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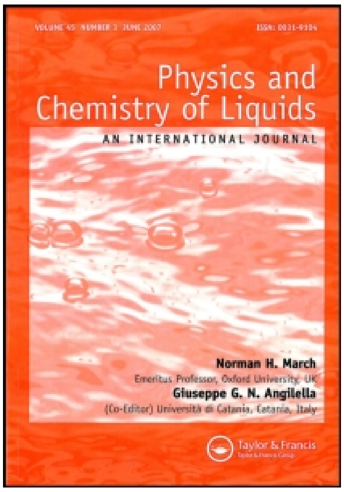

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Neutron scattering measurements from liquid na-k alloys and associated Interionic potentials

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Neutron Scattering Measurements from Liquid Na–K Alloys and Associated Interionic Potentials

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Liquid static structure factors for Na–K alloys at concentrations of 25, 50 and 75 atomic per cent have been measured by neutron scattering in the range of momentum transfer 0.5–7.5 Å^{-1}. From the 50% alloy, an approximate potential for a reference liquid has been extracted. This is compared with potentials for pure liquid Na and K obtained from available X-ray data by the same approximate analysis.

1 INTRODUCTION

As part of a programme to study the properties of liquid metals and alloys, the liquid structure factors have been measured for sodium, potassium and some of their alloys to investigate their variation as a function of the concentration of the constituents. The properties of the alkali metals and their

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alloys are of fundamental importance in the theory of conducting liquids as well as being of technological interest because of their possible use in fast reactors.

The experimental procedures and final data are summarized in some detail in Sections 2 and 3. In Section 4, a theory based on the Born–Green–Yvon hierarchy is presented which will allow the extraction of approximate interionic potentials from a knowledge of the three partial structure factors $S_{\mathrm{Na-Na}}$, $S_{\mathrm{K-K}}$ and $S_{\mathrm{Na-K}}$. Because the present experiments only allow the determination of the number-number structure factor[1] S_{NN} as a function of momentum transfer (denoted by either Q or by k below) for each alloy, we have then had recourse to the concept of a reference liquid, introduced via conformal solution theory by Longuet–Higgins.[2] From the present measurements on the 50% alloy we have extracted an approximate potential for the reference liquid and have compared it with effective potentials derived by the same method for pure Na and pure K. It may well be possible to generate alloy potentials for Na–K from this reference liquid potential by suitable scaling (cf Eq. (5.1) below). We hope to test this by molecular dynamics calculations in a subsequent paper.

2 EXPERIMENTAL DETAILS

Three samples of sodium-potassium alloy containing 75, 50 and 25 atomic per cent sodium respectively were prepared by mixing the constituents (purity 99.99%) in an argon filled glove box and sealing under an argon atmosphere in silica (sample length 100 mm × 10 mm diameter) using

TABLE 2.1

Sample data and experimental parameters (data on Na–K alloys from Diment and Warwick)[3]

Sample composition (atomic %)	100 Na	75 Na–25 K	50 Na–50 K	25 Na–75 K	100 K
Weight % of sodium	100	64	37	17	0
Melting temperature (°C)	98	31	3	6	64
Measurement temp. (°C)	108 ± 2	41 ± 2	19 ± 1	19 ± 1	74 ± 2
Density at meas. temp. (gm cm^{-3})	0.925	0.910	0.882	0.813	0.815
Coherent scattering X-section (barns)	1.65				1.72
Incoherent scattering X-section barns)	1.7				0.5
Wavelength of incident neutron (Å)		1.37			
Angular resolution		½°–2° over range			
Measuring period days)	3	3	5	3	3

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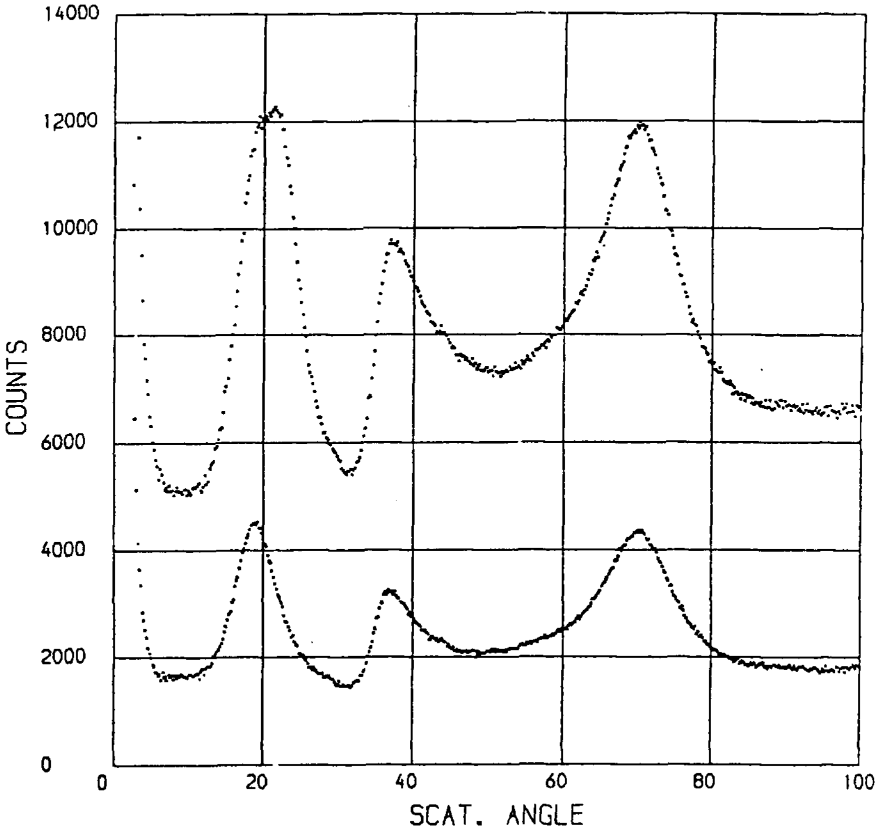

FIGURE 2.1 Detector counts as a function of angle of neutrons scattered by (a) 50% Na-K alloy in a silica tube and (b) silica tube alone.

ground glass stoppers and epoxy resin sealant. Samples of pure sodium and potassium were also prepared.[†] Heating coils were wound above and below the part of the samples being observed (for those samples not liquid at room temperature) and thermocouples were attached to the outside of the tubes G.E. varnish. Heating was maintained by a Eurotherm controller. Neutron scattering spectra from the central 30 mm of samples were measured on the Curran diffractometer on the DIDO reactor at Harwell; spectra were also measured from an empty matching silica tube and a rod of vanadium metal for calibration. The physical data for the samples and the experimental parameters are given in Table 2.1; typical spectra are shown in Figure 2.1.

