

Partial structure factors and diffusion coefficients of liquid potassium-cesium alloys

R. V. Gopala Rao and B. Das Gupta

Physical Chemistry Section, Jadavpur University, Calcutta 700032, West Bengal, India

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With use of the square-well potential as a perturbation on the hard-sphere potential, the partial structure factors defined by Ascroft and Langreth [Phys. Rev. **159**, 500 (1967)] and also the number-number, number-concentration, and concentration-concentration structure factors of Bhatia and Thornton [Phys. Rev. **32**, 3004 (1970)] are calculated for liquid potassium-cesium alloys at various concentrations at 100°C. From the partial structure factors, the total structure factors are also calculated and compared with experimental values. The hard-sphere values are also computed for the same concentrations. The difference plots of the total structure factors of the square well and those of the hard spheres are also presented. The total structure factors obtained from these partial structure factors in the long-wavelength limit are used to calculate the isothermal compressibilities. With the partial structure factors and using Helfand's prescription extended by Davies and Polyvos, we calculate the self-diffusion coefficients. From the self-diffusion coefficients, an estimate of the mutual diffusion coefficients has been made to a good approximation.

I. INTRODUCTION

Extensive investigations by Alblas *et al.*¹ have revealed conclusively that the K-Cs system behaves almost like an ideal solution. The shape of the curve representing the heat of mixing as a function of atomic composition is almost parabolic for the K-Cs system indicating that it forms an ideal mixture.² Hence it is felt appropriate to use the mean spherical model (MSM) approximation with a square-well potential as a perturbation on the hard-sphere potential and obtain the partial structure factors similar to the potentials obtained by Ashcroft and Langreth³ for simple hard sphere mixtures.

The square-well potential is no doubt mathematically convenient, but it is also found that the application of this potential to a number of metals faithfully yielded good structure factors⁴⁻⁷ and transport properties calculated from these structures.^{8,9}

The x-ray experiments for the total structure factors at various concentrations have been reported by Alblas *et al.*¹ As is well known a binary system is characterized by three partial structure factors, namely, $S_{11}(k)$, $S_{22}(k)$, and $S_{12}(k)$. Hence a unique set of partial structure factors cannot be obtained from a single or even two sets of measurements. Therefore, these model calculations become all the more important. When once the above partial structure factors are available, they can be used to calculate the Bhatia-Thornton partial structure factors,¹⁰ namely, the $S_{NN}(k)$, $S_{CC}(k)$, and $S_{NC}(k)$, the number-number, concentration-concentration, and number-concentration, respectively. The total structure factor can be obtained from the partial structure factors $S_{11}(k)$, $S_{22}(k)$, and $S_{12}(k)$ and compared with experiment. Fur-

ther, the partial structure factors in the long-wavelength limit are used to calculate the isothermal compressibilities at various concentrations.

II. THEORY

As an extension of the MSM approximation for square-well mixtures,^{11,12} we define the direct correlation function as

$$C_{ij}(r) = \begin{cases} C_{ij}^{\text{hs}}(r) = -\frac{U_{ij}(r)}{k_B T}, & 0 < r < \sigma_{ij} \\ \frac{\epsilon_{ij}}{k_B T}, & \sigma_{ij} < r < A_{ij}\sigma_{ij} \\ 0, & r > A_{ij}\sigma_{ij} \end{cases} \quad (1)$$

where $C_{ij}^{\text{hs}}(r)$ stands for the hard-sphere solution of the Percus-Yevick equation for binary mixtures as given by Lebowitz. σ_{ij} , ϵ_{ij} , and A_{ij} stand for hard-sphere diameter, depth, and breadth of the square well, respectively, used for the species i . The mixed parameters are determined by Lorentz-Berthelot mixing rules and they are given by

$$\begin{aligned} \sigma_{12} &= (\sigma_{11} + \sigma_{22})/2, \\ \epsilon_{12} &= (\epsilon_{11}\epsilon_{22})^{1/2}, \\ A_{12} &= (A_{11}\sigma_{11} + A_{22}\sigma_{22})/(\sigma_{11} + \sigma_{22}). \end{aligned} \quad (2)$$

The Fourier transform of $C_{11}(r)$ and $C_{12}(r)$ can be written as

$$\rho_{ii}\hat{C}_{ii}(k) = \frac{24\eta_i}{(k\sigma_{ii})^6} \left[a_i(k\sigma_{ii})^3[\sin(k\sigma_{ii}) - k\sigma_{ii}\cos(k\sigma_{ii})] + \beta_i(k\sigma_{ii})^2[2k\sigma_{ii}\sin(k\sigma_{ii}) - (k^2\sigma_{ii}^2 - 2)\cos(k\sigma_{ii}) - 2] \right. \\ \left. + \gamma_i[(4k^3\sigma_{ii}^3 - 24k\sigma_{ii})\sin(k\sigma_{ii}) - (k^4\sigma_{ii}^4 - 12k^2\sigma_{ii}^2 + 24)\cos(k\sigma_{ii}) + 24] \right. \\ \left. - \left[\frac{\epsilon_{ii}}{k_B T} \right] (k\sigma_{ii})^3[-A_{ii}k\sigma_{ii}\cos(A_{ii}k\sigma_{ii}) + \sin(A_{ii}k\sigma_{ii}) + k\sigma_{ii}\cos(k\sigma_{ii}) - \sin(k\sigma_{ii})] \right], \quad (3)$$

