Quantum corrections to the thermodynamic properties of a two-dimensional fluid with hard-core potential

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Abstract. A simple theory, based on the physical interpretation of the reciprocal of activity, is developed to evaluate the thermodynamic properties of a two-dimensional fluid in the semi-classical limit. The theory is applied to calculate the quantum corrections to the equation of state and excess free energy of two-dimensional fluids, whose molecules interact *via* hard-disc and square-well potential. It is found that the quantum effect increases with the increase of density and decrease of temperature.

Keywords. Equation of state; excess free energy; quantum corrections; two-dimensional fluid.

1. Introduction

The problem of calculating the properties of a two-dimensional fluid has been a subject of considerable interest in recent years. This is partly because of the fact that a two-dimensional picture has been used in predicting the properties of adsorbed films (Dash 1975; Steele 1974). Another reason for this is to know the effect of the dimensionality on the nature of these properties (Taxvaerd 1980; Abraham 1980; Baker *et al* 1981). Considerable progress has been made in recent years in the study of classical fluids. (Lado 1968; Henderson 1975, 1977; Steele 1976; Andrews 1976; Kratky 1978; Glandt and Fitts 1978). However, our understanding of the two-dimensional quantum fluid is not satisfactory (Siddon and Shick 1974). Recently the problem of calculating the equilibrium properties of two-dimensional fluids in the semi-classical limit has been a subject of considerable interest (Sinha and Singh 1981; Sinha *et al* 1981), but almost all these attempts have been confined to low density limit.

The purpose of this paper is two fold: one is to calculate the quantum corrections to the thermodynamic properties of a two-dimensional hard-core fluid at high temperature. The other is to know the extent to which the dimensionality of the system affects the nature of quantum effect.

A simple theory has recently been developed to evaluate the thermodynamic properties of three-dimensional semi-classical fluids, based on a physical interpretation of the reciprocal of activity (Singh and Sinha 1977, 1978, 1979).

In this paper, the theory, developed for the three-dimensional fluid, has been extended to the two-dimensional fluid.

In § 2, we outline the general theory for calculating the thermodynamic properties of a two-dimensional hard-core fluid in the semi-classical limit. Expressions are given in simple forms for the equation of state and excess free energy. § 3 is devoted to the classical two-dimensional fluid. The results for two-dimensional fluids with hard-disc and square-well potential are discussed in § 4.

2. A brief out-line of the theory

The thermodynamic properties of a two-dimensional fluid in the semi-classical limit can be calculated on the basis of the physical interpretation of the activity. Thus, the equation of state is given by (Singh and Sinha 1977)

$$\frac{\beta P}{\rho} = \frac{\beta P^c}{\rho} + \frac{1}{2} A + \frac{1}{3} B + \ldots, \tag{1}$$

and the excess free energy per particle is (Singh and Sinha 1978)

$$\beta f_E = \beta f_E^c + \tfrac{1}{2} A + \tfrac{1}{6} B + \ldots, \tag{2}$$

where

$$A = -\rho \int_d^\tau f_{12}^{\mathrm{II}} (1 + f_p^c(1,2)) \, d\bar{r}_{12}, \tag{3}$$

$$B = -\rho^2 \int_d^\tau f_{123}^{\mathrm{III}} (1 + f_{12}^c)(1 + f_{13}^c) \, d\bar{r}_{12} \, d\bar{r}_{13}, \tag{4}$$

P^c and f_E^c are respectively the pressure and excess free energy of a classical system, d is the hard-disc diameter and τ the potential cut off. For hard-disc plus attractive tail potential, f^l is given by

$$f^l = f_{\mathrm{hd}}^l + [1 + f_{\mathrm{hd}}^l] f_p^l, \tag{5}$$

where f_{hd}^l and f_p^l are the l-particle 'modified' Mayer functions, due to hard-disc potential (Sinha and Singh 1977 a, b) and due to perturbation potential (Sinha *et al* 1981) respectively. For a hard-disc system f_p^l reduces to zero.

With the help of (5), equations (3) and (4) can be evaluated in a series of λ/d. Equation (4) first contributes in the order of $(\lambda/d)^2$. The $(\lambda/d)^2$–contribution of the integral involving $f_{\mathrm{hd}}^{\mathrm{III}}$ of (4) comes from the cluster formation of three discs 1, 2, 3 in a plane in which two distances r_{12} and r_{13} lie within d and $d + \lambda$, while the third distance $r_{23} > d + \lambda$. Then, following the method of Sinha and Singh (1981), A and B are evaluated.

$$A = (\rho d^2) \left[C (\lambda/d) + D (\lambda/d)^2 + \ldots \right], \tag{6}$$

$$B = (\rho d^2)^2 E (\lambda/d)^2, \tag{7}$$

where C, D and E are functions of temperature (kT/ϵ) and depend upon the nature of u_p. For hard discs, they are independent of kT/ϵ.