[†] We are indebted to Dr. J. T. Diment and his group in Metallurgy Division at Harwell for the preparation of these samples.

3 DATA REDUCTION

Liquid structure factors were extracted from the measured spectra, the reader being referred to Page[4] for details of processing the data. Some difficulties were encountered in this processing, including: (a) the silica tubes-tubes superimposed a liquid-like structure pattern (see Figure 2.1) on the data which made the subtraction of the spectra sensitive to the absorption and multiple scattering corrections and (b) the coherent scattering cross-sections for the sample were small and the incoherent cross-section relatively large (see Table 2.1 which meant the statistical spread (±5%) of the final data points after all subtractions was relatively poor. However, as the data are smoothly varying, a cubic spline function could be fitted which gives a greater degree of confidence. Figure 3.1 shows the data points from a single day's run of the structure factor $S(Q)$ for the 50 Na-50 K sample. To check the data, the structure factors for the pure metals were compared with those

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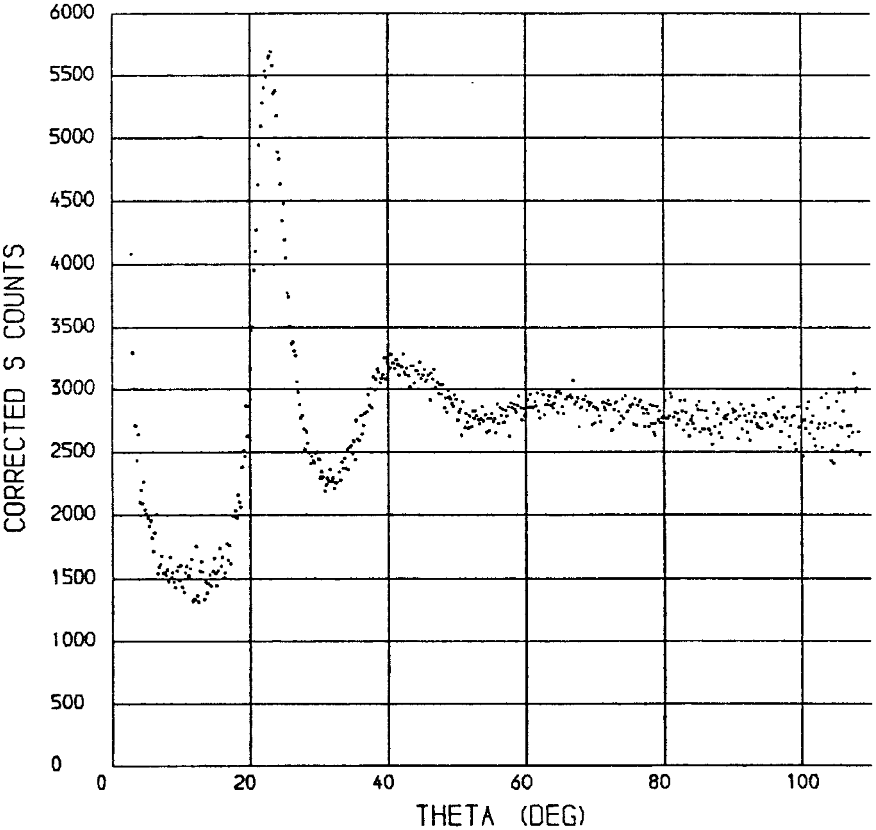

FIGURE 3.1 $S(Q)$ data for a single run from the 50% Na-K alloy after all corrections have been applied.

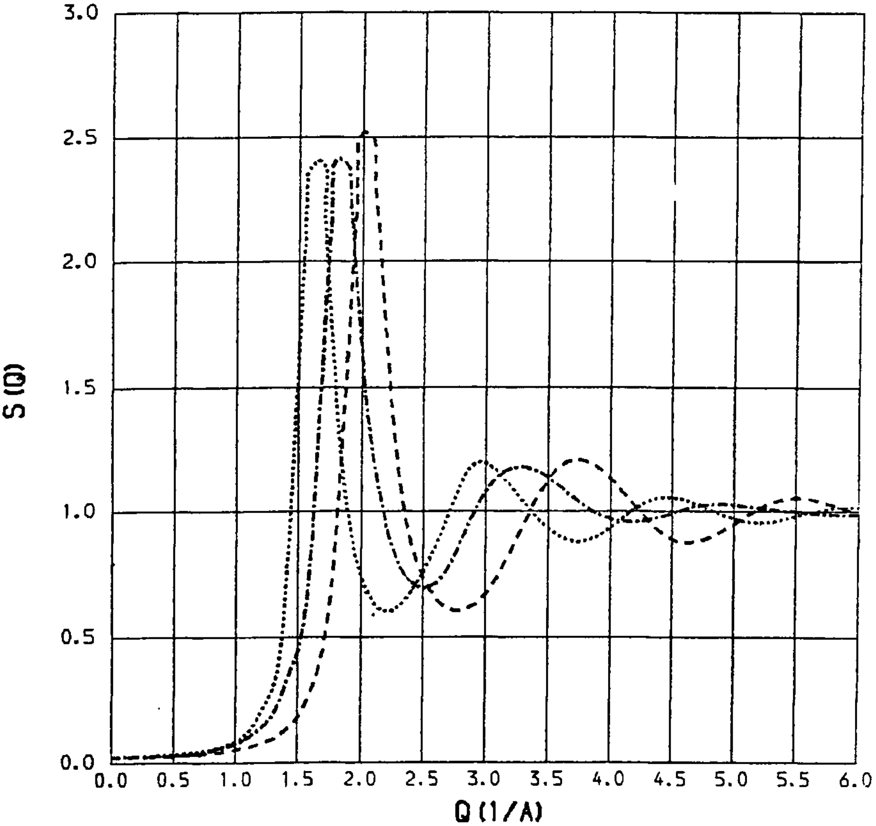

FIGURE 3.2 Smoothed structure factors for Na at 108°C (......), 50% Na-K alloy at 19°C (— · — · —) and K at 74°C(———).

