^c - A_{hd}^c}{kT} = -\beta\epsilon \langle n \rangle_0 - \frac{1}{2}(\beta\epsilon)^2 [\langle n^2 \rangle_0 - \langle n \rangle_0^2], \quad (14)$$

where $\langle n \rangle_0$ is the mean number of molecules in the range σ to $\xi\sigma$ and is given by

$$\langle n \rangle_0 = \pi N \rho \int_{\sigma}^{\xi\sigma} g_{hd}^c(r) r dr. \quad (15)$$

Here $g_{hd}^c(r)$ is the RDF of the classical hard-disc fluid. The fluctuation of the number is given by

$$\langle n^2 \rangle_0 - \langle n \rangle_0^2 = \langle n \rangle_0 kT (\partial\rho/\partial P_{hd}^c)_\beta, \quad (16)$$

where $(\partial\rho/\partial P_{hd}^c)_\beta$ is the macroscopic isothermal compressibility. One can obtain better result by replacing $(\partial\rho/\partial P_{hd}^c) g_{hd}^c(r)$ in (16) by

$$\frac{\partial}{\partial P_{hd}^c} [\rho g_{hd}^c(r)]$$

(Barker and Henderson 1967). Thus the expression for the Helmholtz free energy for a classical 2-D sw fluid can be written as

$$\begin{aligned} \frac{A^c - A_{hd}^c}{N kT} &= -\pi(\beta\epsilon)\rho \int_{\sigma}^{\xi\sigma} g_{hd}^c(r) r dr \\ &\quad - \frac{1}{2}\pi(\beta\epsilon^2)\rho \left(\frac{\partial\rho}{\partial P_{hd}^c} \right) \frac{\partial}{\partial\rho} \left[\rho \int_{\sigma}^{\xi\sigma} g_{hd}^c(r) r dr \right], \end{aligned} \quad (17)$$

where

$$kT \left(\frac{\partial\rho}{\partial P_{hd}^c} \right) = 1 + 2\pi\rho \int_0^{\infty} [g_{hd}^c(r) - 1] r dr. \quad (18)$$

Using (2), the RDF of classical 2-D sw fluid can be written as

$$g^c(r) = g_{hd}^c(r) + (\beta\epsilon) g_1^c(r) + \dots, \quad (19)$$

where $g_1^c(r)$ is the first order perturbation correction to the RDF. Equation (19) can be used to obtain the Helmholtz free energy as (Barker and Henderson 1976)

$$\begin{aligned} \frac{A^c - A_{hd}^c}{N kT} &= -\pi(\beta\epsilon)\rho \int_{\sigma}^{\xi\sigma} g_{hd}^c(r) r dr \\ &\quad - \frac{1}{2}\pi(\beta\epsilon)^2\rho \int_{\sigma}^{\xi\sigma} g_1^c(r) r dr. \end{aligned} \quad (20)$$

Comparing (17) and (20)

$$g_1^c(r) = kT (\partial\rho/\partial P_{hd}^c) \frac{\partial}{\partial\rho} [\rho g_{hd}^c(r)]. \quad (21)$$

Equation (21) is not expected to provide good result for the RDF as it predicts incorrectly that $g_1^c(r) = 0$ beyond the range of $u_p(r)$ (Barker and Henderson 1976). However it may be used to calculate the quantum corrections to the thermodynamic properties.

Now we solve (17) to obtain an analytic expression for the free energy. To evaluate the integral of (17), we write

$$\int_{\sigma}^{\xi\sigma} g_{\text{hd}}^c(r) r dr = \int_0^{\infty} [g_{\text{hd}}^c(r) - 1] r dr - \int_{\xi\sigma}^{\infty} [g_{\text{hd}}^c(r) - 1] r dr + \int_0^{\xi\sigma} r dr. \quad (22)$$

If we approximate $g_{\text{hd}}^c(r) \approx 1$ for $r > \xi\sigma$, we can neglect the second integral in (22) and write

$$\int_{\sigma}^{\xi\sigma} g_{\text{hd}}^c(r) r dr = \int_0^{\infty} [g_{\text{hd}}^c(r) - 1] r dr + \frac{1}{2} \xi^2 \sigma^2. \quad (23)$$