and

$$\hat{C}_{12}(k) = - \left[\frac{4\pi}{k^6} \right] \{ k^2[a_1 + 2b\sigma_{11} + 4d\sigma_{11}^2(\sigma_{12} + 2\lambda)] - 24d\sigma_{12} \} k \sin(k\sigma_{12}) \\ + \{ k^2(2b + 12d\sigma_{11}\sigma_{22}) - k^4[a_1\sigma_{12} + b\sigma_{11}^2 + d\sigma_{11}^3(\sigma_{12} + 3\lambda)] - 24d \} \cos(k\sigma_{12}) \\ + (24d - 2bk^2)\cos(\lambda k) + 24\lambda dk \sin(\lambda k) \\ - (\epsilon_{12}/k_B T)k^3[-A_{12}k\sigma_{12}\cos(A_{12}k\sigma_{12}) + k\sigma_{12}\cos(k\sigma_{12}) + \sin(A_{12}k\sigma_{12}) - \sin(k\sigma_{12})], \quad (4)$$

where $\eta_{ii} = (\pi\rho_{ii}\sigma_{ii}^3)/6$, $\lambda = (\sigma_{22} - \sigma_{11})/2$.

Here ρ_{ii} is the number density of the i th constituent. The various constants that enter into Eqs. (3) and (4) are given by Lobowitz, which are put together for convenience and written as

$$\eta = \eta_1 + \eta_2, \quad (5)$$

$$\alpha = \sigma_{11}/\sigma_{22}, \quad (6)$$

$$a_1 = \{(\eta_1 + \alpha^3\eta_2)(4 + 4\eta + \eta^2) - 3\eta_2(1 - \alpha)^2[1 + \eta_1 + \alpha(1 + \eta_2)](1 + 2\eta_1 - \eta_2) + (1 - \eta^3) - 3\eta_1\eta_2(1 - \eta)(1 - \alpha)^2\} / (1 - \eta)^{-4}. \quad (7)$$

Again we have

$$\alpha^3 a_2 = \{(\eta_1 + \alpha^3\eta_2)(4 + 4\eta + \eta^2) - 3\eta_1(1 - \alpha)^2(1 - \eta_1 + 2\eta_2)[1 + \eta_1 + \alpha(1 + \eta_2)] + (1 - \eta^3)\alpha^3 - 3\eta_1\eta_2(1 - \alpha)^2\alpha(1 - \eta)\} / (1 - \eta)^{-4}, \quad (8)$$

$$\beta_1 = b_1\sigma_{11} = -6[\eta_1(g'_{11})^2 + \eta_2(1 + \alpha)^2\alpha(g'_{12})^2/4], \quad (9)$$

$$\beta_2 = b_2\sigma_{22} \quad (10)$$

$$= -6[\eta_2(g'_{22})^2 + \eta_1(1 + \alpha)^2 + (g'_{12})^2/4\alpha^3], \quad (11)$$

$$\gamma_1 = d\sigma_{11}^3 = (\eta_1 a_1 + \alpha^3\eta_2 a_2)/2 = \alpha^3\gamma_2, \quad (12)$$

$$b\sigma_{22} = -3(1 + \alpha)(\eta_1 g'_{11}/\alpha^2 + \eta_2 g'_{22})g'_{12}. \quad (13)$$

Further,

$$g'_{11} = [(1 + \eta/2) + 3\eta_2(\alpha - 1)/2](1 - \eta)^{-2}, \quad (14)$$

$$g'_{22} = [(1 + \eta/2) + 3\eta_1(1 - \alpha)/2\alpha](1 - \eta)^{-2}, \quad (15)$$

$$g'_{12} = [(1 + \eta/2) + 3(1 - \alpha)(\eta_1 - \eta_2)(2 + 2\alpha)^{-1}](1 - \eta)^{-2}. \quad (16)$$

Here g'_{ij} are not to be confused with the radial distribution functions $g_{ij}(r)$. The g'_{ij} are just constants. The partial structures $S_{ij}(k)$ are now related to the direct correlation $C_{ij}(k)$ functions (DCF) as³

$$S_{11}(k) = \{1 - \rho_{11}\hat{C}_{11}(k) - \rho_{11}\rho_{22}\hat{C}_{12}^2(k)/[1 - \rho_{22}\hat{C}_{22}(k)]\}^{-1}, \quad (17)$$

$$S_{22}(k) = \{1 - \rho_{22}\hat{C}_{22}(k) - \rho_{11}\rho_{22}\hat{C}_{12}^2(k)/[1 - \rho_{11}\hat{C}_{11}(k)]\}^{-1}, \quad (18)$$

$$S_{12}(k) = (\rho_{11}\rho_{22})^{1/2}\hat{C}_{12}(k)\{[1 - \rho_{11}\hat{C}_{11}(k)][1 - \rho_{22}\hat{C}_{22}(k)] - \rho_{11}\rho_{22}\hat{C}_{12}^2(k)\}^{-1}. \quad (19)$$

Now, the total structure factor $S(k)$ in terms of these partial structure factors is given by¹³

$$S(k) = \sum_{i=1}^2 \sum_{j=1}^2 C_i^{1/2} C_j^{1/2} \frac{f_i(k) f_j(k)}{C_1 f_1^2(k) + C_2 f_2^2(k)} S_{ij}(k), \quad (20)$$

where $f_1(k)$ and $f_2(k)$ are the atomic scattering factors and C_1 and C_2 are the atomic fractions of components 1 and 2, respectively.

