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Computation of total and partial structure factors, coordination number, and compressibility with self- and mutual-diffusion coefficients of Hg-In alloy

R. V. Gopala Rao and R. Venkatesh
Division of Physical Chemistry, Jadavpur University, Calcutta 700 032, India

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Hg-In alloy consisting of Hg, which shows several anomalous features in its properties and In, has been studied with a square-well attractive tail as an interaction potential between the atoms in the amalgam. The partial and the total interference functions have been computed with the Lebowitz hard-sphere mixture solution for the Percus-Yevick equation with an attractive square-well potential over a hard-sphere mixture. In addition, the Bhatia-Thoronton correlation functions have also been calculated. From the partial structure factors the number of nearest neighbors has been calculated. All the computed results have been found to be in very good agreement with the x-ray diffraction results obtained by Halder and Wagner [Z. Naturforsch. **22a**, 1489 (1967)] except at 62% atomic fraction of indium. All these results were computed purely from the potential parameters of the pure metals. The alloy is found to show a shoulder in the $S_{NC}(K)$ cross correlation function. This may be due to either compound formation or internal segregation, even though the metals mix freely at all concentrations. The compressibilities at various concentrations of In have been computed from the Kirkwood-Buff formula. The diffusion coefficients have been calculated from Helfand's linear-trajectory principle. The self-diffusion coefficients as evaluated correctly predict them for both metals because of the attractive wells associated with these metals. Thus Hg, in spite of its heavy mass, has a comparatively higher diffusion coefficient than In, which has a lower mass. The melt appears to form a regular solution, as predicted by Bearman and Jones.

I. INTRODUCTION

Mercury amalgams present a long-standing puzzle. Hg is a polyvalent element that has anomalous effective mass[1] and thermoelectric power[2,3] and various other peculiar properties.[2] Mercury forms a variety of pseudocompounds with indium.[4] The structure factor of the Hg-In alloy at various concentrations of Hg has been extensively investigated by Halder and Wagner.[5]

In the present investigation we derive the partial structure factors, the associated Bhatia-Thoronton structure factors, and other thermodynamic and transport properties of the alloy at various concentrations of Hg.

II. THEORY

We use the well-known Lebowitz solution of hard-sphere mixtures along with a square-well attractive tail in arriving at the partial structure factors. Thus in the evaluation of the direct correlation function between i and j atoms we choose

$$C_{ij}(r)=\begin{cases} C_{ij}^{0}(r), \quad 0<r<\sigma_{ij} & \text{(1a)} \\ -\beta\varepsilon_{ij}(r), \quad \sigma_{ij}\le r\le A_{ij}\sigma_{ij} & \text{(1b)} \\ 0, \quad r>A_{ij}\sigma_{ij} \; . & \text{(1c)} \end{cases}$$

Here $C_{ij}^{0}(r)$ stands for the hard-sphere solution of the Percus-Yevick equation for binary mixture as obtained by Lebowitz.[6] Equation (1b) is formed under the mean-spherical-model approximation. Here σ_{ij}, ε_{ij}, and A_{ii} are the hard-sphere diameter, potential-energy depth, and breath of the square-well potential of the ith species, respectively. The hybrid parameters have been computed through Lorentz-Berthelot rules,

$$\begin{aligned} \sigma_{ij}&=(\sigma_{ii}+\sigma_{jj})/2 \; , \\ \varepsilon_{ij}&=(\varepsilon_i\varepsilon_j)^{1/2} \; , \\ A_{ij}&=(A_{ii}\sigma_{ii}+A_{jj}\sigma_{jj})/2\sigma_{ij} \; . \end{aligned} \tag{2}$$

The $C_{ij}(r)$ were obtained by Lebowitz and have been discussed already in detail.[7,8] The Fourier transforms of the direct correlation function $C_{ii}(r)$ and $C_{12}(r)$ have also been given previously.[9,10] The partial structure factors in terms of $C_{ij}(K)$ can be written in a straightforward manner[11] as

$$S_{11}(k)=\{1-\rho_1C_{11}(K) -\rho_1\rho_2C_{12}^2(K)/[1-\rho_2C_{22}(K)]\}^{-1} \; , \tag{3}$$

$$S_{22}(K)=[1-\rho_1C_{11}(K)]S_{11}(K)/[1-\rho_2C_{22}(K)] \; , \tag{4}$$

$$S_{12}(K)=(\rho_1\rho_2)^{1/2}C_{12}(K)S_{11}(K)/[1-\rho_2C_{22}(K)] \; . \tag{5}$$