The equation of state for a hard-disc fluid is given by (Henderson 1975)

$$(\beta P_{\text{hd}}^c / \rho) = (1 + \frac{1}{8} \eta^2) / (1 - \eta)^2, \quad (24)$$

where $\eta = \pi \rho \sigma^2 / 4$. This leads to the compressibility equation for the hard discs as

$$(\partial \rho / \partial P_{\text{hd}}^c) = \beta / a, \quad (25)$$

where

$$a = \frac{1 + \eta + \frac{3}{8} \eta^2 - \frac{1}{8} \eta^3}{(1 - \eta)^3}. \quad (26)$$

From (18) and (25), we get

$$\int_0^{\infty} [g_{\text{hd}}^c(r) - 1] r dr = \left(\frac{1 - a}{8\eta a} \right) \sigma^2, \quad (27)$$

Substituting (27) in (23) we get

$$\int_{\sigma}^{\xi\sigma} g_{\text{hd}}^c(r) r dr = \left[\frac{1 - a}{8\eta a} + \frac{1}{2} \xi^2 \right] \sigma^2. \quad (28)$$

Substituting (28) in (17), we obtain an analytic expression for the Helmholtz free energy of the classical 2-D sw fluid

$$\frac{A^c}{NkT} = \frac{A_{\text{hd}}^c}{NkT} + (\beta\epsilon) \frac{A_1^c}{NkT} + (\beta\epsilon)^2 \frac{A_2^c}{NkT}, \quad (29)$$

where

$$\frac{A_1^c}{NkT} = -\eta \left[2\xi^2 + \frac{1 - a}{2\eta a} \right], \quad (30)$$

$$\frac{A_2^c}{NkT} = -\frac{\eta}{a} \left[\xi^2 - \frac{\left(1 - \frac{11}{16}\eta\right)}{a^2 (1 - \eta)^4} \right], \quad (31)$$

and A_{hd}^c is given by (Henderson 1975)

$$\frac{A_{hd}^c}{NkT} = \frac{9}{8} \frac{\eta}{(1-\eta)} - \frac{7}{8} \ln(1-\eta). \quad (32)$$

Equation (32) is valid for $\eta < 1$. Hence (29) is correct even for high density ($\rho\sigma^2 < 4/\pi$).

The equation of state for the classical sw fluid can be obtained from the relation

$$\beta P^c/\rho = \frac{\beta P_{hd}^c}{\rho} + \eta \frac{\partial}{\partial \eta} \left[\frac{A^c - A_{hd}^c}{NkT} \right]. \quad (33)$$

Substituting (29), we obtain

$$(\beta P^c/\rho) = \frac{\beta P_{hd}^c}{\rho} + (\beta\epsilon)(\beta P_1^c/\rho) + (\beta\epsilon)^2(\beta P_2^c/\rho), \quad (34)$$

where

$$\begin{aligned} (\beta P_1^c/\rho) &= -2\eta \left[\xi^2 - \frac{\left(1 + \frac{11}{16}\eta\right)}{a^2(1-\eta)^4} \right], \quad (35) \\ (\beta P_2^c/\rho) &= -\frac{\eta}{a} \left\{ \left[\xi^2 - \frac{\left(1 + \frac{11}{16}\eta\right)}{a^2(1-\eta)^4} \right] \left[1 - 4 \frac{\eta\left(1 + \frac{11}{16}\eta\right)}{a(1-\eta)^4} \right] \right. \\ &\quad \left. + \frac{\eta}{a^3} \left[8 \frac{\left(1 + \frac{11}{16}\eta\right)^2}{(1-\eta)^8} - \frac{3}{16} a \frac{(25 + 11\eta)}{(1-\eta)^5} \right] \right\}, \quad (36) \end{aligned}$$

and P_{hd}^c is given by (24).

