

Kirkwood-Buff theory

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by
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Kirkwood-Buff theory

- Introduction to the Kirkwood-Buff integrals
- Inversion of Kirkwood-Buff theory
- Thermodynamic properties
- Application: urea–water mixture, KBFF for urea

Kirkwood-Buff theory

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The Statistical Mechanical Theory of Solutions. I

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(Received March 26, 1951)

A general statistical mechanical theory of solutions is developed with the aid of the theory of composition fluctuations in the grand canonical ensemble. It is shown that the derivatives of the chemical potentials and osmotic pressure with respect to concentrations, the partial molar volumes, and compressibility may be expressed in terms of integrals of the radial distribution functions of the several types of molecular pairs present in the solution. Explicit coefficients of a q -fraction expansion of the thermodynamic variables are presented in a detailed treatment of the two-component system.

I

THIS paper will be concerned with the development of a general statistical mechanical theory of solutions which is applicable to all types of intermolecular interaction and is valid both classically and quantum mechanically. The theory of the grand canonical ensemble is employed on the one hand to relate composition fluctuations to derivatives of the chemical potentials of the components and on the other hand to

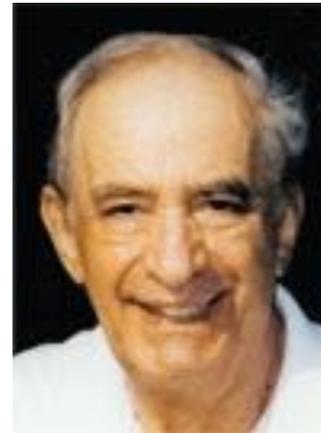
of composition fluctuations in the grand ensemble. The results are subsequently employed to evaluate important thermodynamic variables of a multicomponent system in terms of integrals of the radial distribution functions. The theory provides an alternative to the familiar charging process encountered in electrolyte theory, while in the absence of long-range intermolecular forces, expansions of the excess chemical potentials, partial molar volumes and compressibility in terms of the q -fractions of the solute components may be ob-

Kirkwood-Buff theory



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1907 – 1959

Cornell University,
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Frank P. Buff
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1907 — 1959

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of Chemistry (1947—1956); Cornell University
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National Academy of Sciences as Foreign
Secretary (1954—1955); U.S. United States
Government as Scientific Consultant (1941—1953);
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LARS ONSAGER

1903 — 1966

BORN OSLO, NORWAY

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K. ASAKA

PROFESSOR OF
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BORN IN HIJIMA
DECEMBER 20
DIED WASHINGTON
AUGUST 18

WASEDA UNIVERSITY
HARD MOUTH COLLEGE, SUIT
YALE UNIVERSITY

MIRIAM DING

HER WIFE
REMAINS HERE
VERGREEN CE

WILSON

BORN
APR. 20, 1849,
DIED
JULY 16, 1923

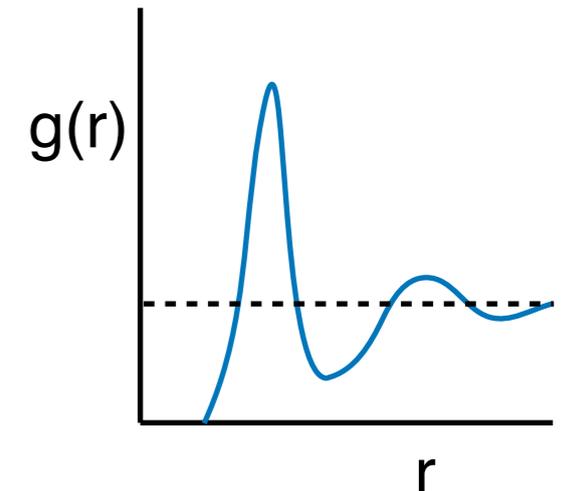
Kirkwood-Buff theory

Kirkwood-Buff Integral:

$$G_{ij} = 4\pi \int_0^{\infty} [g_{ij}(r) - 1] r^2 dr$$

g_{ij} is the radial distribution function of particle i with respect to particle j

G_{ij} has dimension of volume



Interpretation:

- Assuming that particle-particle correlations are local, G_{ij} measures the change in the volume taken by particles j in a local region if a particle i were inserted at the center of this region.
- Or, $\rho_j G_{ij}$ measures the change in the number of j particles in this region....
- Far from the critical point, fluctuations are typically local within a radius of about 1 nm.