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obtained using X-radiation by Greenfield, Wellendorf and Wiser[5] and with the early neutron data of Gingrich and Heaton.[6] The agreement is within our estimated error of ±3% with the exception that the principal maxima in the neutron data were 10 ± 1% lower than those for the X-ray data. For a discussion and interpretation of the point, reference should be made to the work of Egelstaff, March and McGill.[7]

For scattering angles <6°, interference from the main beam in the spectrometer made the neutron data unreliable and in this region the X-ray data of Greenfield, Wellendorf and Wiser[5] have been used for the pure metals while the alloy data were extrapolated to the time intercept at $Q = 0$ $(S(0) = 0.025)$ as for the pure metals.

Figure 3.2 shows the spline fitted structure factors for the 100% and 50% samples. The intermediate concentration samples fall midway in their relative ranges and, within experimental error, the whole family of curves

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varied smoothly as a function of concentration. The structure factor for the 50% alloy is not an average of those for the pure metals in that: (a) the main peak is slightly lower than that of either of the two components and (b) the oscillations at higher Q-values are also slightly lower than those of the components.

Table 3.1 lists the values of the structure factors for the pure metals and the 50% alloy; the data for the 25–75% alloys can be interpolated from these.

TABLE 3.1

Structure factors for pure metals and 50% alloy

Q	Na	Na/K	K	Q	Na	Na/K	K
0.0	0.024	0.026	0.025	1.90	1.799	2.219	0.953
0.05	0.024	0.026	0.025	1.95	2.238	1.930	0.823
0.10	0.024	0.026	0.026	2.00	2.518	1.623	0.738
0.15	0.025	0.027	0.027	2.05	2.519	1.377	0.678
0.20	0.025	0.027	0.028	2.05	2.519	1.377	0.678
0.25	0.026	0.028	0.029	2.10	2.298	1.196	0.637
0.30	0.026	0.028	0.030	2.15	1.984	1.056	0.613
0.35	0.027	0.029	0.031	2.20	1.666	0.943	0.603
0.40	0.028	0.029	0.032	2.25	1.381	0.855	0.607
0.45	0.029	0.030	0.034	2.30	1.155	0.790	0.622
0.50	0.030	0.031	0.036	2.35	0.989	0.745	0.646
0.55	0.031	0.032	0.038	2.40	0.871	0.717	0.679
0.60	0.032	0.034	0.040	2.45	0.790	0.702	0.718
0.65	0.033	0.036	0.043	2.50	0.734	0.696	0.762
0.70	0.035	0.039	0.046	2.55	0.690	0.700	0.811
0.75	0.037	0.043	0.049	2.60	0.655	0.715	0.865
0.80	0.039	0.049	0.054	2.65	0.629	0.740	0.926
0.85	0.041	0.054	0.059	2.70	0.612	0.778	0.991
0.90	0.044	0.060	0.066	2.75	0.603	0.827	1.055
0.95	0.048	0.067	0.073	2.80	0.604	0.882	1.113
1.00	0.052	0.075	0.083	2.85	0.613	0.939	1.160
1.05	0.058	0.086	0.098	2.90	0.627	0.993	1.189
1.10	0.063	0.100	0.121	2.95	0.646	1.042	1.199
1.15	0.070	0.118	0.157	3.00	0.671	1.083	1.194
1.20	0.077	0.140	0.204	3.05	0.704	1.116	1.180
1.25	0.086	0.164	0.252	3.10	0.744	1.142	1.159
1.30	0.097	0.196	0.332	3.15	0.789	1.160	1.133
1.35	0.111	0.247	0.452	3.20	0.839	1.171	1.103
1.40	0.129	0.318	0.696	3.25	0.891	1.177	1.072
1.45	0.153	0.386	1.133	3.30	0.945	1.177	1.040
1.50	0.186	0.485	1.633	3.35	0.997	1.173	1.009
1.55	0.229	0.632	2.092	3.40	1.046	1.164	0.980
1.60	0.285	0.845	2.390	3.45	1.092	1.151	0.954
1.65	0.356	1.259	2.410	3.50	1.130	1.135	0.930
1.70	0.463	1.734	2.150	3.55	1.161	1.117	0.911
1.75	0.647	2.164	1.771	3.60	1.184	1.097	0.896
1.80	0.945	2.482	1.423	3.65	1.198	1.076	0.885
1.85	1.341	2.408	1.151	3.70	1.206	1.056	0.879

TABLE 3.1 (*continued*)

Q	Na	Na/K	K	Q	Na	Na/K	K
3.75	1.207	1.036	0.878	5.50	1.055	0.999	0.982
3.80	1.202	1.018	0.881	5.55	1.054	0.997	0.988
3.85	1.192	1.002	0.889	5.60	1.051	0.995	0.995
3.90	1.177	0.989	0.901	5.65	1.046	0.993	1.001
3.95	1.158	0.978	0.916	5.70	1.039	0.991	1.006
4.00	1.134	0.970	0.933	5.75	1.032	0.989	1.010
4.05	1.109	0.964	0.953	5.80	1.024	0.988	1.013
4.10	1.080	0.960	0.973	5.85	1.017	0.987	1.015
4.15	1.051	0.959	0.993	5.90	1.010	0.987	1.016
4.20	1.022	0.959	1.012	5.95	1.003	0.987	1.016
4.25	0.993	0.961	1.028	6.00	0.996	0.988	1.015
4.30	0.966	0.965	1.041	6.05	0.990	0.989	1.014
4.35	0.941	0.970	1.049	6.10	0.984	0.991	1.013
4.40	0.919	0.977	1.054	6.15	0.979	0.993	1.012
4.45	0.901	0.984	1.056	6.20	0.974	0.995	1.010
4.50	0.887	0.992	1.055	6.25	0.970	0.997	1.009
4.55	0.878	1.000	1.051	6.30	0.967	0.998	1.007
4.60	0.873	1.007	1.045	6.35	0.964	0.999	1.005
4.65	0.873	1.015	1.037	6.40	0.962	1.000	1.004
4.70	0.877	1.020	1.028	6.45	0.961	1.000	1.003
4.75	0.884	1.025	1.017	6.50	0.961	1.000	1.002
4.80	0.894	1.028	1.007	6.55	0.961	1.000	1.001
4.85	0.906	1.029	0.997	6.60	0.963	1.000	1.000
4.90	0.919	1.029	0.987	6.65	0.965	1.000	0.999
4.95	0.934	1.028	0.978	6.70	0.967	1.000	0.999
5.00	0.950	1.026	0.970	6.75	0.970	1.000	0.999
5.05	0.965	1.024	0.964	6.80	0.974	1.000	0.999
5.10	0.981	1.021	0.959	6.85	0.977	1.000	0.999
5.15	0.996	1.017	0.956	6.90	0.981	1.000	0.999
5.20	1.009	1.014	0.955	6.95	0.984	1.000	1.000
5.25	1.022	1.012	0.955	7.00	0.987	1.000	1.000
5.30	1.033	1.009	0.958	7.05	0.990	1.000	1.000
5.35	1.042	1.006	0.962	7.10	0.993	1.000	1.000
5.40	1.049	1.004	0.968	7.15	0.995	1.000	1.000
5.45	1.053	1.002	0.975				

