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Perturbation theory for thermodynamic properties of a ν-dimensional square-well fluid

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Abstract. The Barker-Henderson perturbation theory is used for a ν-dimensional fluid with square-well potential. Analytic expressions are given for the equation of state, excess free energy per particle and internal energy. The numerical results are discussed. A significant feature is the increase of the thermodynamic properties with increasing dimensionality.

Keywords. Perturbation theory; equation of state; excess free energy; internal energy; dimensionality.

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1. Introduction

In recent years theoretical and experimental efforts have been made to understand the structural and thermodynamic properties of ν-dimensional fluids (Baus and Colot 1986, 1987; Colot and Baus 1986). However these efforts are confined to the fluid of hard ν-spheres as they are widely used as the hard-core reference system in ν-dimensional fluids. For a real fluid, an interparticle attraction works as a perturbation over a reference-system potential. The square-well (SW) potential is the simplest model which takes into account both the attractive and repulsive features of the intermolecular interaction. However no attempt has been made to study the ν-dimensional fluid with a potential model having attracting interaction.

In this paper we study the thermodynamic properties of ν-dimensional classical fluid of molecules interacting via the SW potential. The SW potential with $\zeta = 1{\cdot}5$ is a reasonable model for real simple fluid (Henderson *et al* 1976). Moreover, the complicating effects due to a softness of the repulsive part of potential are not present for this model.

For classical SW fluid considerable progress has been made (Hansen and McDonald 1976; Van Kampen *et al* 1967; Barker and Henderson 1967, 1976; Tago 1974; Smith *et al* 1974; Henderson and Chen 1975; Handerson *et al* 1976; Ponce and Renon 1976). But almost all these studies have been confined to the three-dimensional fluid. Mishra and Sinha (1984) have calculated the thermodynamic properties of the two-dimensional SW fluid. However, no work is available for general ν-dimensional fluid.

One of the most successful approaches for dealing with fluids is the Barker-Henderson (BH) perturbation theory (Barker and Henderson 1967). For the SW fluid, the BH perturbation theory can be solved analytically. It has been used to obtain analytic expressions for thermodynamic properties such as the equation of state and free energy for $v = 2$ (Mishra and Sinha 1984) and $v = 3$ (Ponce and Renon 1976). The results for three dimensional SW fluid are found to be in very good agreement with the molecular dynamic results (Alder *et al* 1972). However it has not yet been investigated systematically for different v values.

The purpose of the present investigation is two-fold. First we derive unified analytic expressions for the thermodynamic properties for v-dimensional SW fluid. Second we estimate the effect of dimensionality on the thermodynamic properties of the fluid.

In §2 we discuss the perturbation expansion for thermodynamic functions like free energy of the v-dimensional SW fluid. Analytic expressions for the free energy, pressure and internal energy are presented in §3. Section 4 is devoted to study the thermodynamic properties of the reference system. Results and discussions are presented in §5 and the concluding remarks in §6.

2. Perturbation expansion

We consider a v-dimensional fluid whose molecules interact via a square-well (SW) plus hard-core potential defined by

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

where σ is the diameter of v-dimensional sphere, ε is the well-depth and ζ the potential cut-off. We divide the pair potential $u(r)$ in the form

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

where $u_{\rm hc}(r)$ is the hard-core v-sphere potential

$$\begin{aligned} u_{\rm hc}(r) &= \infty \quad r < \sigma \\ &= 0 \quad r > \sigma \end{aligned} \tag{3}$$

which is treated as a reference potential and

$$\begin{aligned} u_p(r) &= -\varepsilon \quad \sigma < r < \zeta\sigma \\ &= 0 \quad r > \zeta\sigma \end{aligned} \tag{4}$$

is the perturbation.

Barker and Henderson (1967) used their perturbation theory to obtain an expression for the Helmholtz free energy for the three-dimensional SW fluid. We generalize the Barker-Henderson approach to calculate the Helmholtz free energy of a v-dimensional fluid. We expand the Helmholtz free energy A of the system as a Taylor series about the hard v-sphere value $A_{\rm hc}$ as

$$\frac{A - A_{\rm hc}}{kT} = -\beta\varepsilon\langle n\rangle_0 - \frac{1}{2}(\beta\varepsilon)^2[\langle n^2\rangle_0 - \langle n\rangle_0^2], \tag{5}$$

where $\beta = (kT)^{-1}$ (T is the absolute temperature) and $\langle n\rangle_0$ is the mean number of molecules in the range σ and $\zeta\sigma$ and is given by