- $\rho_j g_{ij}(r) 4\pi r^2 dr$ measures the average number of particles j in a spherical shell with width dr around a particle i .
- $\rho_j 4\pi r^2 dr$ measures the average number of particles j in the same spherical shell with random origin.

Hence, $\rho_j (g_{ij}(r) - 1) 4\pi r^2 dr$ gives the excess/deficiency of the number of particles j due to particle i at the sphere center.

ρ_j is the number density (concentration) of particle j

particles i and j may be switched:

$\rho_i g_{ij}(r) 4\pi r^2 dr$
(number of particles i around j)

Note also:

$$G_{ij} = G_{ji}$$

Finally: the KBI measures the average affinity between particles i and j .

Kirkwood-Buff theory

Kirkwood-Buff Integral:

$$G_{ij} = 4\pi \int_0^{\infty} [g_{ij}(r) - 1] r^2 dr$$

Some observations:

The KB theory is a general theory

- no assumptions on the molecules (e.g. spherical shape, Lennard-Jones, ...)
- no assumptions on the mixture (e.g. ideal mixing (Raoult regime, Henry regime), infinite dilution, binary, ...)

Thus ideal for analysis of complex mixtures of solvents

Requires detailed knowledge of the pair-correlation functions

- from MD/MC simulations
- from diffraction experiments

The KBI's can be connected to various thermodynamic quantities (e.g. chemical potentials, partial molar volumes, isothermal compressibility, osmotic pressure,...)

Inverse theory (by A. Ben-Naim) allows to derive KBI's from experimental thermodynamic quantities.

Kirkwood-Buff theory

Fluctuation theory of solutions

Kirkwood-Buff Integrals from particle fluctuations in the grand-canonical ensemble