4 THEORY OF EFFECTIVE INTERIONIC POTENTIALS IN SIMPLE ALLOYS, EXTRACTED FROM STRUCTURE DATA

The experiments described above do not allow, of course, the extraction of the three partial structure factors $S_{\mathrm{Na-Na}}$, $S_{\mathrm{K-K}}$ and $S_{\mathrm{Na-K}}$ for any of the alloys studied. Nevertheless, the problem of determining the interionic potentials in simple metal alloys is sufficiently basic for us to develop the theory below, on the basis of the Born-Green-Yvon hierarchy of classical statistical mechanics.

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Two of us[8] earlier gave a simple approximate procedure for extracting a pair potential from the structure factor for liquid metals like Al or Na. For a one-component system, to which this work applied, the basic equation proposed for extracting a pair potential $\phi(r)$ from the measured structure factor $S(Q)$ and the corresponding radial distribution function $g(r)$ is

$$\phi(r) = U(r) + \frac{k_B T}{8\pi^3 \rho} \int [S(Q) - 1]^2 \exp(i\mathbf{Q} \cdot \mathbf{r})\, d\mathbf{Q}. \tag{4.1}$$

Here the potential of mean force $U(r)$ is related to $g(r)$ through the Boltzmann form

$$g(r) = \exp\left(-\frac{U(r)}{k_B T}\right), \tag{4.2}$$

while ρ is the number density of ions. Immediately below we shall summarize the generalization of Eq. (4.1) to simple binary liquid metal alloys. Following de Angelis and March,[8] we first write down the generalization of the force equation, as set out for example by March,[9] to apply to binary alloys. This is done in the Appendix and when we employ the superposition approximation for alloys in a suitable form we are led to the following approximate equations for the effective interionic pair potentials in an alloy:

$$\begin{aligned}\phi_{aa}(R) = U_{aa}(R) &+ \frac{k_B T \rho_a}{8\pi^3 \rho^2} \int [S_{aa}(Q) - 1]^2 \exp(i\mathbf{Q}\cdot \mathbf{R})\, d\mathbf{Q} \\ &+ \frac{k_B T \rho_b}{8\pi^3 \rho^2} \int [S_{ab}(Q) - 1]^2 \exp(i\mathbf{Q} \cdot \mathbf{R})\, d\mathbf{Q}\end{aligned} \tag{4.3}$$

and

$$\begin{aligned}\phi_{ab}(R) = U_{ab}(R) &+ \frac{k_B T \rho_a}{8\pi^3 \rho^2} \int [S_{aa}(Q) - 1][S_{ab}(Q) - 1] \exp(i\mathbf{Q}\cdot \mathbf{R})\, d\mathbf{Q} \\ &+ \frac{k_B T \rho_b}{8\pi^3 \rho^2} \int [S_{ab}(Q) - 1][S_{bb}(Q) - 1] \exp(i\mathbf{Q} \cdot \mathbf{R})\, d\mathbf{Q}\end{aligned} \tag{4.4}$$

where ρ_a and ρ_b denote the number densities of the separate components and $\rho = \rho_a + \rho_b$. These Eqs. (4.3) and (4.4) give the first order solutions of the force equations for a simple binary metal alloy in terms of measured partial structure factors. They represent for such alloys the direct generalization of the one-component Eq. (4.1), which is recovered from Eq. (4.3) if we put $\rho_b = 0$.

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5 REFERENCE LIQUID POTENTIAL FOR NA-K ALLOYS

The above analysis cannot be applied at present to the liquid Na-K measurements of Sections 2 and 3 because, as we stressed at the outset, complete structural information is not available.

Therefore we shall simplify the discussion of the interionic potentials by appealing to the idea of a reference liquid. This idea can be made precise within the context of the conformal solution theory of Longuet-Higgins,[2] which he applied to calculate thermodynamic properties. This theory was generalized away from the long wavelength limit by Parrinello, Tosi and March[10] and was used with some success by Johnson *et al.*[11] to interpret