$$\langle n\rangle_0 = \frac{1}{2}N\rho \int g_{hc}(r)\,d\bar{r}. \tag{6}$$

Here $g_{hc}(r)$ is the radial distribution function (RDF) of the hard ν-sphere fluid. The fluctuation of the number is given by

$$\langle n^2\rangle_0 - \langle n\rangle_0^2 = \langle n\rangle_0 kT(\partial\rho/\partial P_{hc})_\beta, \tag{7}$$

where $(\partial\rho/\partial P_{hc})_\beta$ is the macroscopic isothermal compressibility. Barker and Henderson (1967) showed that a better result can be obtained by replacing $(\partial\rho/\partial P_{hc})\, g_{hc}(r)$ in (7) by $(\partial(\rho g_{hc}(r))/\partial P_{hc})$.

In the ν-space, we can express (6) as (Baus and Colot 1987)

$$\langle n\rangle_0 = \frac{\nu\pi^{\nu/2}}{2\Gamma(1+\nu/2)}N\rho \int_\sigma^{\zeta\sigma} g_{hc}(r)r^{\nu-1}\,dr, \tag{8}$$

where $\Gamma(l) = l!$ is gamma-function.

Then the expression for the Helmholtz free energy for ν-dimensional SW fluid can be written as

$$\frac{A-A_{hc}}{NkT} = -\frac{\nu\pi^{\nu/2}}{2\Gamma(1+\nu/2)}(\beta\varepsilon)\rho\int_\sigma^{\zeta\sigma} g_{hc}(r)r^{\nu-1}\,dr - \frac{\nu\pi^{\nu/2}}{4\Gamma(1+\nu/2)}(\beta\varepsilon)^2 \times\left(\frac{\partial\rho}{\partial P_{hc}}\right)\frac{\partial}{\partial\rho}\left[\rho\int_\sigma^{\zeta\sigma} g_{hc}(r)r^{\nu-1}\,dr\right], \tag{9}$$

where ρ is the number density. The compressibility equation for hard ν-sphere fluid can be expressed as

$$kT\left(\frac{\partial\rho}{\partial P_{hc}}\right)_\beta = 1 + \frac{\nu\pi^{\nu/2}}{\Gamma(1+\nu/2)}\rho\int_0^\infty [g_{hc}(r)-1]r^{\nu-1}\,dr = 1 + \frac{2^\nu\nu}{\sigma^\nu}\eta\int_0^\infty [g_{hc}(r)-1]r^{\nu-1}\,dr, \tag{10}$$

where

$$\eta = (\pi^{\nu/2}/2^\nu\Gamma(1+\nu/2))\rho\sigma^\nu \tag{11}$$

is the packing fraction in the ν-space (Baus and Colot 1987).

3. Analytic solution

In this section we obtain an analytic expression for the Helmholtz free energy of the ν-dimensional SW fluid. In order to evaluate the integral of (9), we write

$$\int_\sigma^{\zeta\sigma} g_{hc}(r)r^{\nu-1}\,dr = \int_0^\infty [g_{hc}(r)-1]r^{\nu-1}\,dr - \int_{\zeta\sigma}^\infty [g_{hc}(r)-1]r^{\nu-1}\,dr + \int_0^{\zeta\sigma} r^{\nu-1}\,dr. \tag{12}$$

Approximating $g_{\rm hc}(r) \approx 1$ for $r > \zeta\sigma$, we can neglect the second integral of (12) and write

$$\int_{\sigma}^{\zeta\sigma} g(r) r^{\nu-1}\,\mathrm{d}r = \int_{0}^{\infty} [g(r)-1] r^{\nu-1}\,\mathrm{d}r + \zeta^{\nu}\sigma^{\nu}/\nu. \tag{13}$$

From (10) and (13), we get

$$\int_{\sigma}^{\zeta\sigma} g_{\rm hc}(r) r^{\nu-1}\,\mathrm{d}r = \left[\left(\frac{1-a}{2^{\nu}\nu\eta a}\right) + \zeta^{\nu}/\nu\right]\sigma^{\nu}, \tag{14}$$

where

$$kT(\partial\rho/\partial P_{\rm hc}) = a^{-1}. \tag{15}$$

Substituting (14) in (9), we obtain an analytic expression for the Helmholtz free energy of the ν-dimensional SW fluid

$$\frac{A-A_{\rm hc}}{NkT} = (\beta\varepsilon)\left(\frac{A_1}{NkT}\right) + (\beta\varepsilon)^2\left(\frac{A_2}{NkT}\right), \tag{16}$$

where

$$\frac{A_1}{NkT} = -\eta\left[\left(\frac{1-a}{2\eta a}\right) + 2^{\nu-1}\zeta^{\nu}\right] \tag{17}$$

$$\frac{A_2}{NkT} = \frac{\eta}{4a}\left[\frac{1}{a^2}\frac{\partial a}{\partial\eta} - 2^{\nu}\zeta^{\nu}\right]. \tag{18}$$