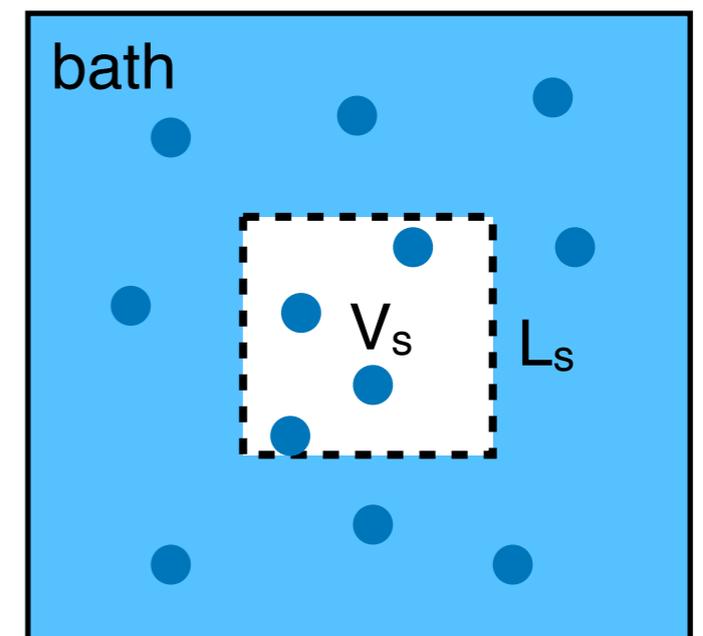
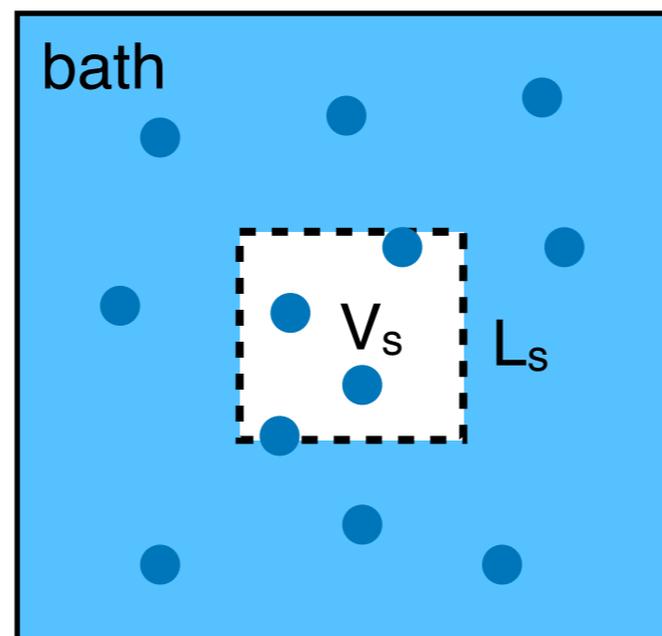
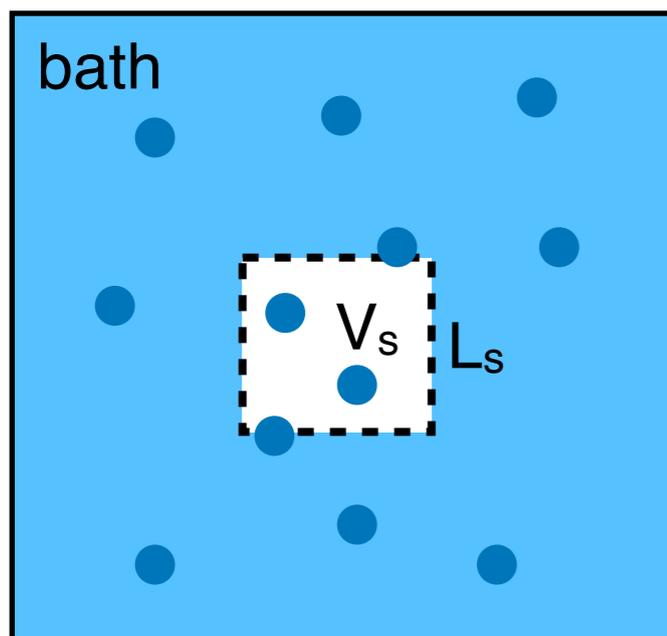
$$G_{ij}(L_s) = V_s \left[\frac{\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle}{\langle N_i \rangle \langle N_j \rangle} - \frac{\delta_{ij}}{\langle N_i \rangle} \right]$$

N_i is the number of particles in the small box with volume V_s

δ_{ij} is de Kronecker delta

Thermodynamic limit from extrapolating from a series of different small box sizes L_s

$$G_{ij} = G_{ij}(L_s) - \frac{c}{L_s}$$



Some thermodynamic relations

For a 2-component mixture: G_{11} , G_{22} , G_{12}

The partial molar volume of component 1:

$$V_1^m = \frac{1 + c_2(G_{22} - G_{12})}{c_1 + c_2 + c_1c_2(G_{11} + G_{22} - 2G_{12})}$$

c is molar concentration

$$c_1V_1^m + c_2V_2^m = 1$$

The compressibility:

$$\kappa_T = \frac{1}{k_B T} \frac{1 + c_1G_{11} + c_2G_{22} + c_1c_2(G_{11}G_{22} + c_1c_2(G_{11}G_{22} - G_{12}^2))}{c_1 + c_2 + c_1c_2(G_{11} + G_{22} - 2G_{12})}$$

The derivative of the osmotic pressure wrt concentration:

$$\left(\frac{\partial \Pi}{\partial c_2} \right)_{T, \mu_2} = \frac{k_B T}{1 + c_2G_{22}}$$

The derivative of the chemical potentials wrt concentration:

$$\frac{1}{k_B T} \left(\frac{\partial \mu_1}{\partial c_1} \right)_{T, op} = \frac{1}{c_1} + \frac{G_{12} - G_{11}}{1 + c_1(G_{11} - G_{12})}$$

Preferential interaction coefficient

Consider a 3-component system:

- solute (S)
- solvent (W) (water)
- cosolute (C)

At low cosolute concentration, the preferential hydration coefficient:

$$\Gamma_W = M_W (G_{WS} - G_{CS})$$

M_W = molarity of water

$\Gamma_W > 0$ Solute is preferentially hydrated by solvent

KB theory is a powerful means for determining if:

- good cosolutes that help to dissolve solutes in bad solvents (e.g. stabilise biomolecules)
- cosolutes that help to precipitate solutes or denature biomolecules

Inversion of the Kirkwood–Buff theory

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Inversion of the Kirkwood–Buff theory of solutions: Application to the water–ethanol system

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(Received 17 March 1977)

A general procedure is outlined whereby experimental data such as partial molar volumes, isothermal compressibilities, and partial vapor pressures may be processed to obtain information on the extent of the affinity between two species in a mixture of two (or more) components. A particular example of the water–ethanol system is processed in this manner to obtain the quantities $G_{\alpha\beta}$ which are integrals over the pair correlation functions between two species α and β . This information is relevant to several topics of interest in the field of aqueous solutions, such as the solvation of solutes, hydrophobic interactions, and structural changes in the solvent brought by the addition of solutes to water. More generally it may be used to characterize the properties of various mixtures on a molecular level.

I. INTRODUCTION

A large body of experimental data exists on the system water–ethanol; this includes thermodynamic, spectroscopic, and transport properties.^{1–3} In addition, a great deal of physicochemical research has been carried out in water–ethanol mixtures as a solvent for various kinetic and thermodynamic measurements, ranging from simple solubilities to complex biochemical processes. In contrast to this vast experimental work, there exist

the next-best information that can be obtained from experimental sources. To this end we propose in this paper to study the behavior of quantities that convey sorts of averages of the pair correlation functions. These quantities have been employed in the Kirkwood–Buff theory of solutions⁶ and are defined for any pair of species α and β by

$$G_{\alpha\beta} = \int_0^{\infty} [g_{\alpha\beta}(R) - 1] 4\pi R^2 dR, \quad (1.1)$$

Inversion of the Kirkwood–Buff theory

The original KBI idea (estimating thermodynamic properties from RDFs) remained dormant for about 25 years.

- seemed unsuitable for study of salt solutions
- required (unknown) RDF data as input

Arieh Ben-Naim (1977): KBI's can be derived from experimental data using KB inversion procedure

(second breakthrough: realistic RDFs from modern computer simulations)

from measurement of isothermal compressibility and molar volumes

$$\kappa_T = \zeta / k_B T \eta$$

in which:

$$V_i = [1 + \rho_j (G_{jj} - G_{ij})] / \eta$$

$$\eta = \rho_i + \rho_j + \rho_i \rho_j (G_{ii} + G_{jj} - 2G_{ij})$$

$$V_j = [1 + \rho_i (G_{ii} - G_{ij})] / \eta$$

$$\zeta = 1 + \rho_i G_{ii} + \rho_j G_{jj} + \rho_i \rho_j (G_{ii} G_{jj} - G_{ij}^2)$$

using constraints:

$$\rho_i \mu_{ii} + \rho_j \mu_{ij} = 0 \quad \rho_i \mu_{ij} + \rho_j \mu_{jj} = 0 \quad \rho_i V_i + \rho_j V_j = 1$$

and chemical potentials

$$\mu_{ii} = \frac{\rho_j k_B T}{\rho_i \eta V} \quad \mu_{jj} = \frac{\rho_i k_B T}{\rho_j \eta V} \quad \mu_{ij} = \mu_{ji} = \frac{-k_B T}{\eta V}$$

Convergence

In finite size systems, the KBI,

$$G_{ij} = 4\pi \int_0^{\infty} [g_{ij}(r) - 1] r^2 dr$$

is replaced by:

$$G_{ij}(R) = 4\pi \int_0^R [g_{ij}(r) - 1] r^2 dr$$

choose sufficiently large value for the integration limit R

- G_{ij} should reach a plateau value
- however, often the convergence is poor...

Ionic systems

In salt solutions, electrolyte solutions, ions pose a problem for the KBI's.

Consider cations A and anions B in water W.