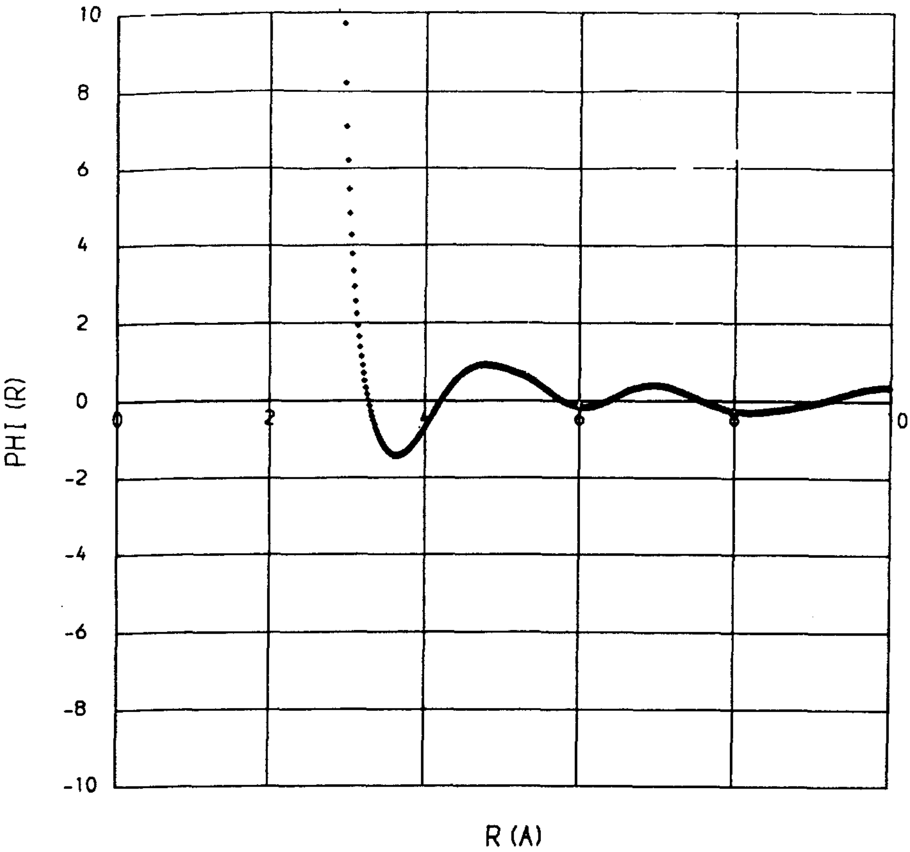

FIGURE 5.1 Effective pair potential $\phi(R)$ for pure liquid Na. This has been calculated by inserting X-ray structure data of Greenfield, Wellendorf, and Wiser[5] into Eq. (4.1). Note that the vertical scale is only to be used for comparison with Figures 5.2 and 5.3; it is not in physically significant units.

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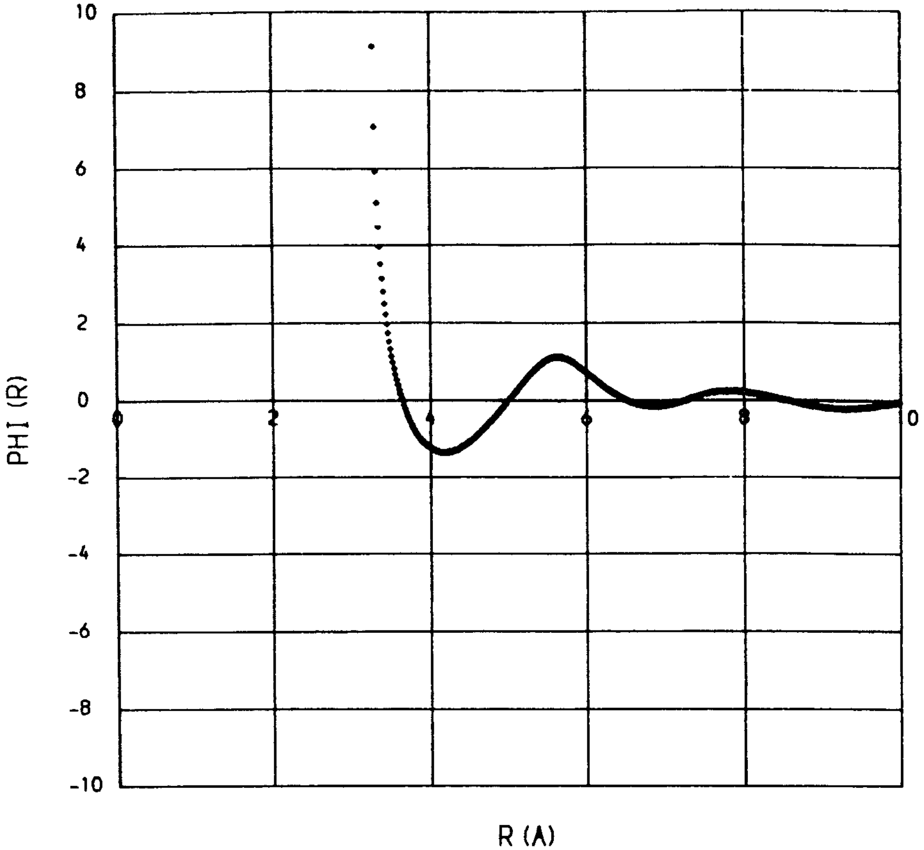

FIGURE 5.2 Reference liquid effective potential $\phi(R)$ extracted from the 50% liquid Na-K alloy data in Table 3.1. This was inserted into Eq. (4.1).

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wavelength dependent concentration fluctuations in Li-Pb (see also the very recent work of Soltwisch *et al.*[12]) and Cu_6Sn_5 alloys. This approximation was also successfully applied to explain in liquid Na-K alloys the very marked variation with concentration of the long wavelength limit of the partial structure factors $S_{Na-Na}(O)$, $S_{K-K}(O)$ and $S_{Na-K}(O)$. This variation was exhibited by McAlister and Turner[13] using measured thermodynamic data and Bhatia, Hargrove and March[14] accounted for it by conformal solution theory. However, the fact that the volume of a K atom in pure liquid K is about twice that of a Na atom in pure liquid Na proved to be important and this indicates that size effects should be included when the generalization away from $Q = 0$ is effected.

Therefore below we retain the idea of a reference liquid, but attempt to transcend the basic assumption of conformal solution theory that we can