In this connection, we felt it necessary to see how much

the hard-sphere contributes to the total structure function [Fig. 1(b)] and to get an idea of the contribution of the attractive part, the difference plots are also given in Figs. 1(c), 1(d), 1(e), and 1(f), while that of the square well is given in Fig. 1(a). It may be noted from Fig. 1(b) that the hard-sphere structure factors give low values for the total structures at the first peak and the difference plot gives mainly a positive contribution except at 0.95 concentration. With increase in K concentration the negative contribution increases.

In the long-wavelength limit, Eqs. (3) and (4) reduce to

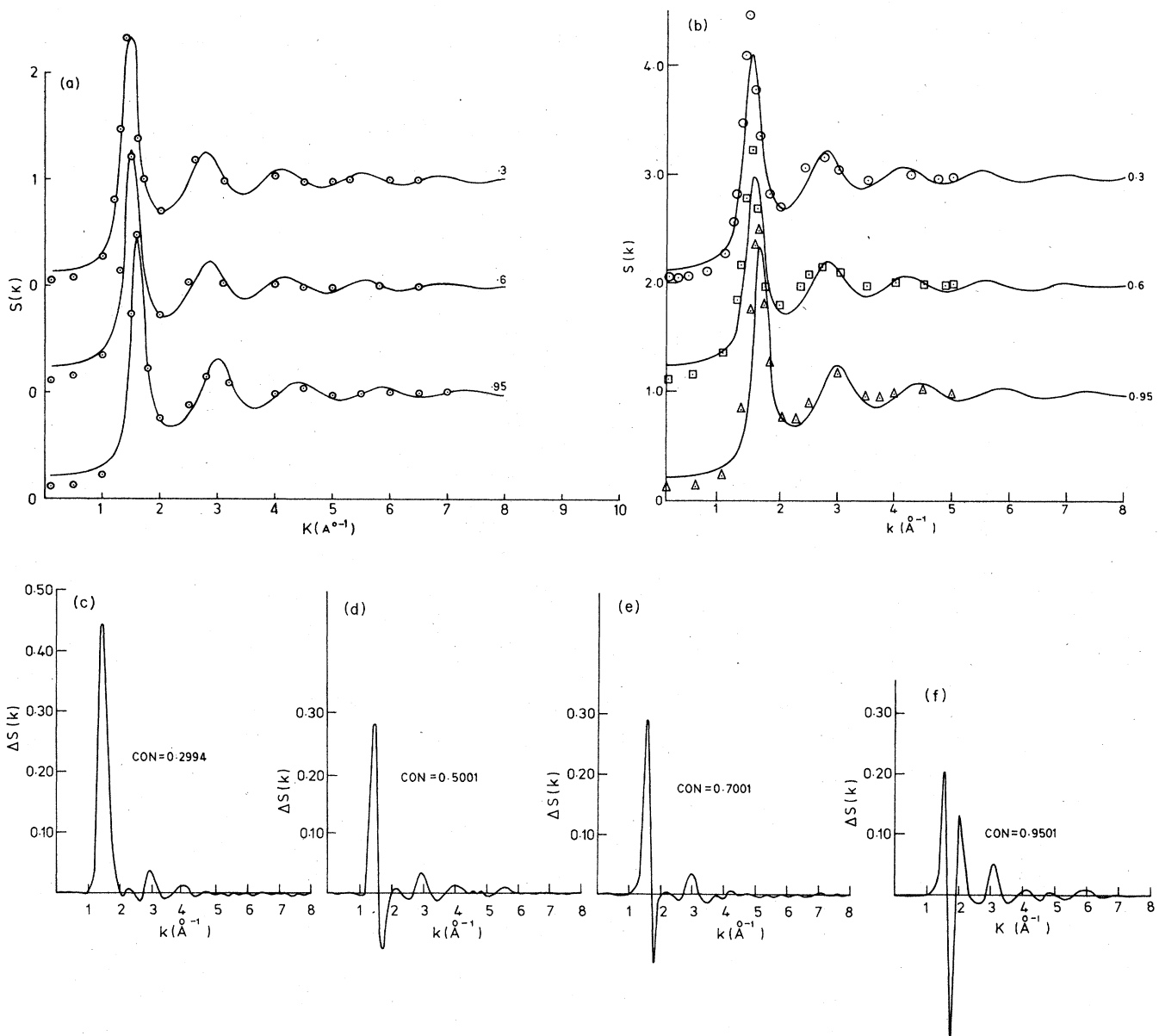


FIG. 1. (a) Total structure factor $S(k)$ at different atom fractions of potassium, calculated results (—) compared with experimental results ($\odot\odot\odot$). (b) Total structure factor $S(k)$ at different atom fractions of potassium, calculated hard-sphere results (—) compared with experimental results [$\odot\odot\odot$, concentration (CON) = 0.3; $\square\square\square$, concentration = 0.6; $\triangle\triangle\triangle$, concentration = 0.95]. (c)–(f) Difference $\Delta S(k)$ of total structure factor of square well and total structure factor of hard sphere marked against the curves as the atom fraction of potassium.