The equation of state for the ν-dimensional SW fluid can be obtained using the relation

$$\frac{\beta P}{\rho} - \frac{\beta P_{\rm hc}}{\rho} = \eta\frac{\partial}{\partial\eta}\left[\frac{A-A_{\rm hc}}{NkT}\right]. \tag{19}$$

Substituting (16), we obtain an analytic expression for the equation of state of the SW fluid

$$\frac{\beta P}{\rho} = \frac{\beta P_{\rm hc}}{\rho} + (\beta\varepsilon)\left(\frac{\beta P_1}{\rho}\right) + (\beta\varepsilon)^2\left(\frac{\beta P_2}{\rho}\right), \tag{20}$$

where

$$\frac{\beta P_1}{\rho} = \eta\left[\frac{1}{2a^2}\frac{\partial a}{\partial\eta} - 2^{\nu-1}\zeta^{\nu}\right] \tag{21}$$

$$\frac{\beta P_2}{\rho} = \frac{\eta}{4a}\left[\frac{1}{a^2}\left\{\eta\frac{\partial^2 a}{\partial\eta^2} - 3\frac{\eta}{a}\left(\frac{\partial a}{\partial\eta}\right)^2 + \frac{a}{\eta}\right\} + 2^{\nu}\zeta^{\nu}\left\{\frac{\eta}{a}\left(\frac{\partial a}{\partial\eta}\right) - 1\right\}\right]. \tag{22}$$

The internal energy U_i of the ν-dimensional SW fluid is given by (Barker and Henderson 1976)

$$\frac{U_i}{NkT} = (\beta\varepsilon)\frac{A_1}{NkT} + (\beta\varepsilon)^2\frac{A_2}{NkT}. \tag{23}$$

The theory developed here requires the knowledge of the thermodynamic properties of hard ν-sphere fluid.

4. Reference system

The thermodynamic properties of the hard ν-sphere fluid can be calculated from the equation of state, which is available for $1 \leqslant \nu \leqslant 5$. The equation of state is known exactly for hard rods ($\nu = 1$) (Zernike and Prins 1927; Herzfeld and Mayer 1934; Tonk 1936) and approximately for hard discs ($\nu = 2$) (Henderson 1975) and hard spheres ($\nu = 3$) (Carnahan and Starling 1969). Recently Baus and Colot (1987) have expressed the equation of state analytically for $\nu = 4$ and 5. The equation of state for hard ν-sphere fluid is given by a single expression

$$\frac{\beta P_{\mathrm{hc}}}{\rho} \equiv Z_{\mathrm{hc}}(\eta) = \frac{1 + \sum_{n \geqslant 1} C_n \eta^n}{(1-\eta)^\nu}. \tag{24}$$

The coefficients C_n for $1 \leqslant \nu \leqslant 5$ are available and are reported in Table 1. From $Z_{\mathrm{hc}}(\eta)$ we can calculate a and f_{hc} for hard ν-sphere fluid (f_{hc} being the free energy per particle of the hard ν-sphere fluid). Thus (Baus and Colot 1987)

$$a = \beta\left(\frac{\partial P_{\mathrm{hc}}}{\partial \rho}\right) = \frac{\partial}{\partial \eta}[\eta Z_{\mathrm{hc}}(\eta)] \tag{25}$$

$$\beta f_{\mathrm{hc}} \equiv \frac{A_{\mathrm{hc}}}{NkT} = \ln[(\lambda/\sigma)^\nu 2^\nu \Gamma(1+\nu/2)\pi^{-\nu/2}] + \ln \eta - 1 + \beta f^E_{\mathrm{hc}}, \tag{26}$$

where f^E_{hc} is the excess free energy per particle of the hard ν-sphere fluid and is given by

$$\beta f^E_{\mathrm{hc}} = \int_0^\eta \left[\frac{Z_{\mathrm{hc}}(\eta') - 1}{\eta'}\right] \mathrm{d}\eta'. \tag{27}$$

From (25) and (27) one can obtain expressions of a and βf^E_{hc} for different values of ν. These quantities are known for hard rods ($\nu = 1$) (Tonk 1936)

$$a = (1-\eta)^{-2} \tag{28}$$

$$\beta f^E_{\mathrm{hc}} = -\ln(1-\eta); \tag{29}$$

Table 1. Coefficients C_n.