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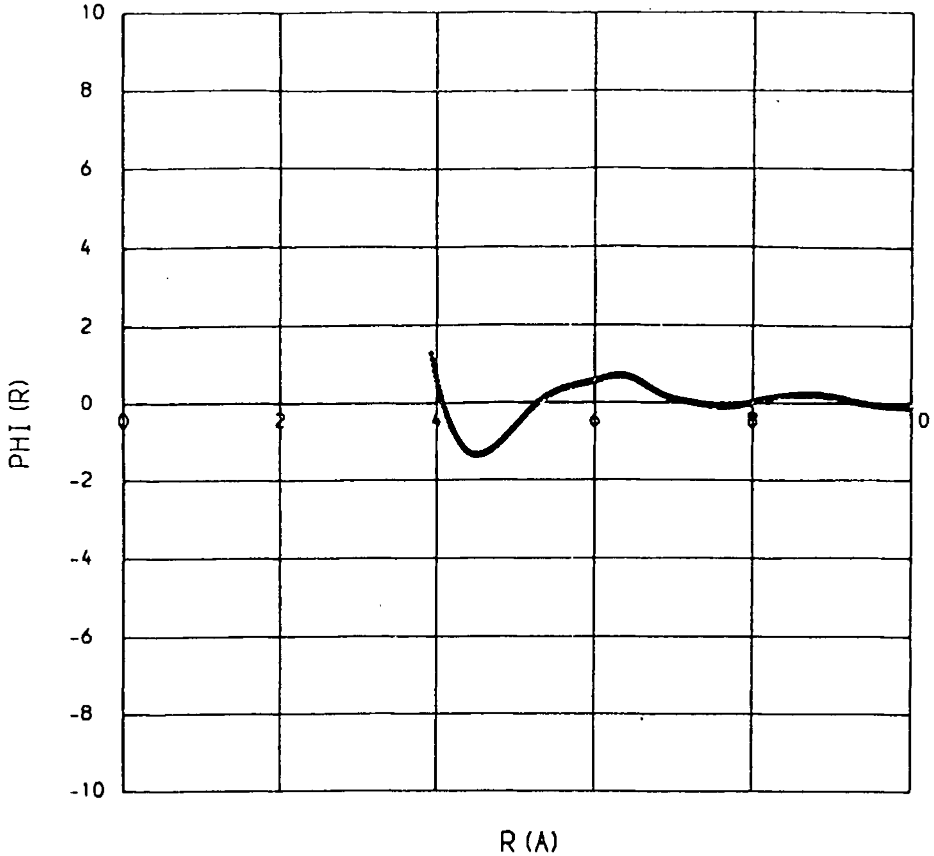

FIGURE 5.3 Same as Figure 5.1 but for pure liquid K. X-ray data of Ref. 5 was again used.

obtain the interionic potentials by small scaling changes from the pair potential $\phi(r)$ of the reference liquid through

$$\phi_{ij}(r) = A_{ij}\phi(\lambda_{ij}r). \tag{5.1}$$

As indicated above, this form will be retained, but we shall not assume that A_{ij} and λ_{ij} are necessarily near to unity, which was the approximation of conformal solution theory.[2] We shall now concentrate solely on the measured data for liquid Na–K alloys recorded in Sections 2 and 3.

The first basic assumption of our analysis of liquid Na–K alloys is that the number-number structure factor $S_{NN}(Q)$ for the 50 Na–50 K alloy can be identified with the structure factor of the reference liquid. Secondly, we adopt Eq. (4.1) as a basis for extracting a pair potential for the reference liquid. While this equation may not lead to fully quantitative potentials (we

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anticipate that it will be best for high density liquid metals like Al), nevertheless we expect it to be meaningful to treat the alloys and the pure liquids on a common footing by adopting this approximate method.

Therefore we have used the neutron data in Table 3.1 to extract the interionic potential of the reference liquid. For the pure metals Na and K we have however employed the X-ray structure data of Ref. 5. The three pair potentials obtained in this way for pure Na, the reference liquid and pure K are plotted in Figures 5.1–5.3 respectively. As already mentioned, we believe that comparison of these potentials is significant even though they cannot be expected individually to be fully quantiative.

6 SUMMARY

Results of neutron scattering experiments have been presented which determine S_{NN} as a function of momentum transfer Q for 25, 50 and 75% alloys of Na and K. †In Section 5, an approximate liquid pair potential has been extracted from the structure data for the 50% alloy using the approximate one-component Eq. (4.1). Using the same approximate framework, this is then compared with Na and K effective pair potentials in Figures 5.1–3.

If we added the assumption that A_{ij} and λ_{ij} are near to unity in Eq. (5.1), the reference liquid potential could be used to calculate the interchange energy w of the conformal solution model.[2] We have not done this because: (i) we regard our description of the reference liquid as still not fully quantitative and (ii) we think one ought to allow for A_{ij} and λ_{ij} appreciably different from unity. Therefore, the most useful way to estimate w is still semi-empirical, as discussed by Bhatia, Hargrove and March;[14] the same interchange energy then generating correctly the liquidus curves for the eutective Na–K.[15]

In conclusion, we must mention, of course, that electron theory affords a first principles route to calculate interionic pair potentials in simple metals and their alloys. Unfortunately, for alloys this approach leads to potentials which are different for every different concentration and though fundamental this seems to us to be too complicated a description for many purposes. We think the reference liquid approach may well be a viable alternative in Na–K alloys which should therefore be fully explored.

† Note added in proof

Alblas and Van der Lugt have reported X-ray measurements on Na-K alloys (J. Phys. F-**10**, 531, 1980)

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We wish to thank Dr M. Dixon for some useful discussions.

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Appendix

FORCE EQUATIONS AND HIGHER-ORDER CORRELATION FUNCTIONS IN BINARY ALLOYS

Let us consider a binary liquid alloy in which there are N atoms of type a at $\mathbf{R}_1, \ldots, \mathbf{R}_N$ and n atoms of type b at $\mathbf{r}_1, \ldots, \mathbf{r}_n$, with number densities $\rho_a = N/V$ and $\rho_b = n/V$, V being the total volume of the liquid alloy.

We shall assume the force field to be usefully described by effective interionic pair potentials and we therefore write for the total potential energy of the system:

$$\Phi(R, r) = \sum_{i \neq j} \phi_{aa}(R_{ij}) + \sum_{i \neq j} \phi_{bb}(r_{ij}) + \sum_{i, j} \phi_{ab}(\mathbf{R}_i \mathbf{r}_j) \tag{A1}$$

where $\phi_{\alpha\beta}$ is the pair potential between atoms α and β.

At this point, we define the potential of mean force (cf. Eq. (4.2) $U_{\alpha\beta}$ for ions α and β from the pair correlation function $g_{\alpha\beta}$ through

$$g_{\alpha\beta}(r) = \exp\left(-\frac{U_{\alpha\beta}}{k_B T}\right). \tag{A2}$$

A generalization of the single-component theory requires an explicit formulation of the "force equation" for the two cases aa and ab (the bb case being obtained trivially from aa). We present below a simple physical argument to derive the force equations in the liquid binary alloy.

