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THE TEMPERATURE DEPENDENCE OF THE HARD SPHERE DIAMETER

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ABSTRACT

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The temperature dependence of the equivalent hard sphere diameter is analyzed using statistical mechanics. The analysis shows that algebraic equations for the hard sphere diameter which were developed by previous workers are not consistent with the statistical mechanics at high temperature. An algebraic equation which is consistent with the statistical mechanics is developed.

INTRODUCTION

Several researchers in recent years have suggested making the hard sphere diameter temperature dependent. Nakamura et al. (1976), Fermeglia (cf. Skjold-Jorgensen, 1983) and DeSantis et al. (1976) suggested several different functional forms for the temperature dependence. Naturally, introducing more parameters into the equation of state enabled a better fit of the macroscopic properties but there was a lack of resolution to the question of proper functional form. It seems unlikely that the question can be resolved without appealing to microscopic arguments and statistical mechanics. The hard sphere diameter is one of the microscopic properties which characterizes the molecules. Many different models of the microscopic properties might describe the macroscopic properties equally well. Statistical mechanical theory permits one to discern which models are physically meaningful.

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THE EQUIVALENT HARD SPHERE DIAMETER FROM PERTURBATION THEORY

Barker and Henderson (1967) presented in their perturbation theory one way in which statistical mechanics could explain the temperature dependence of the hard sphere diameter. In a perturbation theory, the equation of state is divided into a repulsive part and an attractive part. The repulsive part is given by the equation of state of a suitably chosen reference fluid and this part is responsible for the importance of the hard sphere diameter. The approach of Barker and Henderson can be briefly described as follows. Two dummy parameters, α and γ, are introduced into the potential function such that, when these parameters are equal to zero, a hard sphere potential is obtained and when the parameters are equal to one, the original potential is obtained.

$$\begin{aligned} v(r) &= u[d^{\mathrm{hs}} + (r - d^{\mathrm{hs}})/\alpha] && d^{\mathrm{hs}} + (r - d^{\mathrm{hs}})/\alpha < \mu \\ &= 0 && \mu < d^{\mathrm{hs}} + (r - d^{\mathrm{hs}})/\alpha < d^{\mathrm{hs}} \\ & && + (\mu - d^{\mathrm{hs}})/\alpha \\ &= \gamma u(r) && \mu < r \end{aligned} \tag{1}$$

The parameter d^{hs} is the diameter of the hard-sphere reference fluid, so far unspecified; μ is a parameter such that the potential is steep for $r < \mu$ and small for $r > \mu$. Barker and Henderson (1967) chose $\mu = \sigma$, because the potential they used for their reference fluid was best related to this choice of μ. Nezbeda and Aim (1984) have discussed another choice of reference fluid associated with the choice of $\mu = r_{\mathrm{m}}$ where r_{m} is the distance to the minimum in the potential. They have referred to this choice as the hybrid Barker–Henderson (hBH) approach. However, they did not obtain an algebraic equation for the hard sphere temperature dependence based on the hBH approach. The hBH approach is considered in the discussion below.

At this point, the Helmholtz free energy may be expanded in a double Taylor series in α and γ about the point $\alpha = \gamma = 0$ (Barker and Henderson, 1967). If d is chosen by the condition

$$d^{\mathrm{hs}} = \int_0^{\mu} [1 - \exp\{-u(Z)/kT\} \mathrm{d}Z \tag{2}$$

then terms of order α and $\alpha\gamma$ vanish identically. Thus, if terms of order α^2, $\alpha^2\gamma$, $\alpha\gamma^2$, α^3 and all higher order terms are neglected and α and γ are put equal to unity to recover the original potential, then the Helmholtz energy of the reference fluid can be equated to the Helmholtz energy of an equivalent hard sphere fluid

$$A^{\mathrm{rep}} = A^{\mathrm{ref}} = A^{\mathrm{hs}}(d^{\mathrm{hs}}) \tag{3}$$

where A^{rep} is the repulsive part of the equation of state, A^{ref} is the Helmholtz energy of the reference fluid and A^{hs} is the Helmholtz energy of the hard sphere equation of state with hard sphere diameter d^{hs}. If the Carnahan–Starling (1969) equation is chosen to give the equation of state of hard spheres, then

$$(A^{\text{hs}} - A^{\text{id}})/NkT = (4y - 3y^2)/(1-y)^2 \tag{4}$$

where $y = \pi p (d^{\text{hs}})^3/6$ (5)

and the equation of state is given by

$$\left(\frac{A + A^{\text{id}}}{NkT}\right) = \left(\frac{A^{\text{rep}} - A^{\text{id}}}{NkT}\right) + \left(\frac{A^{\text{att}} - A^{\text{id}}}{NkT}\right) \tag{6}$$

Thus, in a statistical mechanical consideration of perturbation theory, one would expect a reasonably accurate expression for the hard sphere diameter to be given by eqn. (2). Unfortunately, eqn. (2) requires numerical integration to be evaluated and is not very convenient for applications. A reasonable compromise between the algebraic equations of previous researchers and the statistical mechanical results of the hBH approach might be reached if an algebraic equation could be suggested which is consistent with eqn. (2).