ν \ C_n	C_1	C_2	C_3	C_4
1	0	0	0	0
2	0	0·1250	0	0
3	1	1·0000	−1·0000	0
4	4	6·4057	−8·1170	0
5	11	36·0000	−74·4380	347·12

for hard discs ($\nu = 2$) (Henderson 1975; Mishra and Sinha 1984)

$$a = \frac{1 + \eta + 0{\cdot}375\eta^2 - 0{\cdot}125\eta^3}{(1-\eta)^3} \tag{30}$$

$$\beta f^E_{\text{hc}} = \frac{9}{8}\frac{\eta}{(1-\eta)} - \frac{7}{8}\ln(1-\eta) \tag{31}$$

and for hard spheres ($\nu = 3$) (Ponce and Renon 1976; Carnahan and Starling 1969)

$$a = (1 + 2\eta)^2/(1-\eta)^4 \tag{32}$$

$$\beta f^E_{\text{hc}} = \frac{\eta(4 - 3\eta)}{(1-\eta)^2}. \tag{33}$$

For higher dimension ($\nu \geqslant 4$) a and f^E_{hc} are not known. We can calculate these quantities by substituting (24) in (25) and (27). Thus for $\nu = 4$, a and βf^E_{hc} are given by

$$a = \frac{1 + 11\eta + 27{\cdot}217\eta^2 - 26{\cdot}062\eta^3}{(1-\eta)^5} \tag{34}$$

$$\beta f^E_{\text{hc}} = \frac{7\eta(1 - 0{\cdot}7568\eta - 0{\cdot}0866\eta^2)}{(1-\eta)^3} + \ln(1-\eta) \tag{35}$$

and for $\nu = 5$

$$a = \frac{1 + 26\eta + 141\eta^2 - 225{\cdot}752\eta^3 + 1661{\cdot}212\eta^4}{(1-\eta)^6} \tag{36}$$

$$\beta f^E_{\text{hc}} = \frac{15\eta(1 - 0{\cdot}8667\eta - 0{\cdot}9431\eta^2 + 5{\cdot}9878\eta^3)}{(1-\eta)^4} + \ln(1-\eta). \tag{37}$$

Equations for βf^E_{hc} discussed above are valid for $\eta < 1$. Hence (16) is correct even for high density ($\eta < 1$). However we use the equations to calculate the free energy up to the packing fractions as high as $\eta < \eta_{\text{cp}}$ because $\eta \gtrsim \eta_{\text{cp}}$ are unphysical, where η_{cp} is the packing fraction at close packing. The value of η_{cp} decreases with increase of ν. For example, $\eta_{\text{cp}} \approx 0{\cdot}9068$ for $\nu = 2$ and $\eta_{\text{cp}} \approx 0{\cdot}38$ for $\nu = 5$.

5. Results and discussions

We have calculated the thermodynamic properties such as equation of state, excess free energy and internal energy of the ν-dimensional SW fluid ($1 \leqslant \nu \leqslant 5$). We choose $\zeta = 1{\cdot}5$ in our calculation, since the three-dimensional SW potential with $\zeta = 1{\cdot}5$ is a qualitatively reasonable model for real fluids (Henderson *et al* 1976).

The values of the first and second order perturbation corrections to the free energy, A_1/NkT and A_2/NkT, are reported in figure 1 as a function of η for $1 \leqslant \nu \leqslant 5$, which shows that the magnitude of the corrections increases with increase of dimension. Further $A_1/NkT > A_2/NkT$ in all the dimensions considered.