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Consider first the mixed case ab. For a configuration in which atom a is at $\mathbf{R}_1$ and atom b is at $\mathbf{r}_1$, we wish to write down an equation for the mean force $-\partial U_{ab}(\mathbf{R}_1\mathbf{r}_1)/\partial\mathbf{R}_1$ acting on atom a. First of all there is a direct interaction from atom b at $\mathbf{r}_1$, namely $-\partial\phi_{ab}(\mathbf{R}_1\mathbf{r}_1)/\partial\mathbf{R}_1$ and secondly there is a contribution from the rest of the system. This latter contribution is calculated by considering a second atom of type a at $\mathbf{R}_2$ acting with a force $-\partial\phi_{aa}(\mathbf{R}_1 - \mathbf{R}_2)/\partial\mathbf{R}_1$ and a second atom of type b at $\mathbf{r}_2$, with resulting force $-\partial\phi_{ab}(\mathbf{R}_1\mathbf{r}_2)/\partial\mathbf{R}_1$. We must then sum these contributions, multiply by the probability of this four atom configuration:

$$\rho^{(4)}_{abab}(\mathbf{R}_1\mathbf{r}_1\mathbf{R}_2\mathbf{r}_2)/\rho^{(2)}_{ab}(\mathbf{R}_1\mathbf{r}_1)$$

where $\rho^{(n)}$ denotes the n-particle distribution function, and finally integrate over the positions of the second type of atom. The result is

$$-\frac{\partial U_{ab}(\mathbf{R}_1\mathbf{r}_1)}{\partial\mathbf{R}_1} = -\frac{\partial\phi_{ab}(\mathbf{R}_1\mathbf{r}_1)}{\partial\mathbf{R}_1} - \iint \frac{\rho^{(4)}_{abab}(\mathbf{R}_1\mathbf{r}_1\mathbf{R}_2\mathbf{r}_2)}{\rho^{(2)}_{ab}(\mathbf{R}_1\mathbf{r}_1)} \times \left[\frac{\partial\phi_{aa}(\mathbf{R}_1 - \mathbf{R}_2)}{\partial\mathbf{R}_1} + \frac{\partial\phi_{ab}(\mathbf{R}_1\mathbf{r}_2)}{\partial\mathbf{R}_1}\right] \mathrm{d}\mathbf{R}_2\,\mathrm{d}\mathbf{r}_2, \tag{A3}$$

The double integral in Eq. (A3) can be written as:

$$\int \mathrm{d}\mathbf{R}_2 \frac{\partial\phi_{aa}(\mathbf{R}_1 - \mathbf{R}_2)}{\partial\mathbf{R}_1} \int \mathrm{d}\mathbf{r}_2\,\rho^{(4)}_{abab}(\mathbf{R}_1\mathbf{r}_1\mathbf{R}_2\mathbf{r}_2) + \int \mathrm{d}\mathbf{r}_2 \frac{\partial\phi_{ab}(\mathbf{R}_1\mathbf{r}_1)}{\partial\mathbf{R}_1} \times \int \mathrm{d}\mathbf{R}_2\,\rho^{(4)}_{abab}(\mathbf{R}_1\mathbf{r}_1\mathbf{R}_2\mathbf{r}_2). \tag{A4}$$

Since the three-atom correlations $\rho^{(3)}$ are related to $\rho^{(4)}$ by

$$\rho^{(3)}_{aba}(\mathbf{R}_1\mathbf{r}_1\mathbf{R}_2) = \int \rho^{(4)}_{abab}(\mathbf{R}_1\mathbf{r}_1\mathbf{R}_2\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_2 \tag{A5}$$

and

$$\rho^{(3)}_{abb}(\mathbf{R}_1\mathbf{r}_1\mathbf{r}_2) = \int \rho^{(4)}_{abab}(\mathbf{R}_1\mathbf{r}_1\mathbf{R}_2\mathbf{r}_2)\,\mathrm{d}\mathbf{R}_2, \tag{A6}$$

Eq. (A3) becomes

$$-\frac{\partial U_{ab}(\mathbf{R}_1\mathbf{r}_1)}{\partial\mathbf{R}_1} = -\frac{\partial\phi_{ab}(\mathbf{R}_1\mathbf{r}_1)}{\partial\mathbf{R}_1} - \int \frac{\rho^{(3)}_{aab}(\mathbf{R}_1\mathbf{r}_1\mathbf{R}_2)}{\rho^{(2)}_{ab}(\mathbf{R}_1\mathbf{r}_1)} \frac{\partial\phi_{aa}(\mathbf{R}_1 - \mathbf{R}_2)}{\partial\mathbf{R}_1}\,\mathrm{d}\mathbf{R}_2 - \int \frac{\rho^{(3)}_{abb}(\mathbf{R}_1\mathbf{r}_1\mathbf{r}_2)}{\rho^{(2)}_{ab}(\mathbf{R}_1\mathbf{r}_1)} \frac{\partial\phi_{ab}(\mathbf{R}_1\mathbf{r}_2)}{\partial\mathbf{R}_1}\,\mathrm{d}\mathbf{r}_2. \tag{A7}$$

Introducing the usual correlation functions g through

$$\rho^{(3)}_{aab}(\mathbf{R}_1\mathbf{R}_2\mathbf{r}_1) = \rho_a^2\rho_b g^{(3)}_{aab}(\mathbf{R}_1\mathbf{R}_2\mathbf{r}_1), \tag{A8}$$

$$\rho^{(3)}_{abb}(\mathbf{R}_1\mathbf{r}_1\mathbf{r}_2) = \rho_a\rho_b^2 g^{(3)}_{abb}(\mathbf{R}_1\mathbf{r}_1\mathbf{r}_2) \tag{A9}$$

and

$$\rho^{(2)}_{ab}(\mathbf{R}_1\mathbf{r}_1) = \rho_a\rho_b g_{ab}(\mathbf{R}_1\mathbf{r}_1), \tag{A10}$$

we have finally

$$\frac{\partial\phi_{ab}(\mathbf{R}_1\mathbf{r}_1)}{\partial\mathbf{R}_1} = \frac{\partial U_{ab}(\mathbf{R}_1\mathbf{r}_1)}{\partial\mathbf{R}_1} - \rho_a\int\frac{g^{(3)}_{aab}(\mathbf{R}_1\mathbf{R}_2\mathbf{r}_1)}{g_{ab}(\mathbf{R}_1\mathbf{r}_1)}\frac{\partial\phi_{aa}(\mathbf{R}_1-\mathbf{R}_2)}{\partial\mathbf{R}_1}\,d\mathbf{R}_2$$
$$-\rho_b\int\frac{g^{(3)}_{abb}(\mathbf{R}_1\mathbf{r}_1\mathbf{r}_2)}{g_{ab}(\mathbf{R}_1\mathbf{r}_1)}\frac{\partial\phi_{ab}(\mathbf{R}_1\mathbf{r}_2)}{\partial\mathbf{R}_1}\,d\mathbf{r}_2. \tag{A11}$$