Using (6) and (7), the results for the thermodynamic properties of a two-dimensional fluid can be obtained. Thus

$$\frac{\beta P}{\rho} = \frac{\beta P^c}{\rho} + P_{\mathrm{I}} (\lambda/d) + P_{\mathrm{II}} (\lambda/d)^2 + \ldots, \tag{8}$$

where $\quad P_{\mathrm{I}} = \tfrac{1}{2} (\rho d^2) C, \tag{9a}$

$$P_{\mathrm{II}} = \tfrac{1}{2} (\rho d^2) D + \tfrac{1}{3} (\rho d^2)^2 E, \tag{9b}$$

and

$$\beta f_E = \beta f_E^c + F_{\mathrm{I}} (\lambda/d) + F_{\mathrm{II}} (\lambda/d)^2 + \ldots, \tag{10}$$

where $\quad F_{\mathrm{I}} = \tfrac{1}{2} (\rho d^2) C, \tag{11a}$

$$F_{\mathrm{II}} = \tfrac{1}{2} (\rho d^2) D + \tfrac{1}{6} (\rho d^2)^2 E. \tag{11b}$$

One can easily express the thermodynamic properties in terms of reduced quantities $T^* = kT/\epsilon$ and $\pi^* = h/d (m \epsilon)^{1/2}$.

3. Classical two-dimensional fluid

In this section, we consider a two-dimensional classical fluid, whose molecules interact *via* a pair potential, given by

$$u(r) = u_{\mathrm{hd}}(r) + u_p(r), \tag{12}$$

where $\quad u_{\mathrm{hd}}(r) = \infty, \; r < d,$

$$= 0, \; r > d, \tag{13}$$

is the hard-disc potential, treated as a reference potential and $u_p(r)$ is the perturbation.

Andrews (1976) has obtained the thermodynamic properties of the classical fluid.

$$\frac{\beta P^c}{\rho} = \frac{\beta P_{\mathrm{hd}}^c}{\rho} + a, \tag{14}$$

and $\quad \beta f_E^c = \beta [f_E^c]_{\mathrm{hd}} + a, \tag{15}$

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$$\text{where} \qquad \alpha = -\pi \rho \int_d^\tau \{\exp[-\beta u(r)] - 1\} r \, d \, r. \qquad (16)$$

For a classical hard-disc fluid, Andrews (1976) has obtained an analytical equation for pressure, based on the third and fourth virial coefficients. The theory was further extended, based on the fifth virial coefficient, by Kratky (1978), who has given an analytic expression for the equation of state. We can obtain the excess free energy per particle for the classical hard-disc fluid, using the Kratky equation of state by the relation

$$\beta f_E^c = \int_0^\rho \left(\frac{\beta P^c}{\rho'} - 1 \right) \frac{d\rho'}{\rho'}. \qquad (17)$$

4. Results and discussion

4.1 *Hard-disc model*

Here, we consider a two-dimensional fluid, whose molecules interact *via* a hard-disc potential (12). In this case, $u_p = 0$ and the values of C, D and E can be obtained from (3) and (4) respectively

$$C = \pi/\sqrt{2}, \qquad (18a)$$

$$D = 1/3, \qquad (18b)$$

$$E = 0.46698 \, \pi^2. \qquad (18c)$$

The values of $\beta P/\rho$ and βf_E (obtained from (8) and (10) respectively) for a hard-disc fluid are reported in figures 1 and 2 respectively for $\lambda/d = 0.2$ and 0.5. The classical values are also shown in the figures. In figure 1, the classical value of the equation of state is compared with the hard-disc Monte Carlo values of Henderson (1977). The agreement is good.

We have compared the quantum correction terms for two-and three-dimensional fluids (for three-dimensional fluid, see Singh and Sinha 1977, 1978). We find that for a given density and λ/d, the quantum correction for the two-dimensional fluid is less than that for the three-dimensional fluid.

4.2 *Square well model*

Here, we apply the theory developed in § 4.1 to a two- dimensional fluid whose molecules interact *via* a square well plus hard-core sw potential. The perturbation potential, which is given by