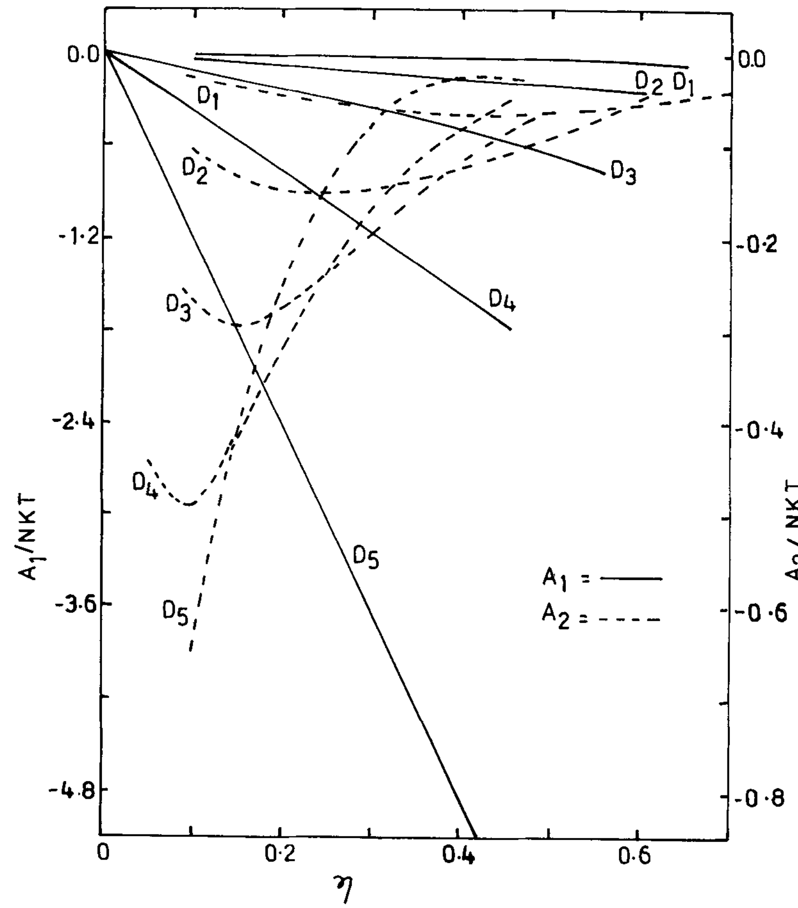

Figure 1. Values of A_1/NkT and A_2/NkT of ν-D SW fluid with $\zeta = 1{\cdot}5$ as a function of η.

The values of the equation of state, $\beta P/\rho$, for the ν-dimensional SW ($1 \leqslant \nu \leqslant 5$) as a function of η are reported in figures 2 and 3 for $\beta\varepsilon = 0{\cdot}75$ and $1{\cdot}25$, respectively. $\beta P/\rho$ first decreases with increase of η, reaching a minimum and then begins to increase. The minimum value of $\beta P/\rho$ increases with the dimensionality. The mimimum point shifts towards the lower value of η when ν increases. This behaviour can be explained by considering the contributions of the repulsive and attractive part of potential. These contributions, which are of opposite signs, increase with η as well as ν. This is the reason that higher the value of ν lower is the minimum point.

Figures 4 and 5 demonstrate the variation of the excess free energy per particle, βf, as a function of η for $\beta\varepsilon = 0{\cdot}75$ and $1{\cdot}25$, respectively. It also decreases with increase of η first reaching to a minimum value and then begins to increase. Like the equation of state, the minimum value of βf increases with increase of ν and shifts towards the lower value of η when ν increases.

In figure 6 the values of the configurational internal energy U_i/NkT are plotted as a function of $\beta\varepsilon$ for $\eta = 0{\cdot}3$. The internal energy increases with the increase of dimension ν.