Expanding (34) in power of η we obtain expression for second and third virial coefficients for the classical sw fluid

$$B_2^c = b_0 [1 - (\xi^2 - 1)(\beta\epsilon)(1 + \beta\epsilon/2)], \quad (37)$$

$$\begin{aligned} B_3^c &= b_0^2 [0.781 - \frac{5}{32}(\beta\epsilon) + 2(\beta\epsilon)^2 \{(\xi^2 - 1) \\ &\quad + \frac{25}{24}\}], \quad (38) \end{aligned}$$

where

$$b_0 = \pi N \sigma^2/2.$$

The internal energy U_i^c and the internal heat capacity C_i^c of the classical sw fluid are given by (Barker and Henderson 1976)

$$U_i^c/NkT = (\beta\epsilon) \frac{A_1^c}{NkT} + 2(\beta\epsilon)^2 \frac{A_2^c}{NkT}, \quad (39)$$

$$C_i^c/Nk = -2(\beta\epsilon)^2 (A_2^c/NkT). \quad (40)$$

4. Quantum-correction to the thermodynamic properties

The first order quantum correction to the free energy equation (11) is given in terms of $g^c(\sigma)$, which can be obtained using (19).

In terms of the quantum parameter $\pi^* = h/\sigma\sqrt{m\varepsilon}$ and $T^* = kT/\varepsilon$, (11) can be written as

$$A_1 = A_1^* \pi^*, \quad (41)$$

with

$$A_1^* = [a_0(\eta) + a_1(\eta)/T^*]/\sqrt{T^*}, \quad (42)$$

where

$$a_0(\eta) = \frac{1}{\sqrt{\pi}} \eta g_{\text{hd}}^c(\sigma), \quad (43)$$

$$a_1(\eta) = \frac{1}{\sqrt{\pi}} \eta g_1^c(\sigma). \quad (44)$$

Using the relation (Barker and Henderson 1976)

$$\beta P_{\text{hd}}^c/\rho = 1 + 2\eta g_{\text{hd}}^c(\sigma), \quad (45)$$

and (24), $g_{\text{hd}}^c(\sigma)$ is expressed as

$$g_{\text{hd}}^c(\sigma) = (1 - \frac{7}{16}\eta)/(1 - \eta)^2, \quad (46)$$

Using (21), one can easily obtain an expression for $g_1^c(\sigma)$. Knowing $g_{\text{hd}}^c(\sigma)$ and $g_1^c(\sigma)$ we can obtain expressions for $a_0(\eta)$ and $a_1(\eta)$ as

$$a_0(\eta) = \frac{1}{\sqrt{\pi}} \eta (1 - \frac{7}{16}\eta)/(1 - \eta)^2. \quad (47)$$

$$a_1(\eta) = \frac{1}{\sqrt{\pi}} \eta (1 + \frac{1}{8}\eta)/(1 + \eta + \frac{3}{8}\eta^2 - \frac{1}{8}\eta^3). \quad (48)$$

Equations (47) and (48) are the coefficients due to the hard-discs and attractive-tail potential respectively. They are valid for $\eta \leq 1$ (which covers the range of density considered in this paper).

For the first quantum correction to the pressure, we find

$$P_1 = P_1^* \pi^*, \quad (49)$$

where

$$P_1^* = \eta \frac{\partial A_1^*}{\partial \eta}. \quad (50)$$

Substituting (42), we obtain

$$P_1^* = [P_0(\eta) + P_1(\eta)/T^*]/\sqrt{T^*}, \quad (51)$$

where

$$P_0(\eta) = \frac{1}{\sqrt{\pi}} \eta (1 + \frac{1}{8}\eta)/(1 - \eta)^3, \quad (52)$$

$$P_1(\eta) = \frac{1}{\sqrt{\pi}} \eta \frac{(1 + \frac{1}{4}\eta - \frac{1}{4}\eta^2 + \frac{1}{4}\eta^3 + \frac{1}{64}\eta^4)}{(1 + \eta + \frac{3}{8}\eta^2 - \frac{1}{8}\eta^3)^2}. \quad (53)$$

From the expression for the pressure, the second and third virial coefficients of the 2-D sw fluid are given by

$$B_2 = B_2^c + B_2^l \pi^*, \quad (54)$$

where

$$B_2^l = \frac{b_0}{2\sqrt{\pi}} \left[1 + \frac{1}{T^*} \right] / \sqrt{T^*} \quad (55)$$

and

$$B_3 = B_3^c + B_3^l \pi^*, \quad (56)$$

where

$$B_3^l = \frac{b_0^2}{32\sqrt{\pi}} \left[25 + \frac{19}{T^*} \right] / \sqrt{T^*}. \quad (57)$$