$$\begin{aligned} u_p(r) &= -\epsilon, \quad d < r < \eta d \\ &= 0, \qquad r > \eta d, \end{aligned} \qquad (19)$$
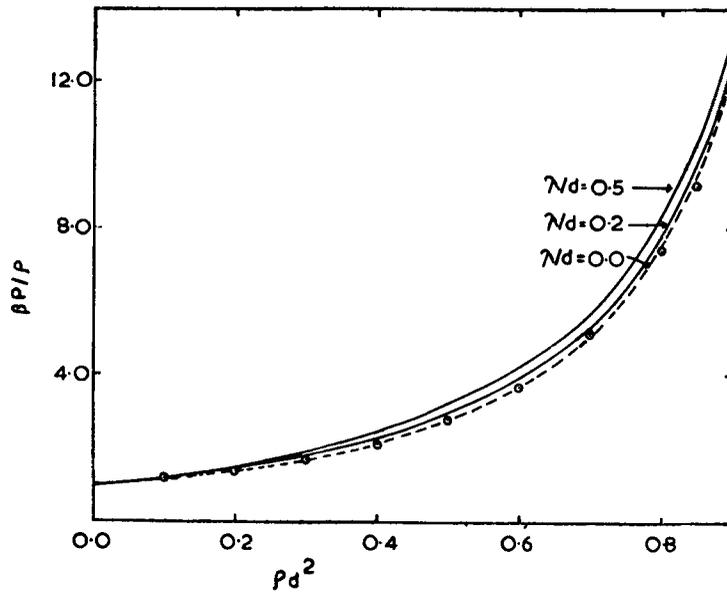
Figure 1. Equation of state $\beta P/\rho$ of a hard-disc fluid in the semi-classical limit for $\lambda/d = 0\cdot0, 0\cdot2$ and $0\cdot5$. MC value of classical equation of state is represented by $\odot$.
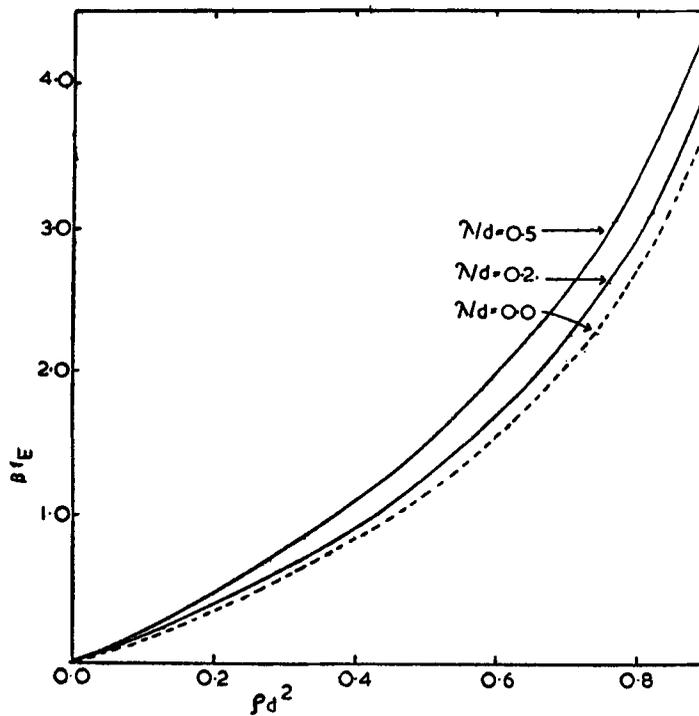

Figure 2. Excess free energy per particle βf_E of a hard-disc fluid in the semi-classical limit for $\lambda/d = 0\cdot0, 0\cdot2$ and $0\cdot5$.

may be expressed in an analytic form (Sinha and Singh 1977c)

$$u_p(r) = \frac{-\epsilon}{\exp\left[\left(\frac{r}{d} - \eta\right)\Big/ Y\right] + 1}, \; r > d, \tag{20}$$

with $Y \to 0$. Further, the sw model has a potential cut-off at $\tau = \eta d$. Then using (5) the integrals appearing in (3) and (4) can be easily evaluated. The last integral may be evaluated following the method of Sinha and Singh (1977c). Thus, the result is

$$C = \frac{\pi}{\sqrt{2}} [1 + (\exp(1/T^*) - 1) \, \mathrm{erf} \, \delta^*], \tag{21a}$$

$$D = \tfrac{1}{3}\Bigg[1 + [\exp(1/T^* - 1)] \, [(1 - \tfrac{3}{4}\exp - \delta^{*2})] \\
+ \frac{\ln 2 - \tfrac{1}{4}}{4} \exp(1/T^*) \left(\frac{1}{T^*}\right)^2 \Bigg], \tag{21b}$$