$$\rho_{ii}\hat{C}_{ii}(0) = -24\eta_i(a_i/3 + b\sigma_{ii}/4 + d\sigma_{ii}^3/6) + 8\eta_{ii}\epsilon_{ii}(A_{ii}^3 - 1)/k_B T,$$

and

$$(21)$$

$$\hat{C}_{12}(0) = 4\pi\epsilon_{12}\sigma_{12}^3(A_{12}^3 - 1)/3k_B T - 4\pi a_1\sigma_{12}^3/3 - 4\pi\sigma_{11}^3[b(\sigma_{11} + 2\sigma_{22})/12 + d\lambda\sigma_{11}(3\sigma_{11} + 5\sigma_{22})/10 + d\sigma_{11}^2(2\sigma_{11} + 3\sigma_{22})/30].$$

The isothermal compressibility β_T for a binary mixture can be written in terms of those DCF's in the long-wave limit as¹⁴

$$\beta_T = [1 - C_1\rho_{11}\hat{C}_{11}(0) - C_2\rho_{22}\hat{C}_{22}(0) - 2C_1C_2\rho_{12}\hat{C}_{12}(0)]^{-1}/\rho k_B T. \quad (22)$$

Three other correlation functions $S_{NN}(k)$, $S_{CC}(k)$, and $S_{NC}(k)$ are also defined by Bhatia and Thornton, which are related to $S_{ij}(k)$ s as¹⁰

$$S_{NN}(k) = C_1S_{11}(k) + C_2S_{22}(k) + 2(C_1C_2)^{1/2}S_{12}(k), \quad (23)$$

$$S_{CC}(k) = C_1C_2[C_2S_{11}(k) + C_1S_{22}(k) - 2(C_1C_2)^{1/2}S_{12}(k)], \quad (24)$$

$$S_{NC}(k) = C_1C_2[S_{11}(k) - S_{22}(k) + S_{12}(k)(C_2 - C_1)/(C_1C_2)^{1/2}]. \quad (25)$$

III. RESULTS AND DISCUSSIONS FOR STRUCTURE FACTORS

The computations have been performed for the K-Cs alloy system at nine concentrations and a typical set of results for four concentrations, namely, 0.3, 0.5, 0.7, and 0.95 atomic fraction potassium, have been presented in Figs. 2(a), 2(b), and 2(c) for the three partial structure factors $S_{11}(k)$, $S_{22}(k)$, and $S_{12}(k)$.

The densities of the mixture were obtained from pure liquid densities assuming ideal mixing.¹⁵ Thus, we have

$$\rho_{11} = C_1\rho_{11}^0\rho_{22}^0/C_1(\rho_{22}^0 - \rho_{11}^0) + \rho_{11}^0,$$

$$\rho_{22} = (1 - C_1)\rho_{11}^0\rho_{22}^0/C_1(\rho_{22}^0 - \rho_{11}^0) + \rho_{11}^0,$$

where ρ_{11}^0 and ρ_{22}^0 are the densities of the pure components under the same conditions, the values of which are 0.01265 and 0.008122, respectively. The potential parameters of each component have been obtained by fitting to the first peak of the experimental pure liquid structure function curves individually. The total structure factors are obtained from the partial structure factors using Eq. (20) and the potential parameters used are those of pure metals. While in the case of hard-sphere Percus-Yevick (HSPY) structure factors evaluated by Alblas *et al.*, the parameter η is obtained by fitting the first peak of each individual alloy composition and hence there is a variation of values ranging from 0.46 to 0.48. The present method uses the Lebowitz equation for hard-sphere mixtures and