For two atoms of type a, an argument paralleling the above leads to:

$$\frac{\partial\phi_{aa}(\mathbf{R}_1-\mathbf{R}_2)}{\partial\mathbf{R}_1} = \frac{\partial U_{aa}(\mathbf{R}_1-\mathbf{R}_2)}{\partial\mathbf{R}_1} - \rho_a\int\frac{g^{(3)}_{aaa}(\mathbf{R}_1\mathbf{R}_2\mathbf{R}_3)}{g_{aa}(\mathbf{R}_1-\mathbf{R}_2)}\frac{\partial\phi_{aa}(\mathbf{R}_1-\mathbf{R}_3)}{\partial\mathbf{R}_1}\,d\mathbf{R}_3$$
$$-\rho_b\int\frac{g^{(3)}_{aab}(\mathbf{R}_1\mathbf{R}_2\mathbf{r}_1)}{g_{aa}(\mathbf{R}_1-\mathbf{R}_2)}\frac{\partial\phi_{ab}(\mathbf{R}_1\mathbf{r}_1)}{\partial\mathbf{R}_1}\,d\mathbf{r}_1. \tag{A12}$$

Equations (A11) and (A12) give the desired generalizations for binary mixtures of the force equation for one-component liquids (see, for example, Ref. 9). Given the assumption (A1) of pair forces, these equations are exact consequences of classical statistical mechanics.

ZEROTH ORDER THEORY

To proceed further, we must, of course, introduce approximations into Eqs. (A11) and (A12). Motivated by the single component theory of de Angelis and March, we take as the zeroth order approximation:

$$-k_BT\ln g_{aa}(r) = U_{aa}(r) \doteqdot \phi_{aa}(r) \tag{A13}$$

and

$$-k_BT\ln g_{ab}(r) = U_{ab}(r) \doteqdot \phi_{ab}(r) \tag{A14}$$

which lead to the identities

$$g_{aa}(\mathbf{R}_1-\mathbf{R}_2)\frac{\partial\phi_{aa}(\mathbf{R}_1-\mathbf{R}_2)}{\partial\mathbf{R}_1} = -\frac{1}{\beta}\frac{\partial}{\partial\mathbf{R}_1}(g_{aa}(\mathbf{R}_1-\mathbf{R}_2)-1) \tag{A15}$$

and

$$g_{ab}(\mathbf{R}_1\mathbf{r}_1)\frac{\partial\phi_{ab}(\mathbf{R}_1\mathbf{r}_1)}{\partial\mathbf{R}_1} = -\frac{1}{\beta}\frac{\partial}{\partial\mathbf{R}_1}(g_{ab}(\mathbf{R}_1\mathbf{r}_1)-1), \tag{A16}$$

with $\beta = (k_BT)^{-1}$.

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For the triplet functions, we shall now assume essentially the Kirkwood superposition approximation, which is consistent with Eqs. (13) and (A14), namely (cf. Ref. 16)

$$g^{(3)}_{aab}(\mathbf{R}_1\mathbf{R}_2\mathbf{r}_1) \doteqdot g_{aa}(\mathbf{R}_1 - \mathbf{R}_2)g_{ab}(\mathbf{R}_1\mathbf{r}_1)g_{ab}(\mathbf{R}_2\mathbf{r}_1). \tag{A17}$$

Use of Eqs. (A15) (A16) and (A17) in the force Eqs. (A11) and (A12) allows us to integrate over $\mathbf{R}_1$ to obtain:

$$\begin{aligned}\phi_{aa}(\mathbf{R}_1 - \mathbf{R}_2) = U_{aa}(\mathbf{R}_1 - \mathbf{R}_2) &+ k_B T\rho_a \int h_{aa}(\mathbf{R}_1 - \mathbf{R}_3)h_{aa}(\mathbf{R}_2 - \mathbf{R}_3)\,\mathrm{d}\mathbf{R}_3 \\ &+ k_B T\rho_b \int h_{ab}(\mathbf{R}_1\mathbf{r}_1)h_{ab}(\mathbf{R}_2\mathbf{r}_1)\,\mathrm{d}\mathbf{r}_1\end{aligned} \tag{A18}$$

and

$$\begin{aligned}\phi_{ab}(\mathbf{R}_1\mathbf{r}_1) = U_{ab}(\mathbf{R}_1\mathbf{r}_1) &+ k_B T\rho_a \int h_{aa}(\mathbf{R}_1 - \mathbf{R}_2)h_{ab}(\mathbf{R}_2\mathbf{r}_1)\,\mathrm{d}\mathbf{R}_2 \\ &+ k_B T\rho_b \int h_{ab}(\mathbf{R}_1\mathbf{r}_2)h_{bb}(\mathbf{r}_1 - \mathbf{r}_2)\,\mathrm{d}\mathbf{r}_2.\end{aligned} \tag{A19}$$

Here $h_{ij}(r) = g_{ij}(r) - 1$ is the so-called total correlation function. Introducing the Fourier transforms

$$\tilde{h}_{ij}(k) = \int \exp(i\mathbf{k}\cdot\mathbf{r})h_{ij}(r)\,\mathrm{d}\mathbf{r} \tag{A20}$$

and the partial structure factors

$$S_{ij}(k) = 1 + \rho\tilde{h}_{ij}(k);\ \rho = \frac{(N+n)}{V} = \rho_a + \rho_b \tag{A21}$$

we obtain the desired results (4.4) and (4.5) of the main text.

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