Further, the total structure factor[12] in terms of partial structure factors can be written as

$$S(K)=\sum_{i=1}^{2}\sum_{j=1}^{2}(C_iC_j)^{1/2}\frac{f_if_j}{C_1f_1^2+C_2f_2^2}S_{ij}(K) \; . \tag{6}$$

Here f_i and f_j are the atomic scattering factors and are taken from the literature[13] and C_i is the atomic fraction of the *i*th species. Thus, for a binary alloy we get for the total structure factor

$$S(K)=\frac{1}{C_1f_1^2+C_2f_2^2}[C_1f_1^2S_{11}(K)+2(C_1C_2)^{1/2}f_1f_2S_{12}(K)+C_2f_2^2S_{12}(K)]\ . \tag{7}$$

The input parameters used in the evaluation of the partial structure factors have been given in Table I.

In order to compute the important thermodynamic properties, for the compressibility we use the Kirkwood-Buff equation,[14] which can be written as

$$\rho k_BT\beta_T=[1-C_1\rho_1C_{11}(0)-C_2\rho_2C_{22}(0)-2\rho_{12}C_1C_2C_{12}(0)]^{-1}\ . \tag{8}$$

Here $C_{ii}(0)$ is the direct correlation function in the long-wavelength limit, and the various expressions for $C_{11}(0)$ and $C_{12}(0)$ have been given already[9,10] and hence will not be repeated here. Here $\rho_{12}=(\rho_1\rho_2)^{1/2}$. The compressibility at various concentrations is given in column 7 of Table II.

The well-known Bhatia-Thoronton[15] correlation functions which are related to the various thermodynamic properties[16] are related to the partial structure factors linearly as

$$S_{NN}(K)=C_1S_{11}(K)+C_2S_{22}(K)+2C_1^{1/2}C_2^{1/2}S_{12}(K)\ , \tag{9}$$

$$S_{CC}(K)=C_1C_2[C_2S_{11}(K)+C_1S_{22}(K)-2(C_1C_2)^{1/2}S_{12}(K)]\ , \tag{10}$$

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

Here $S_{NN}(K)$, $S_{CC}(K)$, and $S_{NC}(K)$ are number-number, concentration-concentration, and cross-correlation functions, respectively. The densities of the alloy are taken from the literature[17] at various concentrations of Hg. From these experimental values the number densities have been calculated.

A. Coordination number

From the partial structure factors the radial distribution functions have been computed by Fourier inversion. Thus we have the partial radial distribution function $g_{ij}(r)$ given by

$$g_{ij}(r)=1+\frac{1}{2\pi^2(\rho_i\rho_j)^{1/2}}\int_0^\infty[S_{ij}(K)-\delta_{ij}]K\sin(kr)dr\ . \tag{12}$$

Here δ_{ij} is the well-known Kronecker delta. From these $g_{ij}(r)$ we obtain the first coordination numbers through the equation

$$\eta_{ij}=4\pi\rho_0\int_0^{r_{\min}}g_{ij}(r)r^2\,dr\ . \tag{13}$$

Here $r_{\min}$ is the first minimum of the partial radial distribution function.

TABLE I. Input parameters used in calculations of Hg-In alloy.

Metal	Temp. (K)	σ_{ii} (Å)	ε_{ii}/k_B (K)	A_{ii}
Hg	298	2.80	100.00	1.73
In	298	2.83	173.76	1.72

III. RESULTS AND DISCUSSION

The calculated partial structure factors $S_{11}(K)$, $S_{22}(K)$, and $S_{12}(K)$ are shown in Figs. 2–5. The total structure factors are shown in Fig. 1 and are compared with experiment. Here subscripts 1 and 2 refer to Hg and In, respectively. $S_{11}(K)$ and $S_{22}(K)$, and also $S(K)$, the total structure factor, show characteristics similar to a single-component system, while $S_{12}(K)$ goes to zero at large K.