Other thermodynamic properties can be similarly calculated. Thus the internal energy U_i and the internal heat capacity C_i of the sw fluid correct to the first order quantum correction are given by

$$U_i/N\varepsilon = (U_i^c/N\varepsilon) + U_1^* \pi^*, \quad (58)$$

where

$$U_1^* = \frac{1}{2} [a_0(\eta) + 3a_1(\eta)/T^*] \sqrt{T^*}, \quad (59)$$

and

$$\frac{C_1}{Nk} = \frac{C_i^c}{Nk} + C_1^* \pi^*, \quad (60)$$

where

$$C_1^* = \frac{1}{4} [a_0(\eta) - 3a_1(\eta)/T^*] / \sqrt{T^*}. \quad (61)$$

5. Results and discussions

We have evaluated the thermodynamic properties such as free energy and equation of state of the 2-D sw fluid with $\xi = 1.5$ in the semi-classical limit. In our calculations, we have used the method developed in §3 to calculate the classical values of the thermodynamic properties. The values of the first and second order perturbation corrections to the free energy A_1^c/NkT and A_2^c/NkT are reported in figure 1 which shows that $A_2^c/NkT < A_1^c/NkT$.

The first order quantum coefficients A_1^* and P_1^* for the free energy and pressure are calculated using (42) and (51) respectively. They are the sum of two terms: one arising due to the hard discs and the other due to the attractive perturbation. From a_n and p_n values ($n = 0, 1$) we find that at high densities ($\rho\sigma^2 \geq 0.5$), the main contribution to the quantum corrections comes from the hard discs while the contribution due to the sw tail is small. However at low density and/or low temperature, their effects are of comparable magnitude.

The A/NkT values for the 2-D sw fluid with $\xi = 1.5$ and the quantum parameter $\pi^* = 0.593$ are calculated using (10). They are shown in figure 2 as a function of $\rho\sigma^2$ for $T^* = 2.74, 1.35$ and 0.75 . The classical values, calculated from (29) are also demonstrated there. In figure 3 the $\beta P/\rho$ values are reported for $T^* = 2.74$, and 0.75 . The classical values are also demonstrated there. We find that the quantum effect increases with increase of density and decrease of temperature.

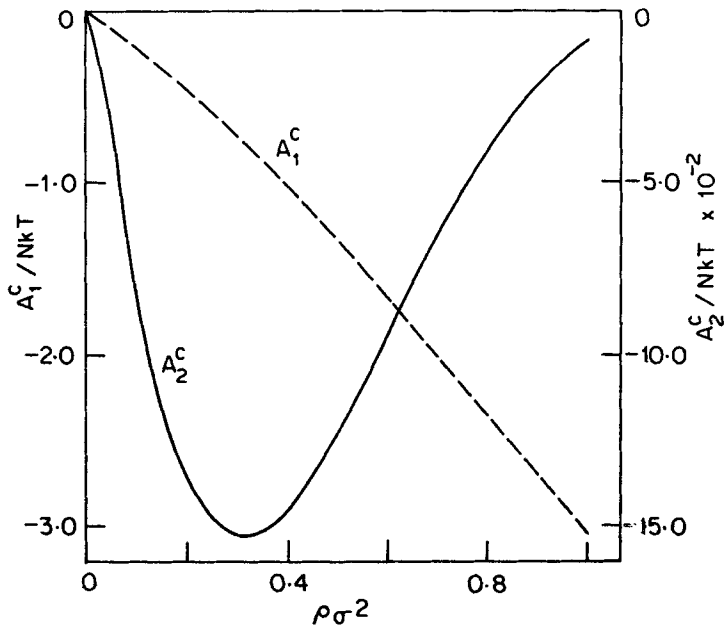


Figure 1. Values of A_1^c and A_2^c of 2-D sw fluid for $\zeta = 1.5$.