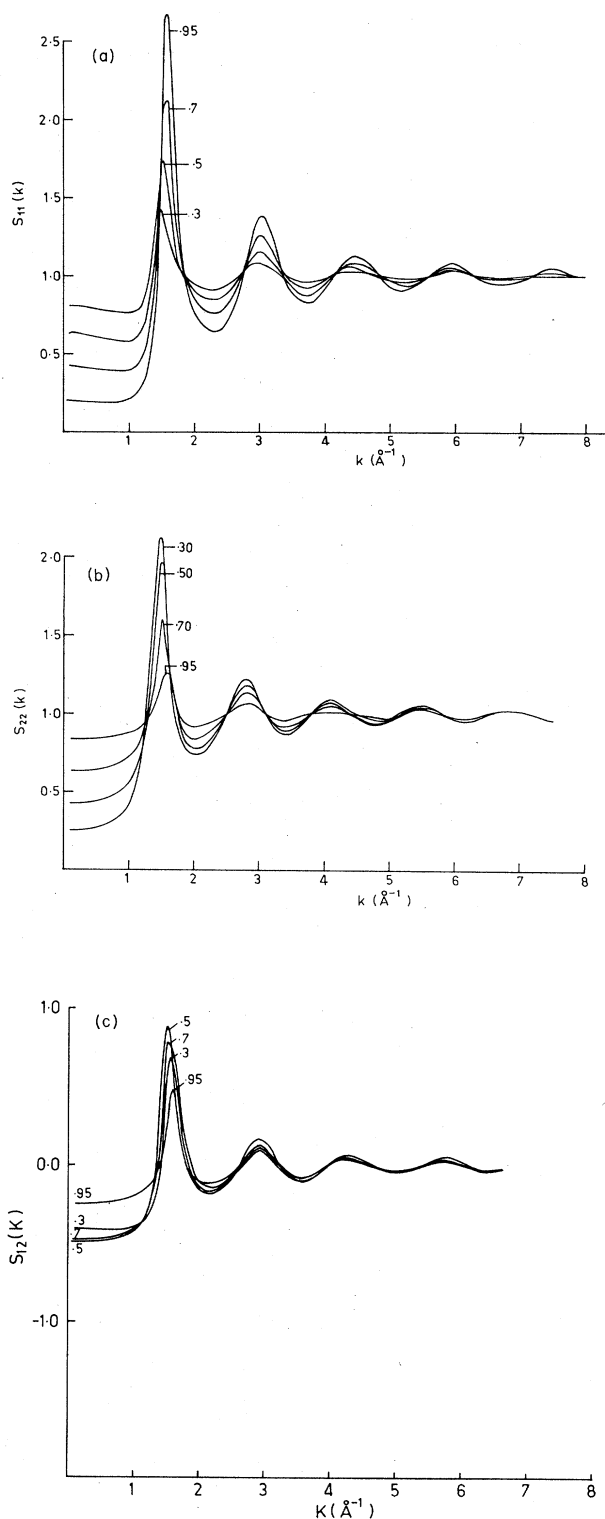


FIG. 2. (a) $S_{11}(k)$ -vs- k curves for different atom fractions of potassium marked against the curves. Subscript 1 denotes K. (b) $S_{22}(k)$ -vs- k curves for different atom fractions of potassium marked against the curves. Subscript 2 denotes Cs. (c) $S_{12}(k)$ -vs- k curves for different atom fractions of potassium marked against the curves.

Berthelot's rules for obtaining the potential parameters. It is seen from Eqs. (2) and (4) the parameters η_1 and η_2 are fixed and the $S_{ij}(k)$ are obtained from Eqs. (17)–(19), (23), and (25). The values obtained and which have been used for the calculation of the $S_{ij}(k)$ of the alloy are

$$\sigma_{11} = 4.220 \text{ \AA}, \quad \epsilon_{11}/k_B = 98.0 \text{ K},$$

$$\sigma_{22} = 4.605 \text{ \AA}, \quad \epsilon_{22}/k_B = 90.0 \text{ K},$$

$$A_{11} = 1.65, \quad T = 373.0 \text{ K},$$

$$A_{22} = 1.60.$$

Here 1 stands for potassium and 2 stands for cesium. It is found that both K and Cs have almost the same principal (S_k) peak values which are 2.8 and 2.6, respectively. Thus in Fig. 2(a) it can be seen that as the concentration of K increases the peak height increases and shifts to the right while with increase in atom fraction of K, the height of $S_{\text{Cs-Cs}}(k)$, i.e., $S_{22}(k)$ decreases [Fig. 2(b)]. It is important to point out that in both $S_{11}(k)$ and $S_{22}(k)$ the region of the principal peak lies between $k=1$ and $k=2.2$ in both the cases. This is also found to be the case in pure metals.¹⁶ In the case of $S_{12}(k)$ the maximum is obtained with equiatomic concentration, and it is found that with maximum concentration of potassium (0.95 at.%) the peak height comes largest at $k=1.6$ and with 0.5 at.% concentration the maximum comes at the value of $k=1.5$. As expected, the $S_{11}(k)$ and $S_{22}(k)$ go to unity at large values of k while in the case of $S_{12}(k)$ it attains a value of zero at large k . It may be noted from Figs. 2(a) and 2(b) the $S(k)$ at low k values is smooth and no shoulders are observed as is found in the case of the Cu-Pb alloy.¹⁷ This again shows that K-Cs forms an ideal alloy. It can also be observed that the k region of the first maximum of $S_{\text{K-K}}(k)$ in both Na-K (Ref. 7) and K-Cs is found to be the same, while that of $S_{\text{Cs-Cs}}(k)$ is also found to be the same in Na-Cs (Ref. 18) and K-Cs alloys. We present the long-wavelength limit of values of $S_{ij}(0)$ and β_T calculated from Eqs. (17)–(19), and (22) in Table I.