From Eqs. (9)–(11) we obtain the Bhatia-Thoronton structure factors which are shown in Figs. 6–10. The number-number correlation function shows a great resemblance to the total structure factor and becomes unity at large K. However, at all concentrations $S_{NN}(K)$ shows two conspicuous first and second peaks, thereby showing a strong number-number correlation in momentum space. The $S_{CC}(K)$ function oscillates around the value of C_1C_2 and shows a comparatively large value at small K, and is shown for clarity in Figs. 9 and 10 separately. The $S_{NC}(K)$ functions oscillate around zero. The graphs also show a shoulder around $K=3.7$ Å^{-1}, indicating the formation of a compound.[4] The peculiar nature of Hg is also observed in the resistivities of Hg amalgams.[2]

Unfortunately, no experimental data are available for comparison of theoretical compressibilities. However, it may be observed that at low concentrations of indium (i.e., at 5 at. % of In) the compressibility of the amalgam is 15.92×10^{-12} cm^2/dyn as compared to pure Hg, whose compressibility is 5.5×10^{-12} cm^2/dyn,[18] and that of In, which is approximately 3.5×10^{-12} cm^2/dyn. This may be due to the presence of a large number of holes present in the amalgam and the loose compound-forming nature of the alloy. Besides, there is a difference in the valencies of these elements. The same observations as to the formation of unstable compounds of Hg amalgams have been made by Faber.[2] Thus, according to him, Na and Hg form a loose compound ($NaHg_2$) which could affect the compressibility. The case must be similar for Hg-In as well, and hence we see the high compressibility exhibited by the alloy. Further, in the case of Hg-In, two anomalies in the sound velocity were observed[4] which may be due to some compound formation, and hence we have the high compressibilities as obtained in the present calculations. However, it may be observed from Table III that the compressibilities smoothly increase with increasing concentration of In, which shows that the two elements mix freely in spite of their valence differences.

The partial coordination numbers at different concentrations are given also in Table II. Here η_{ii} stands for the number of nearest neighbors of the same kind (i.e., first shell) while η_{12} gives the number of nearest neighbors of

TABLE II. Calculated values of the coordination member and isothermal compressibility at various concentrations of Hg-In alloy.

Composition (at. % In)	ρ Atoms (Å^{-3})	η_{11}	η_{22}	η_{12}	η	$S(0)$	$10^{12}X_T$ (cm^2/dyn)
5	0.0405	8.1335	0.4249	1.9136	10.4720	0.0265	15.92
12	0.0404	7.5180	1.0322	2.8511	11.4013	0.0287	17.29
25	0.0401	6.4479	2.1622	3.8295	12.4396	0.0320	19.41
35	0.0398	5.4740	3.0217	4.1357	12.6314	0.0340	20.80
42	0.0396	4.8602	3.6189	4.2617	12.7408	0.0351	21.57
50	0.0393	4.2152	4.3502	4.3495	12.9149	0.0364	22.55
62	0.0389	3.1691	5.3632	4.1876	12.7199	0.0377	23.58

the second kind with respect to the first. As expected, it may be observed that when the concentration of Hg (designated as 1) is high, the number of nearest neighbors is also high, while the reverse is the case with respect to indium, whose concentration is less. Further, as the concentration of In increases, the number of nearest neighbors (NN's) of its own kind increases smoothly. The same trend is also observed in the case of Hg. It may be noticed that at 50 at. % concentration the NN's of the same kind are astonishingly the same. This is expected because the atomic volumes of the elements (In$\approx$15 cm^3/mol, Hg$\approx$14.1 cm^3/mol), and also their compressibilities are nearly equal. Thus, the number of nearest neighbors at 50 at. % is found to be the same. Further, the total number is around 12, which corresponds to a fcc or a hcp structure and is in good agreement with those obtained by Wagner and Halder.[5] The near-equal values of the NN's at 50 at. % concentration is in satisfactory agreement with the fact that the diameters of the atoms are nearly equal.