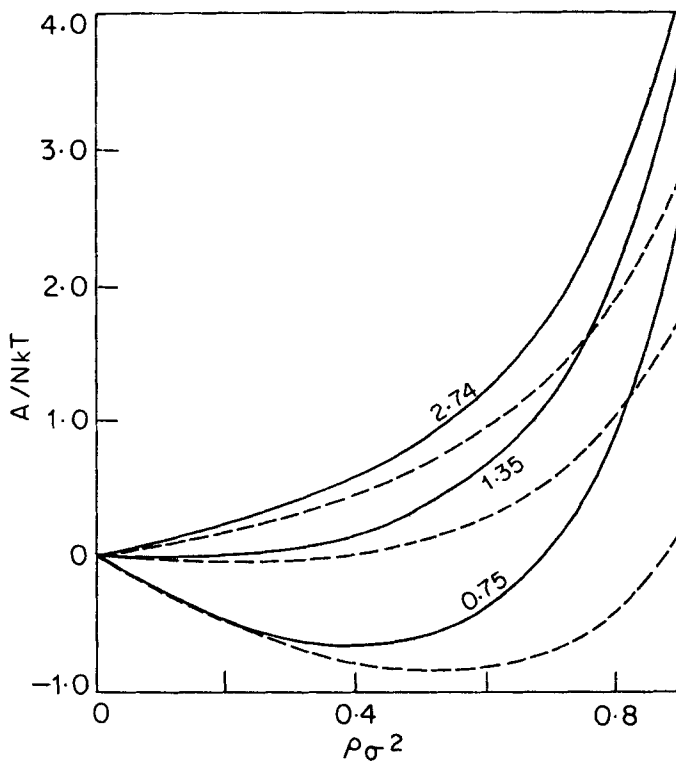


Figure 2. Values of A/NkT for 2-D sw fluid with $\zeta = 1.5$ and $\pi^* = 0.593$ as a function of $\rho\sigma^2$ for $T^* = 2.74, 1.35$ and 0.75 . The classical and semiclassical results are represented by the dashed and solid lines respectively.

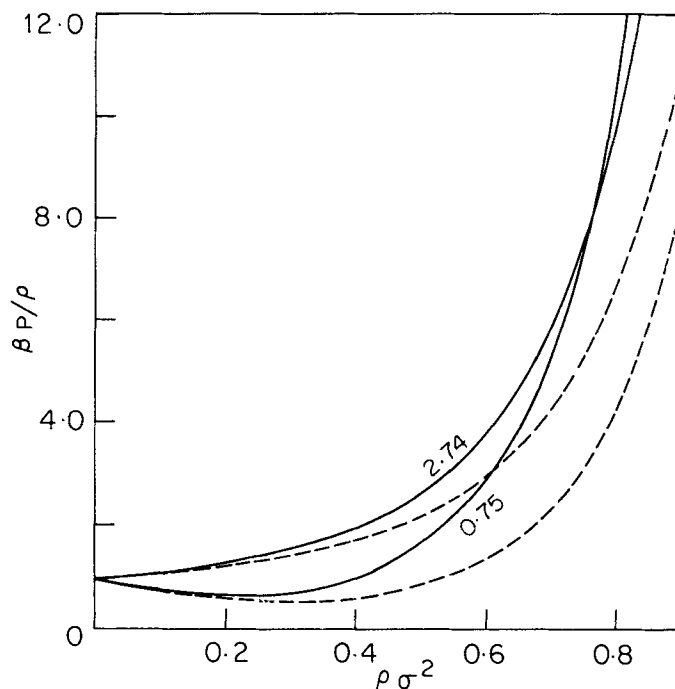


Figure 3. Values of $\beta P/\rho$ for 2-D sw fluid with $\zeta = 1.5$ and $\pi^* = 0.593$ as a function of $\rho\sigma^2$ for $T^* = 2.74$, and 0.75 . (key same as in figure 2).

In figure 4 the $U_i/N\varepsilon$ values are plotted as a function of $1/T^*$ for three values of $\rho\sigma^2$ (0.45, 0.6 and 0.85) and $\pi^* = 0.593$. The classical values are also shown in the figure. Here U_i is the excess internal energy with respect to the ideal gas at the same temperature and density. The excess internal energy increases with increase of temperature; the classical values increase steadily to a finite value as $T^* \rightarrow \infty$, while the quantum value increases faster and tends to infinity as $T^* \rightarrow \infty$.

In figure 5 we compare the internal heat capacity (*ie* heat capacity with respect to the ideal gas at the same density and temperature) C_i/Nk obtained from (60) with the classical values given by (40) for $\rho\sigma^2 = 0.6$ and 0.85 and $\pi^* = 0.593$. From the figure, we find that the quantum effect increases with the increase of density and decrease of temperature.