$$E = 0\cdot46698 \, \pi^2 \exp(2/T^*), \tag{21c}$$
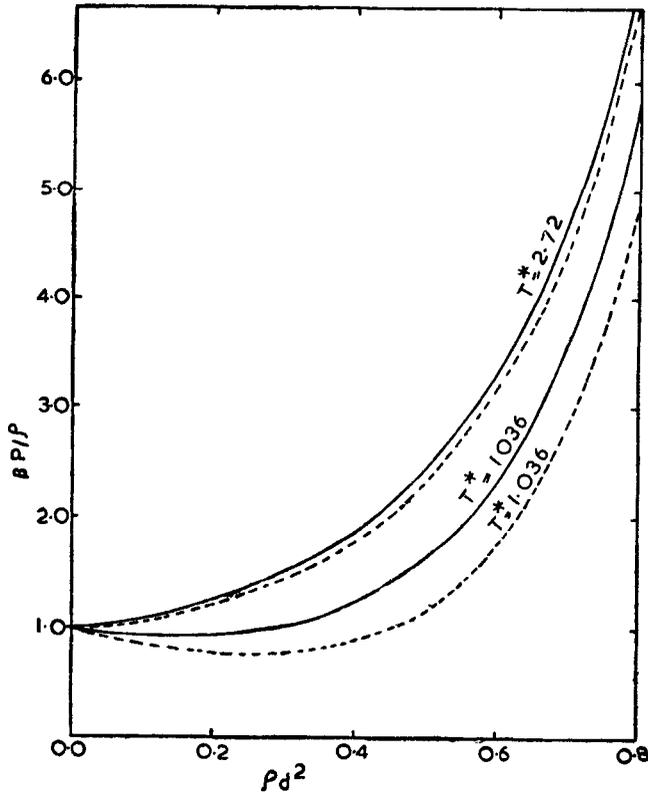
Figure 3. Equation of state $\beta P/\rho$ of a sw fluid with $\eta = 1\cdot50$ for $\pi^* = 0\cdot593$ at $T^* = 1\cdot036$ and $2\cdot72$; ———— $\beta P/\rho$ and — — — $\beta P^c/\rho$
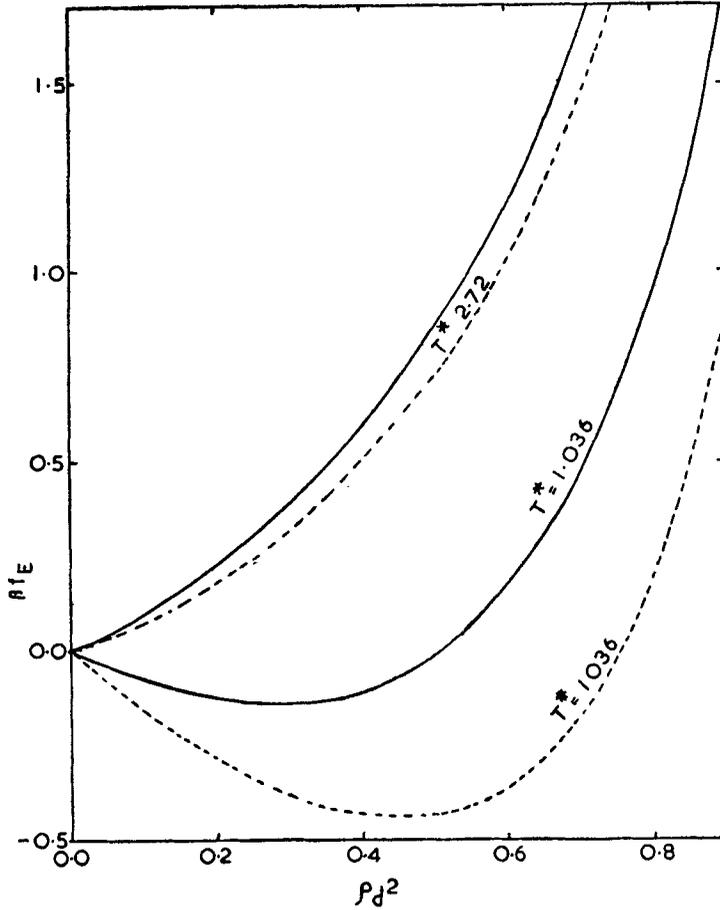
Figure 4. Excess free energy per particle βf_E of a sw fluid with $\eta = 1\cdot50$ for $\pi^* = 0\cdot593$ at $T^* = 1\cdot036$ and $2\cdot72$; ——— βf_E and — — — βf_E^c.

$$\delta^* = 2\pi\,(\eta - 1)\,\sqrt{T^*}/\pi^*. \tag{21d}$$

The values of $\beta\,P/\rho$ and βf_E for the two-dimensional sw fluids with $\eta = 1\cdot50$ are reported in figures 3 and 4 respectively for $\pi^* = 0\cdot593$ (π^* is the quantum parameter) at $T^* = 1\cdot036$ and $2\cdot72$. The classical values are also shown in the figures for comparison. We find that the quantum effect in this case increases with the increase in density and the decrease in temperature qualitatively in the same way as that in the case of the three-dimensional sw fluid (Singh and Sinha 1979). However, the magnitude of quantum corrections for a two-dimensional fluid is less than that for a three-dimensional fluid.

We, therefore come to the conclusion that the quantum effect increases with dimension.

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