IV. COMPUTATION OF TRANSPORT PROPERTIES FROM PARTIAL STRUCTURE FACTORS

In this part of the paper we present computations using the above data to evaluate the diffusion coefficient. We use the linear-trajectory method applied to mixtures.[19,20]

As is well known, the diffusion coefficient of the lth species D_l is connected to the friction constant as

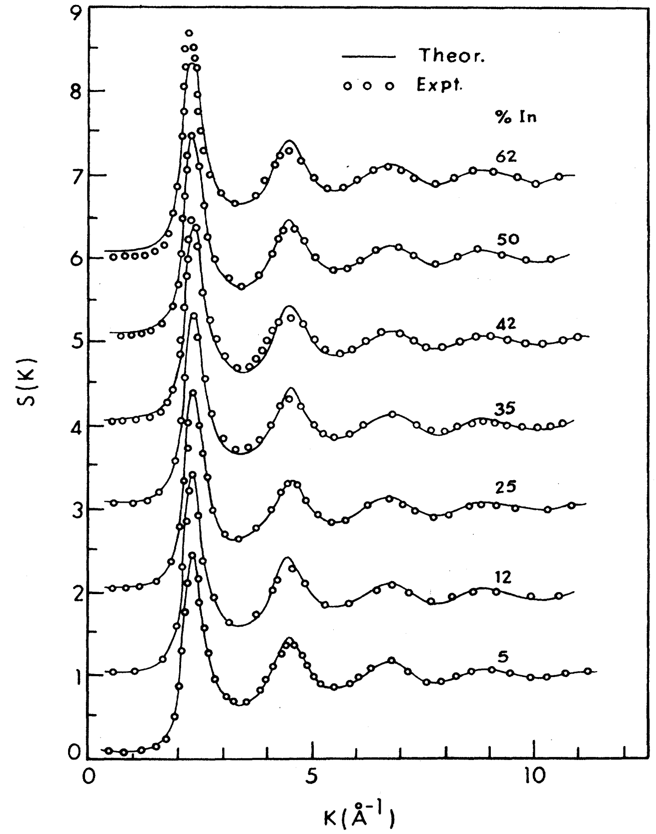

FIG. 1. $S(K)$ vs K at different at. % In.

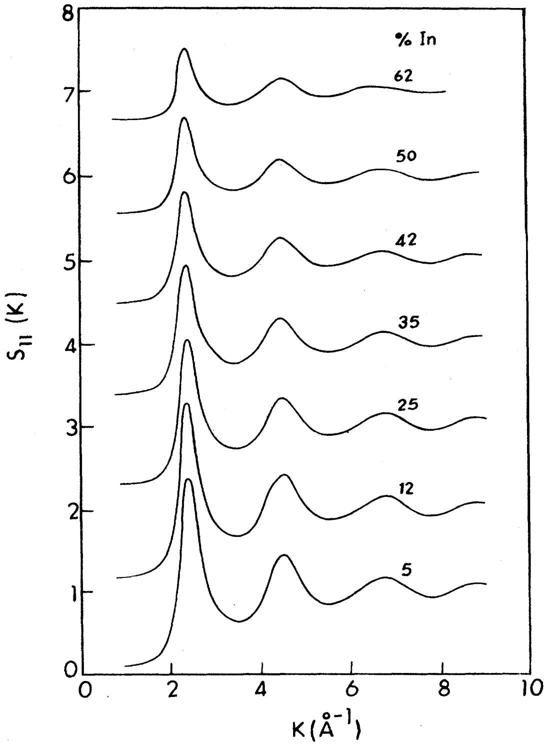

FIG. 2. $S_{11}(K)$ vs K at different at. % In.