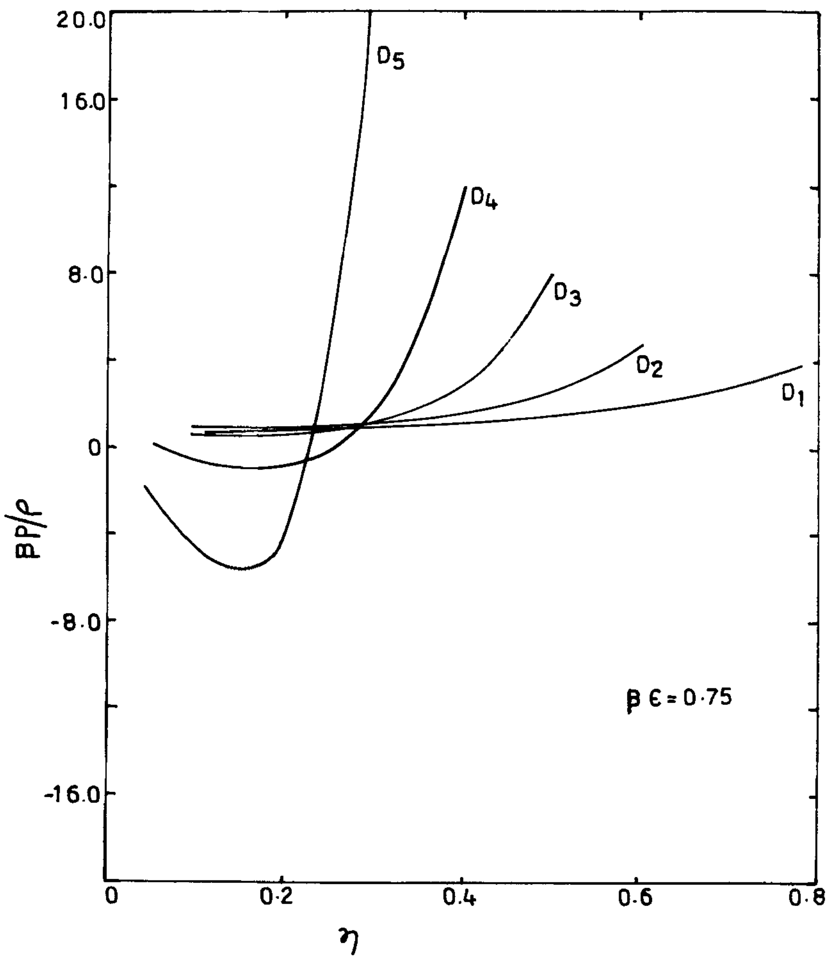

Figure 2. Values of $\beta P/\rho$ for ν-D SW fluid with $\zeta = 1{\cdot}5$ at $\beta\varepsilon = 0{\cdot}75$ as a function of η.

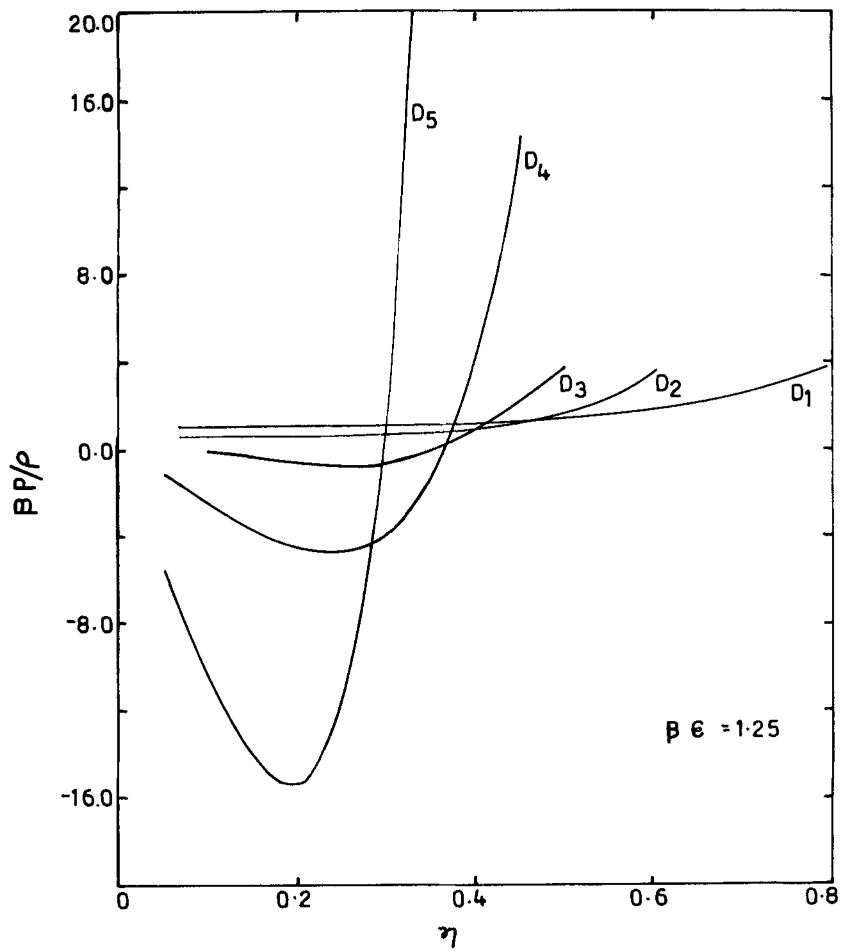

Figure 3. Values of $\beta P/\rho$ for ν-D SW fluid with $\zeta = 1{\cdot}5$ at $\beta\varepsilon = 1{\cdot}25$ as a function of η.