An algebraic equation which is consistent with eqn. (2) can be developed by computing values numerically and regressing constants in an equation which is capable of representing the temperature range from zero to infinity. This broad temperature range is not typically of practical interest but the upper and lower limits provide convenient boundary conditions in the analysis of eqn. (2). Over the temperature range of practical interest (reduced temperature of 0.5–3.0) the shape given by eqn. (2) is very simple and it is difficult to distinguish between most of the functional forms.

It was determined that an exponential functional form was not capable of matching eqn. (2) over the entire temperature range. Instead, eqn. (7) is suggested

$$\frac{d^{\text{hs}}}{r_{\text{m}}} = \left(a(T^*)^2 + bT^* + 1\right)^{-1/C} \tag{7}$$

where $T^* = kT/\epsilon$

To consider the temperature dependence of the hard sphere diameter, one must adopt a model of the intermolecular potential function. The Mie (n–6) potential was used for this investigation. This potential is given for general values of n by eqn. (8). The Lennard–Jones (12–6) potential is an example of a Mie potential with $n = 12$.

$$u(r) = \epsilon(n^n/6^6)^{1/(n-6)}/(n-6)\left[(\sigma/r)^n - (\sigma/r)^6\right] \tag{8}$$

A simple form of eqn. (7) provided an accurate representation of numeri-

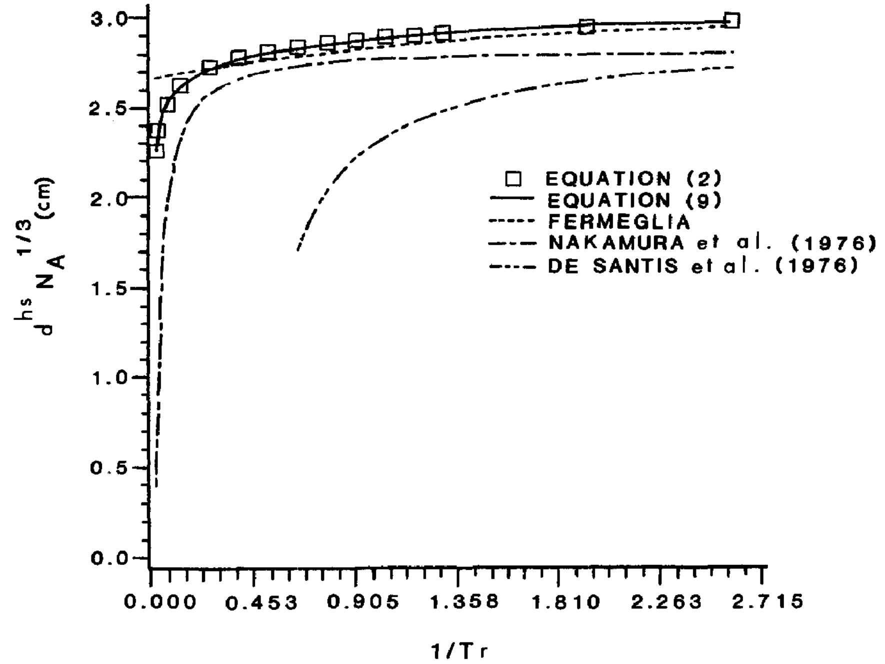

Fig. 1. Comparison of different correlations of the hard sphere diameter.

cally calculated values of eqn. (2) for values of n equal to 12, 20, 30, 40, 50, 60 and 70. This form is given by eqn. (9)

$$\frac{d^{\mathrm{hs}}}{r_{\mathrm{m}}} = \left(n(0.0093n - 0.0592)(T^*)^2 + (n-1)T^* + 1\right)^{-1/(2n+1)} \tag{9}$$

Argon was selected as the substance for making comparisons between eqn. (2), eqn. (9) and the correlations of previous workers. The complete correlation for argon could be easily obtained for each previous correlation from the data in the literature references. The previous correlations considered were those of Fermeglia (cf. Skjold-Jørgensen, 1983), Nakamura et al. (1976) and DeSantis et al. (1976). The correlations for the temperature dependence of the hard sphere diameter of argon are given in eqns. (10)–(12) below. For eqns. (2) and (9), a value of $n = 12$ was used with $r_{\mathrm{m}} = 2^{1/6}$, $\sigma = 0.3822$ nm and $\epsilon/k = 117.2$ K. These are values which are commonly used for the potential of argon. All the correlations are compared in Fig. 1 and Table 1.