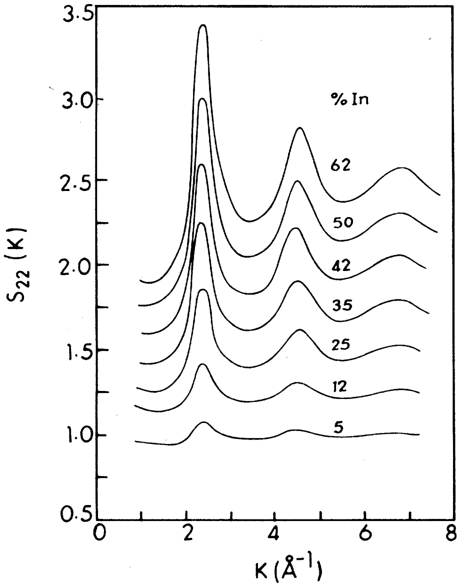

FIG. 3. $S_{22}(K)$ vs K at different at. % In.

$$D_l=\frac{k_B T}{\xi_l} . \tag{14}$$

The friction constant can be written as a sum of three contributions, namely

$$\xi_l=\xi_l^H+\xi_l^S+\xi_l^{SH} . \tag{15}$$

Here ξ_l^H, ξ_l^S, and ξ_l^{SH} are the hard sphere, soft part, and cross coefficient of the friction constant, given by the following equations:

$$\xi_l^H=\sum_{m=1}^{2}\tfrac{8}{3}\sigma_{lm}^2 g_{lm}(\sigma_{lm})\rho_m(2\pi u_{lm}k_B T)^{1/2} , \tag{16}$$

$$\xi_l^S=-\sum_{m=1}^{2}\frac{\rho_m}{3}\left[\frac{2\pi u_{lm}}{k_B T}\right]^{1/2}\left[\frac{1}{(2\pi)^2}\right] \times\int_0^\infty K^3\hat{V}_{lm}^S(K)\hat{G}_{lm}(K)dk , \tag{17}$$

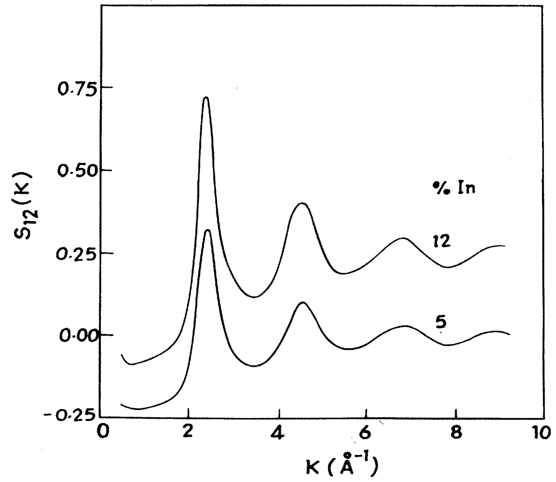

FIG. 4. $S_{12}(K)$ vs K for 5 and 12 at. % In.

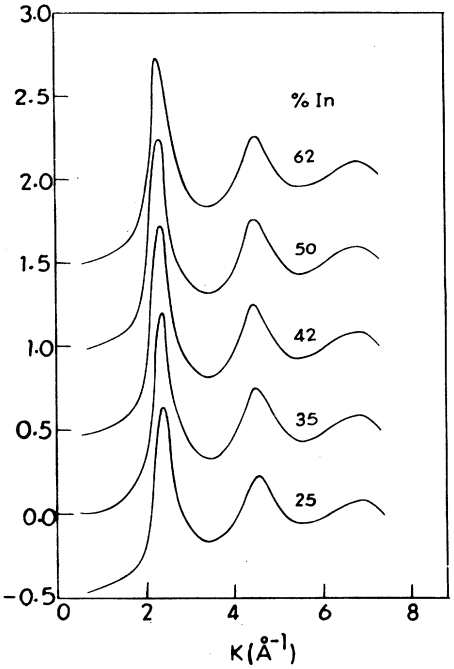

FIG. 5. $S_{12}(K)$ vs K for different concentrations of In.