In Fig. 1(a) the total structure function calculated from the theoretical $S_{ij}(k)$ using Eq. (20) at three typical concentrations 0.3, 0.6, and 0.95 have been shown. It is seen

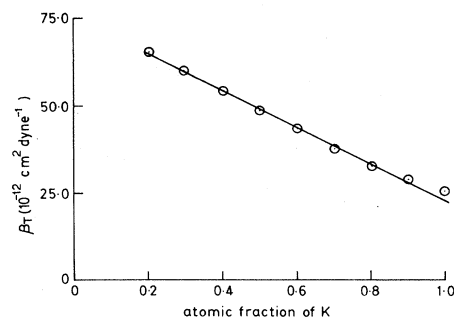


FIG. 3. Isothermal compressibility vs atom fractions of potassium, calculated using the present model results.

that the calculated values agree very well with experiment¹ except at low k . Even in this range the agreement is fair.

In Fig. 3 we give the variation of compressibility as a function of concentration of potassium. In this connection, it may be pointed out that alkali metals are difficult to deal with in theoretical calculations except, though, perhaps for the recent calculations of Singh and Holz,¹⁹ who used a pseudopotential approach and a k -dependent dielectric function. Hence the present calculations become all the more important and the agreement of $S(k)$ between the computed and the experimental values is gratifying.

We give in Figs. 4(a), 4(b), and 4(c) the Bhatia-Thornton structures $S_{\text{NN}}(k)$, $S_{\text{CC}}(k)$, and $S_{\text{NC}}(k)$ for four concentrations. In the case of $S_{\text{NN}}(k)$, the highest peak was obtained with 0.95 atomic fraction potassium, and its variation is similar to that of $S(k)$ in a pure liquid. The $S_{\text{CC}}(k)$ and $S_{\text{NC}}(k)$ oscillate around $C_1 C_2$ and 0, respectively. It may also be noted that $S_{\text{NC}}(k)$ goes to zero while $S_{\text{NN}}(k)$ attains unity at large k . Further, from Fig. 4(b), it can be noted that for 0.3 and 0.7 concentrations of K the $S_{\text{CC}}(k)$ are coincident. At 0.95 atomic fraction of K the concentration-concentration fluctuations are negligible and it remains almost constant around 0.0475. A similar trend has been observed in the case of gold-cobalt alloy at 0.9 atomic fraction of cobalt.²⁰ The present studies were extended up to 0.95 atom fraction of K in the K-Cs alloy and the fluctuations are negligible.

TABLE I. Ashcroft-Langreth partial structure factors in the long-wavelength limit and isothermal compressibilities for liquid potassium-cesium alloys at different atom fractions of potassium.

Concentration (atomic fraction of K)	$S_{11}(0)$	$S_{22}(0)$	$S_{12}(0)$	$\beta_T (10^{12} \text{ cm}^2 \text{ dyn}^{-1})$
0.2000	0.8773	0.1703	-0.3400	65.78
0.2994	0.8060	0.2480	-0.4075	60.18
0.4000	0.7220	0.3316	-0.4565	54.42
0.5001	0.6324	0.4200	-0.4880	48.71
0.6004	0.5326	0.5218	-0.5011	43.08
0.7004	0.4220	0.6291	-0.4910	37.65
0.8003	0.2297	0.7449	-0.4483	32.48
0.8746	0.2006	0.8364	-0.3841	28.84
0.9501	0.0926	0.9337	-0.2609	25.83