Fermeglia (cf. Skjold-Jørgensen, 1983)

$$d^{\mathrm{hs}} = 1.65655 d_{\mathrm{c}}\left(1 - 0.12\exp(-2/(3T_{\mathrm{r}})\right); \quad d_{\mathrm{c}} = (0.08943RT_{\mathrm{c}}/P_{\mathrm{c}})^{1/3} \tag{10}$$

TABLE 1

Comparison of correlations for the equivalent hard sphere diameter (for argon)

T_r	eqn. (2)	eqn. (9)	eqn. (10)	eqn. (11)	eqn. (12)
77.6879	2.25846	2.25933	2.66606	0.39312	–
38.8440	2.37044	2.37497	2.66914	1.05748	–
15.5376	2.51629	2.52222	2.67821	1.91477	–
7.7688	2.62234	2.62525	2.69282	2.33381	–
3.8844	2.72227	2.72002	2.72023	2.57656	–
2.5896	2.77706	2.77211	2.74538	2.66296	–
1.9422	2.81403	2.80783	2.76846	2.70724	–
1.5538	2.84154	2.83491	2.78965	2.73416	1.70979
1.2948	2.86321	2.85666	2.80909	2.75226	2.03812
1.1098	2.88096	2.87479	2.82694	2.76526	2.22015
0.9711	2.89591	2.89031	2.84331	2.77505	2.33928
0.8632	2.90875	2.90385	2.85834	2.78269	2.42418
0.7769	2.91996	2.91584	2.87214	2.78881	2.48805
0.5179	2.96068	2.96083	2.92585	2.80727	2.66230
0.3884	2.98721	2.99150	2.96082	2.81654	2.74147

Nakamura et al. (1976)

$$d^{hs} = (3b/2\pi)^{1/3}; \quad b = 10**(-1.3169 - 0.03319T_r) \tag{11}$$

DeSantis et al. (1976)

$$d^{hs} = (3b/2\pi)^{1/3}; \quad b = 0.026(1.927 - T_r)/(1.927 - 1) \tag{12}$$

The correlation of DeSantis et al. (1976) illustrates the fallacy of proposing a correlation for an equation of state constant without a careful analysis of proper functional form. Their equation cannot be applied above a reduced temperature of 1.972. Furthermore, the curvature of their equation is incorrect in the range of temperatures to which their equation should apply.

The equations of Nakamura et al. and Fermeglia are more reasonable than the equation of DeSantis et al. but still have certain shortcomings. The equation of Nakamura et al. is too nearly constant at low temperature and varies too rapidly at high temperatures. The equation of Fermeglia has roughly the right curvature at low temperature but it indicates a finite value in the high temperature limit. Equation (2) in conjunction with the (n–6) Mie potential indicates that the hard sphere diameter should approach zero at high temperature thus the Fermeglia correlation is in disagreement. If one would like to assume that molecules possess some hard inner core, then that assumption should be expressed in the choice of potential model. Equation (2) could then be applied to the alternative potential model. For example, consider the Kihara potential model which has a hard core. Equation (9) could easily be applied to the $(n-6)$ outer shell of the Kihara potential and the hard core thickness simply added. The Nakamura et al. correlation could be similarly adapted but it would suffer the same problems as before. The Fermeglia çorrelation, on the other hand, indicates a much higher ratio of hard core thickness to soft shell thickness than is typical of applications of the Kihara potential. Thus the approach developed here can be generalized to other potential models and still present advantages over previous correlations.

TEST OF THE NEW CORRELATION AT HIGH TEMPERATURE

At high temperatures, it is possible to obtain the temperature dependence of the hard sphere diameter by a different approach from that of Barker and Henderson (1967). The kinetic energy of the molecules varies with temperature. As the temperature rises, the kinetic energy of the molecules rises and they are enabled to penetrate each other's soft repulsiveness more and more. Although it requires considerable energy to penetrate the Mie potential, the energy is not infinite as in, say, a square-well potential. Thus, the Mie potential is relatively soft. This softness is responsible for the temperature dependence of the equivalent hard sphere diameter in the first place. Another effect of high temperature is that the attractive part of the potential contributes little to the thermodynamics of the fluid. Thus it is possible to relate the Lennard–Jones (12–6) fluid (for instance) to the hard sphere fluid. An approximate relationship can be established through the virial coefficients.