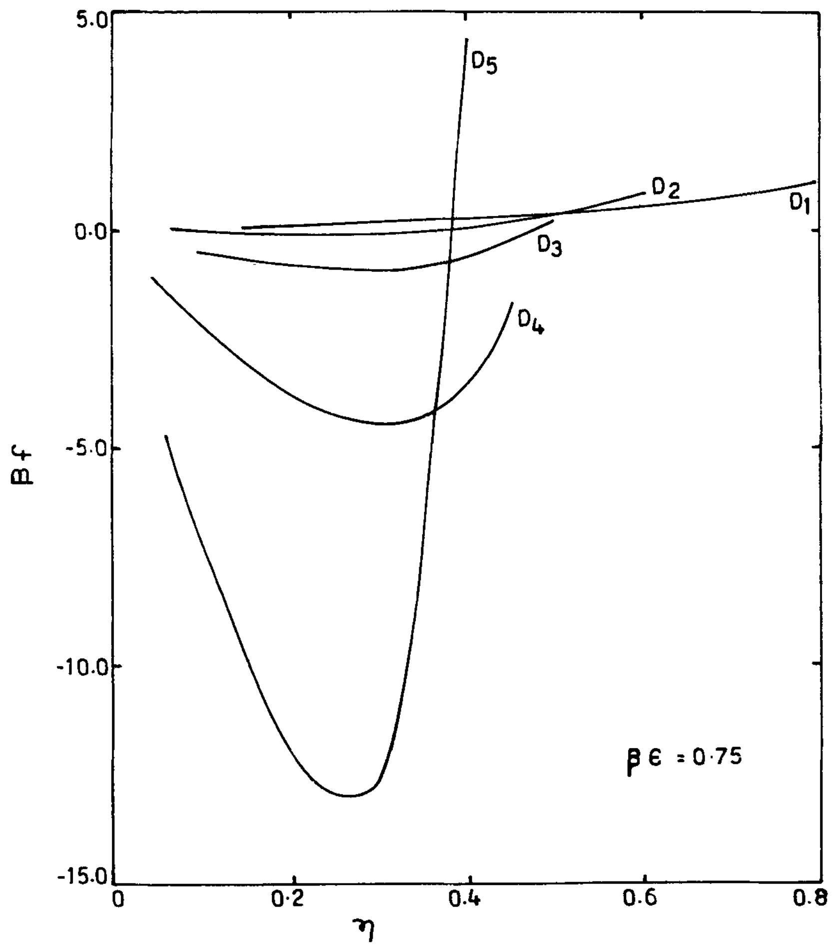

Figure 4. Values of βf for v-D SW fluid with $\zeta = 1{\cdot}5$ at $\beta\varepsilon = 0{\cdot}75$ as a function of η.