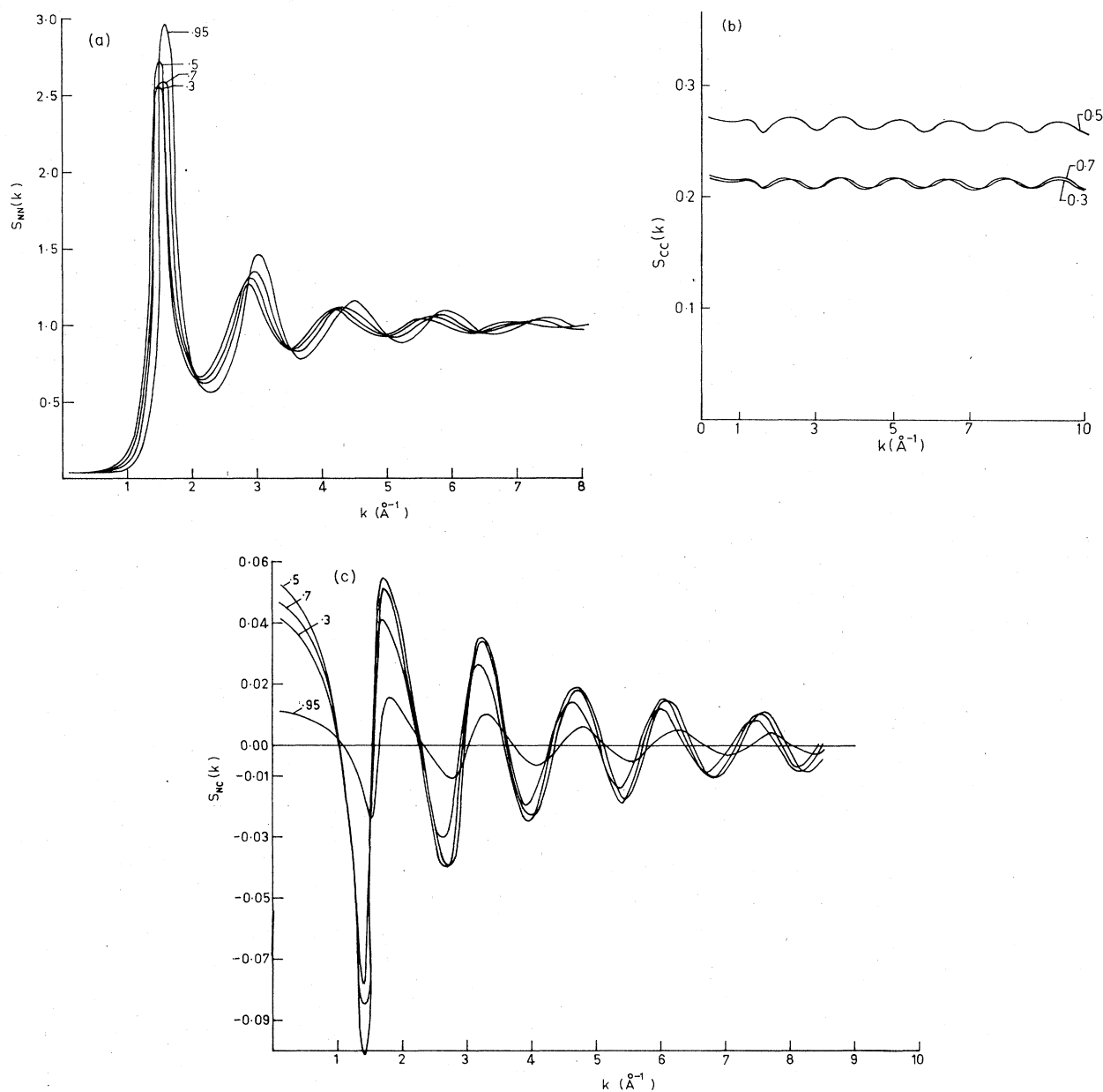


FIG. 4. (a) $S_{NN}(k)$ -vs- k curves for different atom fractions of potassium marked against the curves. (b) $S_{CC}(k)$ -vs- k curves for different atom fractions of potassium marked against the curves. (c) $S_{NC}(k)$ -vs- k curves for different atom fractions of potassium marked against the curves.

IV. RESULTS AND DISCUSSION FOR RADIAL DISTRIBUTION FUNCTIONS

In this section we make a Fourier transformation of the $S_{ij}(k)$ and obtain the radial distribution function $g_{ij}(r)$ using the equation²¹

$$g_{ij}(r) = 1 + \frac{1}{2\pi^2(\rho_i \rho_j)^{1/2}} \times \int_0^\infty [S_{ij}(k) - \delta_{ij}] k^2 \frac{\sin(kr)}{kr} dk. \quad (26)$$

Here δ_{ij} is the well-known Kronecker δ function. We use

the linear trajectory approximation due to Helfand²² extended by Davis and Polyvos^{23,24} to the alloy. We have

$$D_i = \frac{k_B T}{\xi_{ij}}, \quad (27)$$

where D_i is the diffusion coefficient of the i th constituent, k_B is the Boltzmann constant, and ξ_i is the friction coefficient of the i th species, given by

$$\xi_i = \xi_i^H + \xi_i^S + \xi_i^{SH}. \quad (28)$$

In the above equations ξ_i^H , ξ_i^S , and ξ_i^{SH} are the friction coefficients due to repulsive core interactions, soft interac-

TABLE II. Calculated friction coefficients of various liquid K-Cs alloys at 373 K.

Concentration (atomic fraction of K)	$\xi_i^H/k_B T$ (10^5 sec/cm ²)		$\xi_i^S/k_B T$ (10^5 sec/cm ²)		$\xi_i^{SH}/k_B T$ (10^5 sec/cm ²)	
	K	Cs	K	Cs	K	Cs
0.0001	0.1139	0.1882	0.0501	0.0775	0.0891	0.1420
0.1000	0.1177	0.1922	0.0509	0.0780	0.0923	0.1454
0.2001	0.1219	0.1967	0.0517	0.0784	0.0959	0.1491
0.2994	0.1266	0.2015	0.0525	0.0787	0.0949	0.1532
0.4000	0.1320	0.2071	0.0534	0.0789	0.1045	0.1579
0.5001	0.1380	0.2133	0.0545	0.0792	0.1097	0.1632
0.6004	0.1450	0.2203	0.0558	0.0796	0.1157	0.1692
0.7004	0.1531	0.2283	0.0576	0.0804	0.1226	0.1760
0.8003	0.1626	0.2377	0.0600	0.0817	0.1307	0.1840
0.8746	0.1707	0.2454	0.0622	0.0832	0.1377	0.1907
0.8999	0.1737	0.2483	0.0631	0.0839	0.1403	0.1932
0.9501	0.1801	0.2544	0.0649	0.0853	0.1459	0.1985
0.9801	0.1843	0.2583	0.0661	0.0864	0.1494	0.2019
0.9999	0.1872	0.2610	0.0669	0.0870	0.1519	0.2042

tions, and the cross effect between the hard and the soft forces in the potential, respectively. These are given by the equations