For the Lennard–Jones fluid

$$B2 = (2\pi\sigma^3/3)B2^* \tag{13}$$

$$B3 = (2\pi\sigma^3/3)^2 B3^* \tag{14}$$

For the hard sphere fluid

$$B2 = 4\left[\pi(d^{hs})^3/6\right] \tag{15}$$

$$B3 = 10\left[\pi(d^{hs})^3/6\right]^2 \tag{16}$$

Substitution yields

$$\text{from B2;}\quad d^{hs}/\sigma = (B2^*)^{1/3} \tag{17}$$

$$\text{from B3;}\quad d^{hs}/\sigma = (1.6B3^*)^{1/6} \tag{18}$$

TABLE 2

Equivalent hard sphere diameters for the Lennard–Jones potential

T^*	B2*	B3*	d^{hs}/σ		
			from B2	from B3	from eqn. (9)
20	0.5270	0.2464	0.8077	0.8563	0.8752
50	0.5090	0.1853	0.7984	0.8166	0.8244
100	0.4644	0.1425	0.7744	0.7817	0.7855
500	0.3420	0.07106	0.6993	0.6960	0.6958

Where B2* and B3* are the reduced second and third virial coefficients calculated using the Lennard–Jones potential. Comparison of eqn. (9) with the results from the virial coefficients is given in Table 2. As the temperature increases, the agreement between the various estimates improves. Thus, eqn. (9) appears to be accurate at high temperatures. Note that the agreement is not very accurate at temperatures below $T^* = 100$. This means that extremely high temperatures are necessary before attractive effects are actually negligible.

CONCLUSIONS

The temperature dependence of the equivalent hard sphere diameter is best analyzed by using statistical mechanics. The hybrid Barker–Henderson (hBH) approach represents one such analysis and it was considered here along with the virial coefficients at high temperature. A comparison showed that algebraic equations for the hard sphere diameter which were developed by previous workers are not consistent with these analyses. An algebraic equation which is consistent with the statistical mechanics was developed for practical calculations. Most of the correlations agree fairly well over the temperature range where most calculations are performed. On the other hand, a constant value of the hard sphere diameter could perform nearly as well over this temperature range. It is recommended that the equivalent hard sphere diameter be represented by eqn. (2) or eqn. (9) for most general applications.

LIST OF SYMBOLS

A	Helmholtz free energy
B2	second virial coefficient
B3	third virial coefficient
d^{hs}	equivalent hard sphere diameter

k	Boltzmann's constant
n	exponent of the repulsive part of the potential function
N_A	Avogadro's number
r_m	intermolecular distance at the minimum in the potential
T	absolute temperature
T^*	reduced temperature kT/ϵ
T_r	reduced temperature T/T_c
$u(r)$	the potential function

Greek symbols

γ	parameter in the modified potential function of Barker and Henderson
ϵ	energetic parameter in the potential fraction
μ	parameter in the modified potential function of Barker and Henderson
σ	intermolecular distance where the potential is equal to zero

REFERENCES

Barker, J.A. and Henderson, D., 1967. Perturbation theory and equation of state for fluids. II. A successful theory of liquids. J. Chem. Phys., 47: 4714–4721.

Carnahan, N.F. and Starling, K.E., 1969. Equation of state for non-attracting rigid spheres. J. Chem. Phys., 51: 635–636.

DeSantis, R., Gironi, F. and Marelli, L., 1976. Vapor–liquid equilibrium from a hard-sphere equation of state. Ind. Eng. Chem. Fundam., 15: 183–189.

Nakamura, R., Breedveld, G.J.F. and Prausnitz, J.M., 1976. Thermodynamic properties of gas mixtures containing common polar and nonpolar components. Ind. Eng. Chem., Proc. Des. Dev., 15: 557–563.

Nezbeda, I. and Aim, K., 1984. Perturbed hard sphere equation of state of real fluids. II. Effective hard sphere diameters and residual properties. Fluid Phase Equilibria, 17: 1–8.

Skjold-Jorgensen, S., 1983. Gas solubility calculations. II. Application of a new group contribution equation of state. Fluid Phase Equilibria, 16: 317–351.