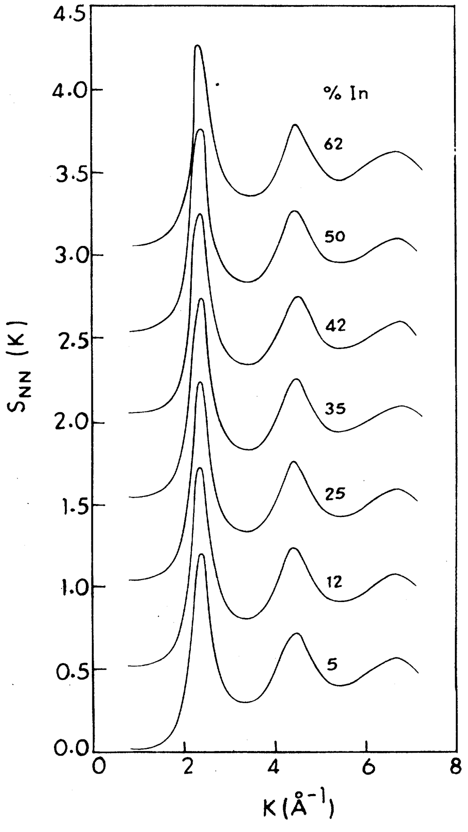

FIG. 6. $S_{NN}(K)$ vs K for different at. % In.

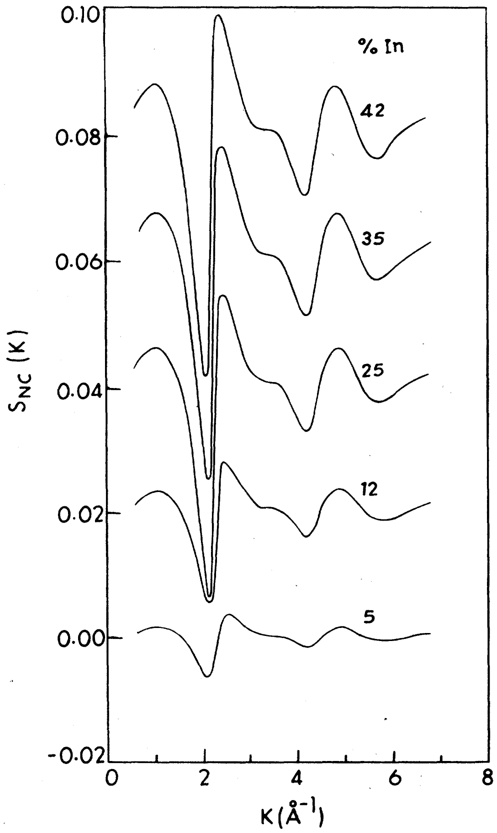

FIG. 7. $S_{NC}(K)$ vs K for 5, 12, 25, 35 and 42 at. % In.

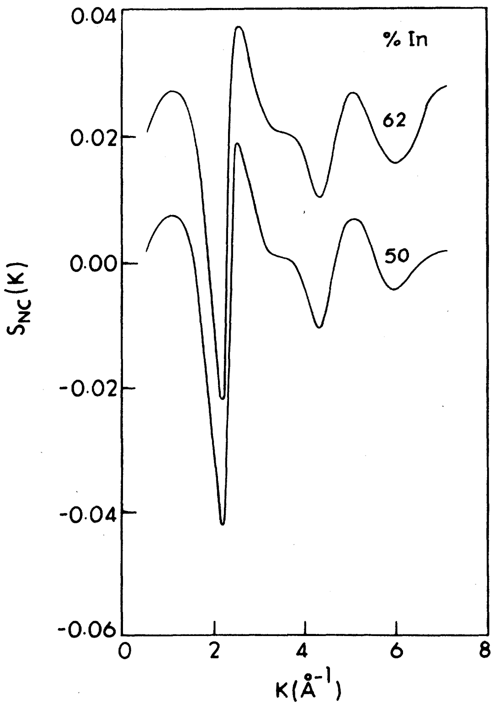

FIG. 8. $S_{NC}(K)$ vs K for 50 and 62 at. % In.

and

$$\xi_l^{SH} = -\sum_{m=1}^{2} \frac{2\rho_l}{3} g_{lm}(\sigma_{lm}) \left[\frac{2u_{lm}}{\pi k_B T} \right]^{1/2} \times \int_0^\infty dk [K\sigma_{lm}\cos(K\sigma_{lm}) - \sin(K\sigma_{lm})] \hat{V}^{S}_{lm}(K) \,. \tag{18}$$