The ion mole fractions are equal (charge neutrality).
Therefore, the RDF's are constrained (in a closed finite system):

$$\rho_i \int_V g_{ij}(r) d\mathbf{r} = N_j - \delta_{ij}$$

This leads to constraints on the KBI's:

$$G_{AW} = G_{BW}$$

$$G_{AA} = G_{BB}$$

$$\rho_A G_{AB} = 1 + \rho_A G_{AA}$$

which leads to a singularity in the equations for calculating macroscopic properties

$$x_A = \frac{N_A}{N_A + N_B + N_W}$$

$$x_B = \frac{N_B}{N_A + N_B + N_W}$$

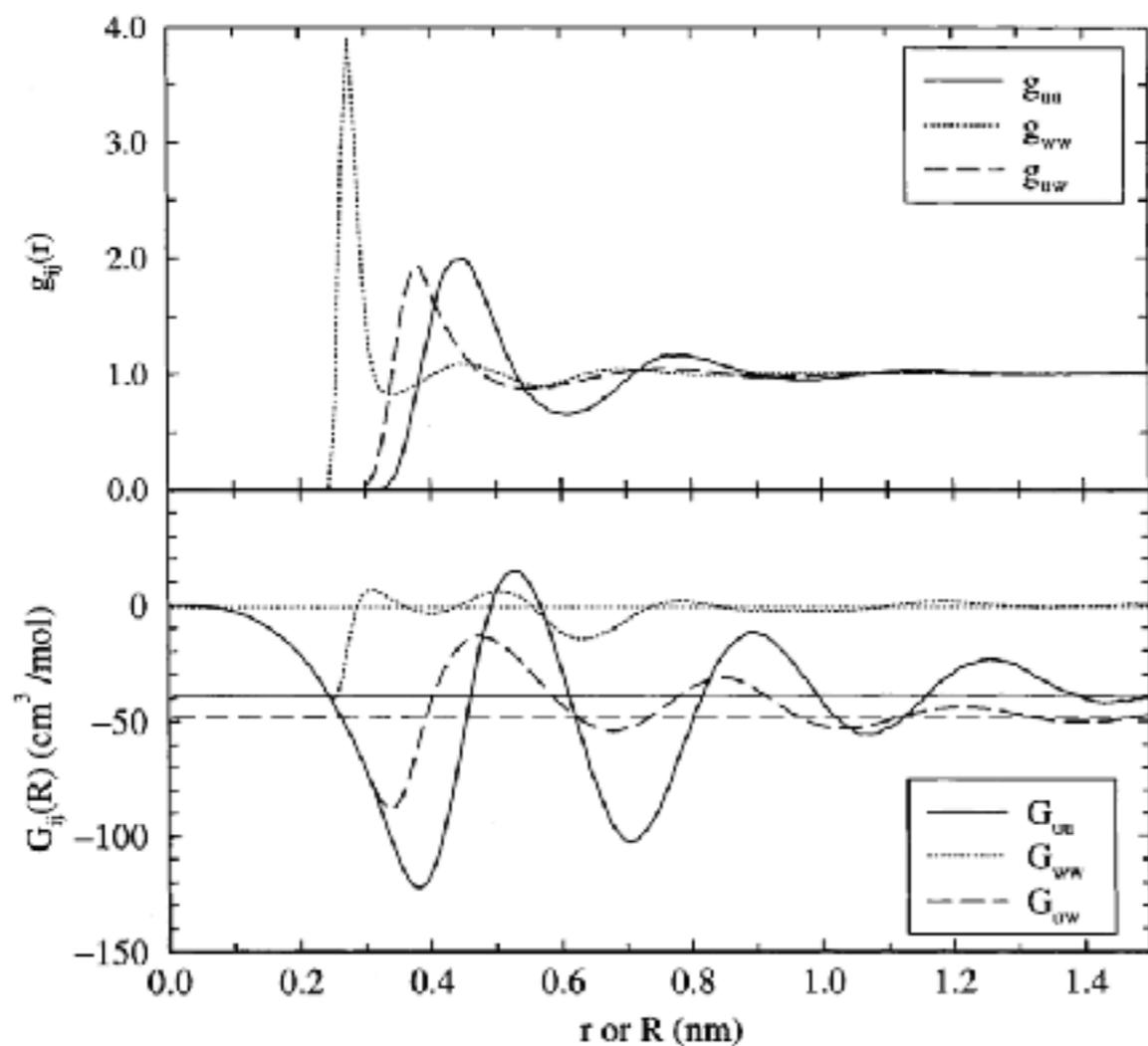
true for all 3-component systems, in which 2 have the same mole fraction (NB KBT independent of interaction types)

not a problem for fluctuations in (semi-) grand-canonical ensemble.