$$\xi_i^H = \sum_{j=1}^2 \frac{8}{3} \sigma_{ij}^2 g_{ij}(\sigma_{ij}) \rho_j (2\pi\mu_{ij}k_B T)^{1/2}, \quad (29)$$

$$\xi_i^S = \sum_{j=1}^2 \frac{\rho_i}{3} (2\pi\mu_{ij}/k_B T)^{1/2} (2\pi)^{-2} \times \int_0^\infty k^3 \hat{\psi}_{ij}^S(k) \hat{h}_{ij}(k) dk, \quad (30)$$

and

$$\xi_i^{SH} = - \sum_{j=1}^2 \frac{2\rho_j}{3} g_{ij}(\sigma_{ij}) (2\mu_{ij}/\pi k_B T)^{1/2} \times \int_0^\infty dk [k\sigma_{ij} \cos(k\sigma_{ij}) - \sin(k\sigma_{ij})] \hat{\psi}_{ij}^S(k). \quad (31)$$

ρ_{ii} is the number density of the i th species. In the above equations $\rho_{ii} \hat{C}_{ij}(k)$ and $\hat{\psi}_{ij}^S(k)$ are the Fourier transforms

of the total correlation function and the soft part of the potential $\psi_{ij}(r)$, respectively. Further, σ_{ii} is the hard-sphere diameter and μ_{ij} is the reduced mass given by

$$\mu_{ij} = \frac{m_i m_j}{m_i + m_j} \quad (32)$$

and

$$h_{ij}(k) = [S_{ij}(k) - \delta_{ij}] (\rho_{ii} \rho_{jj})^{-1/2}.$$

For the square-well potential we have

$$\hat{C}_{ij}(k) = [S_{ij}(k) - \delta_{ij}] (\rho_i \rho_j)^{-1/2}, \quad (33)$$

$$\hat{\psi}_{ij}^S(k) = \frac{4\pi\epsilon_{ij}}{k^3} [A_{ij}k\sigma_{ij} \cos(A_{ij}k\sigma_{ij}) - \sin(A_{ij}k\sigma_{ij}) - k\sigma_{ij} \cos(k\sigma_{ij}) + \sin(k\sigma_{ij})], \quad (34)$$

where ϵ_{ij} and A_{ij} are defined already. The computed results for friction coefficients and the diffusion coefficients

TABLE III. Calculated self-diffusion and mutual diffusion coefficients for liquid K-Cs alloys at 373 K.

Concentration (atomic fraction for K)	D_K	D_{Cs}	D_{K-Cs}	D_K/D_{Cs}
	10^{-5} (cm ² /sec)	10^{-5} (cm ² /sec)	10^{-5} (cm ² /sec)	
0.0001	3.9496	2.452	3.9495	1.61
0.1001	3.8315	2.4038	3.6889	1.59
0.2001	3.7091	2.3573	3.4386	1.57
0.2994	3.5829	2.3068	3.2008	1.55
0.4000	3.4490	2.2526	2.9704	1.53
0.5001	3.3084	2.1947	2.7514	1.51
0.6004	3.1587	2.1318	2.5421	1.46
0.7004	2.9995	2.0630	2.3435	1.45
0.8003	2.8302	1.9870	2.1554	1.42
0.8746	2.6977	1.9253	2.0222	1.40
0.8999	2.6514	1.9032	1.9781	1.39
0.9501	2.5578	1.8576	1.8926	1.38
0.9801	2.5010	1.8293	1.8426	1.37
0.9999	2.4631	1.8101	1.8102	1.36

are given in Tables II and III. There is no experimental data available on diffusion coefficients for the liquid K-Cs alloys.

The ratio D_K/D_{Cs} varies in the present case from 1.6 to 1.4 as the atom fraction of K varies from 0 to 1. Constancy of this ratio is generally expected from the regular solution theory.^{25,26}

In the present case the maximum variation is 0.25 parts in 1.5 (average value), which amounts to a variation of 16% and may be considered fair remembering the fact that alkali metals do not form ideal solutions even though thermodynamically the heat of mixing is nearly parabolic in the present alloy. Thus a variation of 16% can be considered to be fairly constant as is found in rare-gas liquid mixtures.²⁷

Unfortunately there is no theory for the mutual diffusion coefficient. However, several workers have pointed out that the mutual diffusion coefficient can be written as²⁷⁻²⁹

$$D_{12} = C_2 D_1 + C_1 D_2 + \dots, \quad (35)$$

where the ellipsis represents some unspecified correction terms. Unless the solution is very irregular, one can apply

this equation to evaluate the mutual diffusion coefficient. In the present case it is a fairly satisfactory regular solution. The values calculated from the above equation are also presented in Table III.

Thus it may be seen that the various parameters used in these calculations are obtained from the structure factor data of pure components only. These results acquire greater importance in the absence of any experimental results and it also shows the usefulness of the model calculations through which we obtained the compressibilities as a function of concentrations, the diffusion coefficients and the partial radial distribution functions, namely, g_{ij} (σ_{ij}) necessary for the evaluation of the diffusion coefficients. It may also be pointed out that by the Fourier transformation of the $S_{ij}(k)$ curves the $g_{ij}(r)$ curves were obtained.

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