Here ρ_i is the number density of the ith species. $\hat{G}_{lm}(K)$ and $\hat{V}^{S}_{lm}(K)$ are the Fourier transforms of the total correlation function $h(r)$ and the soft part of the potential, $\hat{V}^{S}_{lm}(r)$, respectively. Further, u_{lm} is the reduced mass,

$$u_{lm} = \frac{m_l m_n}{m_l + m_n} \,. \tag{19}$$

In the present case we have

$$\hat{G}_{lm}(K) = [S_{lm}(K) - \delta_{lm}](\rho_l \rho_m)^{1/2} \,, \tag{20}$$

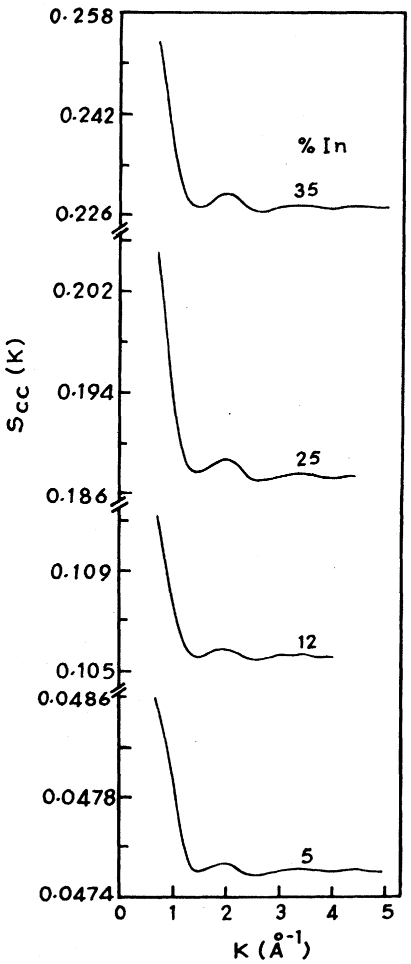

FIG. 9. $S_{CC}(K)$ vs K for 5, 12, 25, and 35 at. % In.

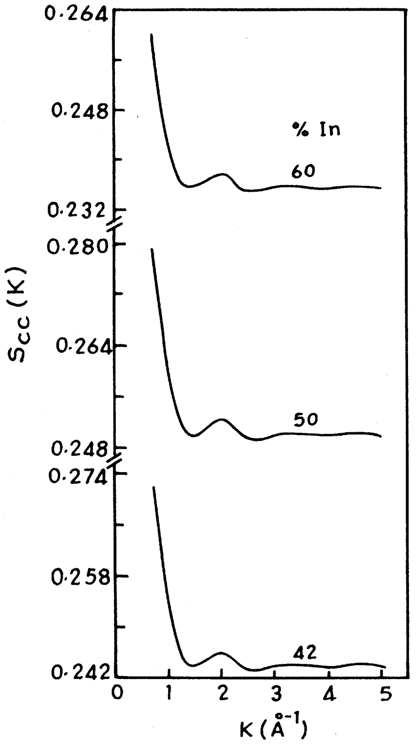

FIG. 10. $S_{CC}(K)$ vs K for 42, 50, and 60 at. % In.

$$\hat{V}^{S}_{lm}(K)=\frac{4\pi\varepsilon_{lm}}{K^3}[A_{lm}K\sigma_{lm}\cos(A_{lm}K\sigma_{lm}) -K\sigma_{lm}\cos(K\sigma_{lm})+\sin(K\sigma_{lm})] . \tag{21}$$

The various contributions to the total friction constant are given in Table III and the self- and mutual-diffusion coefficients are given in Table IV. The approximate mutual-diffusion coefficient is computed from the following equation:

$$D_{12}=C_2D_1+C_1D_2+\text{correction terms} . \tag{22}$$

The self- and mutual-diffusion coefficients as evaluated from Eqs. (14) and (22) are given in Table IV.