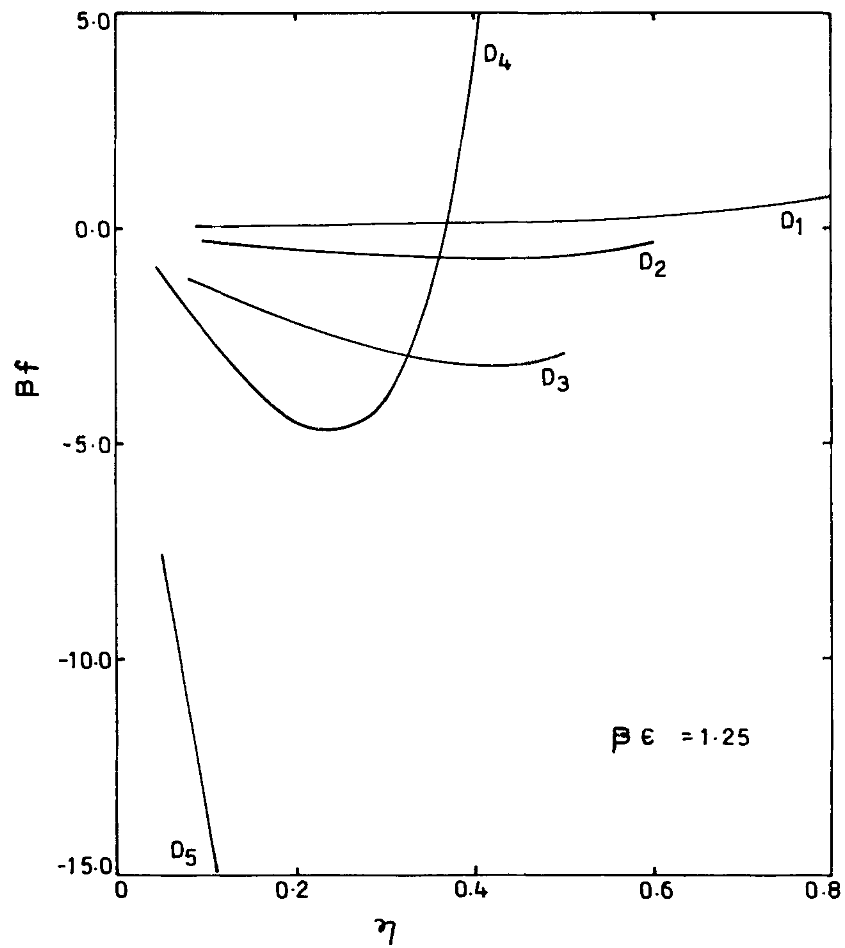

Figure 5. Values of βf for v-D SW fluid with $\zeta = 1{\cdot}5$ at $\beta\varepsilon = 1{\cdot}25$ as a function of η.

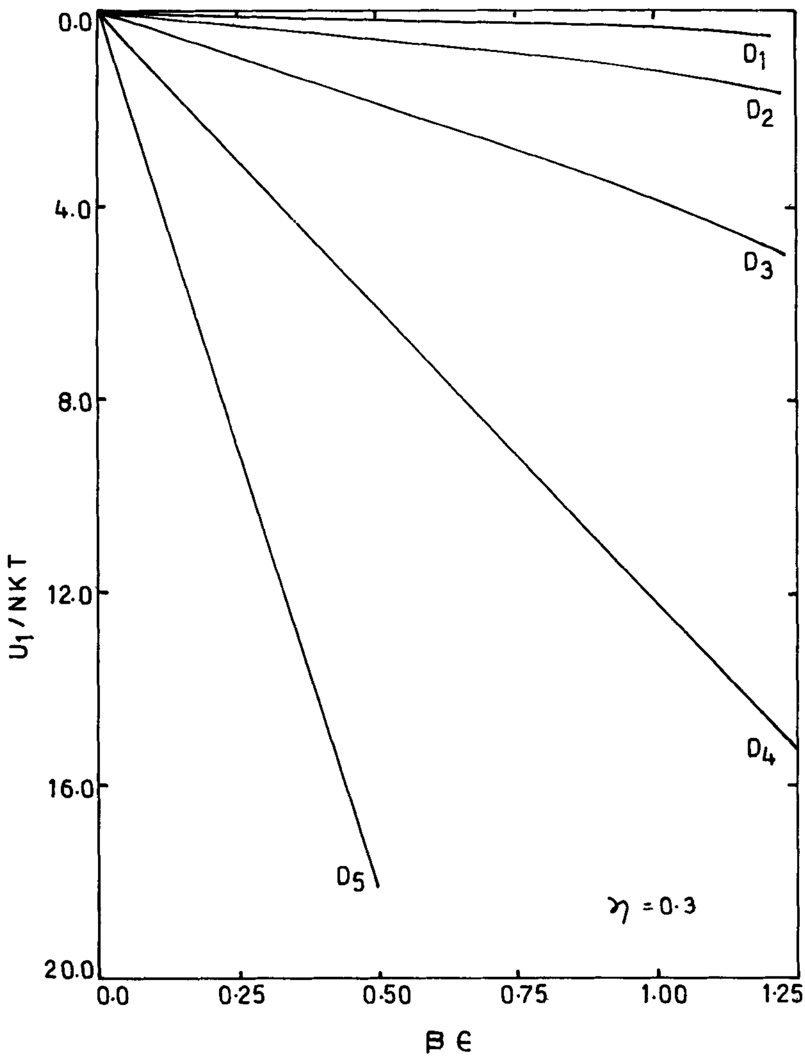

Figure 6. Values of U_i/NkT for ν-*D* SW fluid with $\zeta = 1{\cdot}5$ as a function of $\beta\varepsilon$ for $\eta = 0{\cdot}3$.

6. Concluding remarks

Using the BH perturbation theory, we have given unified analytic expressions for the thermodynamic properties of the ν-dimensional SW fluid and estimated the effect of dimensionality on these thermodynamic properties. The second order perturbation theory provides excellent results for $\nu = 3$. (Barker and Henderson 1976; Ponce and Renon 1976). It is expected to provide good results even for $\nu \geqslant 4$; since the properties of the reference hard-core fluid are in good agreement with the simulation results (Baus and Colot 1987) and the perturbation corrections in this case are expressed in terms of the derivatives of pressure of hard ν-sphere system.

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