6. Conclusion

Using the Barker-Henderson perturbation theory, we have given analytic expressions for the thermodynamic properties of the classical 2-D sw fluid. Like 3-D fluid (Ponce and Renon 1976), this approach is expected to provide good results at high densities. Using the perturbation theory for the RDF of the classical fluid, we have calculated the first quantum correction to the thermodynamic properties. It is found that the main quantum effect arises due to the hard core and contribution due to the attractive tail is small at high density and/or high temperature. At low densities, their contributions are

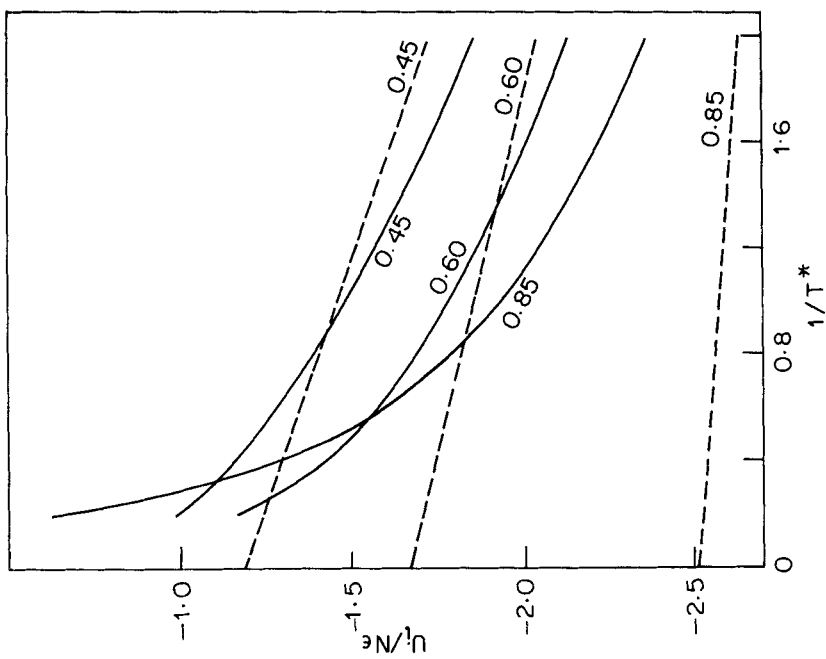


Figure 4. Values of $U_i/N\epsilon$ for 2-D sw fluid with $\xi = 1.5$ and $\pi^* = 0.593$ as a function of $1/T^*$ for $\rho\sigma^2 = 0.45, 0.6$ and 0.85 (key same as in figure 2).

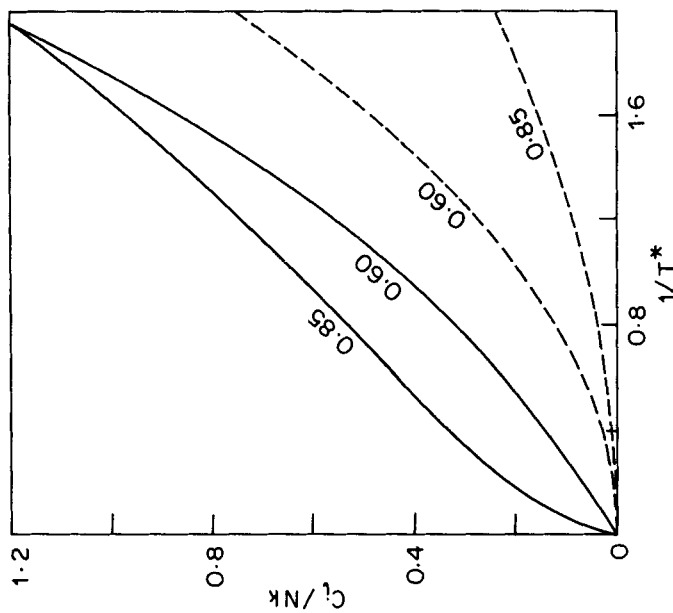


Figure 5. Values of C_i/Nk for 2-D sw fluid with $\xi = 1.5$ and $\pi^* = 0.593$ as a function of $1/T^*$ for $\rho\sigma^2 = 0.6$ and 0.85 (key same as in figure 2).

comparable. However, one should take into account the higher order quantum corrections to estimate the quantum effects at low temperatures.

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