It may be observed from Table III that the hard-sphere part of the friction coefficient is higher for Hg than for In. From Eq. (16) we can easily perceive that the hard-sphere part for Hg should be higher than that of In since the mass of Hg is much higher than In. However, the soft part of In contains $\hat{V}^{S}_{lm}(K)$, which, as can be observed from Eq. (21), has a term ε_{lm} (the potential-energy depth) which is much higher for In than for Hg. Hence ξ^S and ξ^{SH} are higher for In than Hg. Thus the total of ξ_l is nearly the same for both elements, which therefore gives almost the same self-diffusion coefficient. Thus the high potential-energy depth, which is an indication of its attractivity to its cluster, offsets its mobility in spite of its low mass. On the other hand, Hg has a higher mass but also a low potential-energy depth, and hence has a segregating nature. It may be observed from Table IV that at a very low concentration of In (5 at. %) the present computed value is nearly equal to that obtained by Mangelsdorf[21,22] for Hg (1.6×10^{-5} cm^2/sec). In the case of In it was actually reported[22] that its diffusivity is less than Hg. In fact, the observed value of In in liquid Hg was found to be 1.39×10^{-5} cm^2/sec. Thus the present calculated values are interestingly in conformity with the observed values. At the high concentration of 62 at. % atomic fraction of In, the value of its self-diffusion coefficient is 2.3×10^{-5} cm^2/sec, while that of pure In is 1.6×10^{-5} cm^2/sec. The present computed results on diffusion, which are in conformity with experiment,[22] are the result of taking an attractive tail as a perturbation over the hard sphere. If a simple hard-sphere potential is taken into consideration, the computed results are not in conformity with experiment. This can be easily seen from Table III, where ξ^H of mercury is higher than In with the result that the diffusion coefficient would have been less than that of In and hence in contradiction with experiment.

It may be observed from the last column of Table IV that the ratio of the self-diffusion coefficients is nearly constant (within 5%) over the entire range of concentrations. A similar behavior was observed for rare-gas mixtures by Jacucci and McDonald[23] in their computer experiments. From the regular-solution theory of Bearman and Jones,[24] a constancy of ratio is also expected. It was found that the ratio of the diffusion coefficient is inversely proportional to the square of the atomic radii, i.e.,

TABLE III. Computed values of friction constants at various concentrations.

Composition (at. % In)	$10^9\xi^{HS}$ (g/sec) Hg	In	$10^9\xi^{S}$ (g/sec) Hg	In	$10^9\xi^{SH}$ (g/sec) Hg	In
5	1.015	0.8697	0.2993	0.3936	0.4752	0.5400
12	1.001	0.8600	0.3056	0.4033	0.4781	0.5446
25	0.9688	0.8359	0.3171	0.4213	0.4798	0.5493
35	0.9401	0.8139	0.3259	0.4353	0.4789	0.5502
42	0.9206	0.7993	0.3321	0.4452	0.4785	0.5511
50	0.8950	0.7791	0.3393	0.4566	0.4756	0.5493
62	0.8598	0.7518	0.3503	0.4742	0.4727	0.5481

TABLE IV. Calculated self- and mutual-diffusion coefficients at different concentrations.

Composition (at. % In)	In units of 10^{-4} cm^2/sec D_{Hg}	D_{In}	$D_{\mathrm{Hg\text{-}In}}$	$D_{\mathrm{Hg}}/D_{\mathrm{In}}$
5	0.2299	0.2280	0.2281	1.0083
12	0.2304	0.2275	0.2278	1.0127
25	0.2329	0.2276	0.2289	1.0193
35	0.2357	0.2285	0.2310	1.0315
42	0.2375	0.2290	0.2326	1.0371
50	0.2405	0.2304	0.2355	1.0438
62	0.2444	0.2318	0.2396	1.0544

$D_1/D_2=(\sigma_2/\sigma_1)^2$. In the present case $(\sigma_2/\sigma_1)^2=1.02$, while the average value, as seen from Table IV, is 1.03. Thus Hg-In alloy appears to form a regular solution and both the structural and transport properties can be calculated purely from the parametrized potential energy of the simple liquid metals.

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