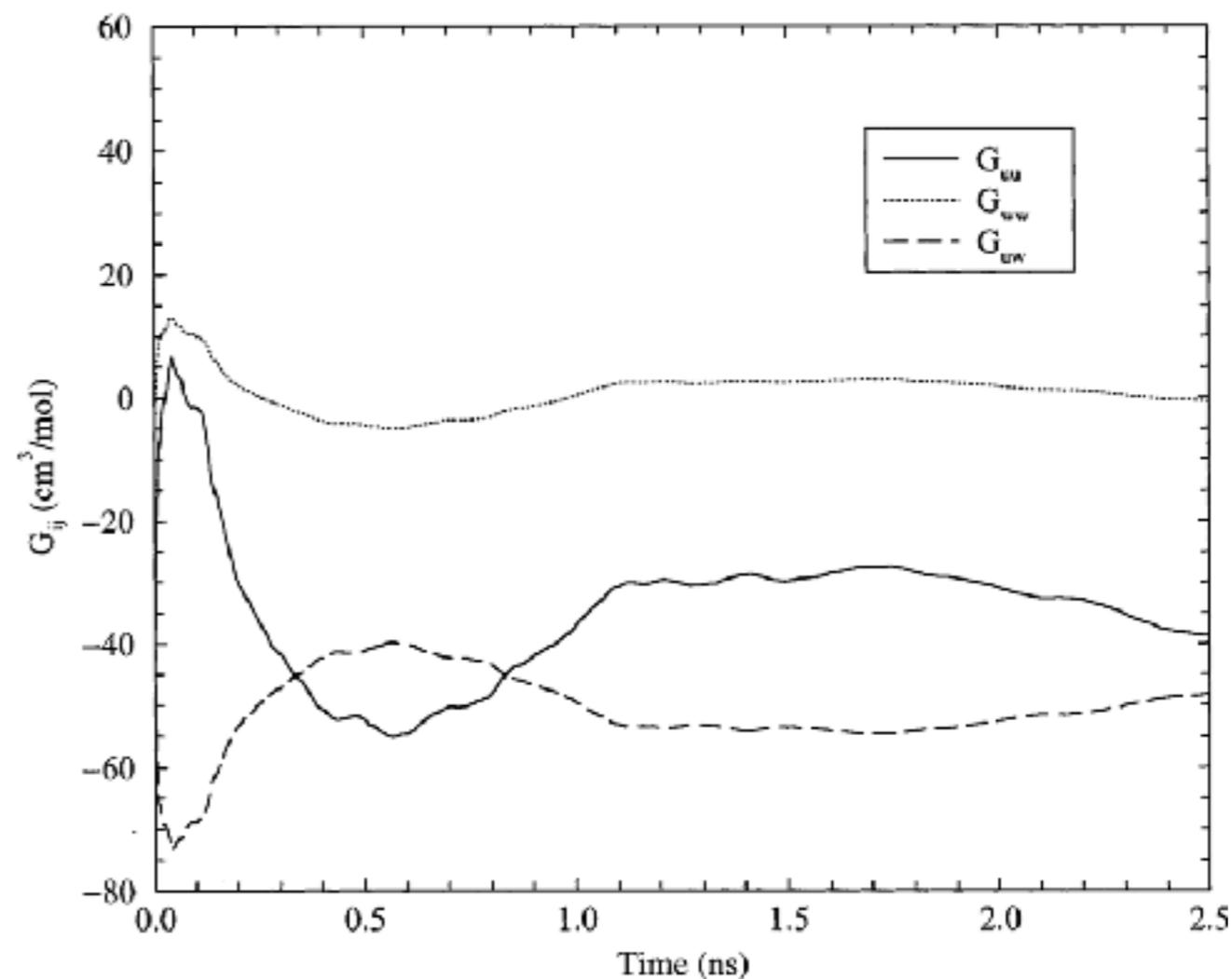
Application: Water urea mixture

- urea is an important denaturant for proteins
- urea (non-bonded) forcefield parameters developed from KBIs

RDFs and KBIs



convergence



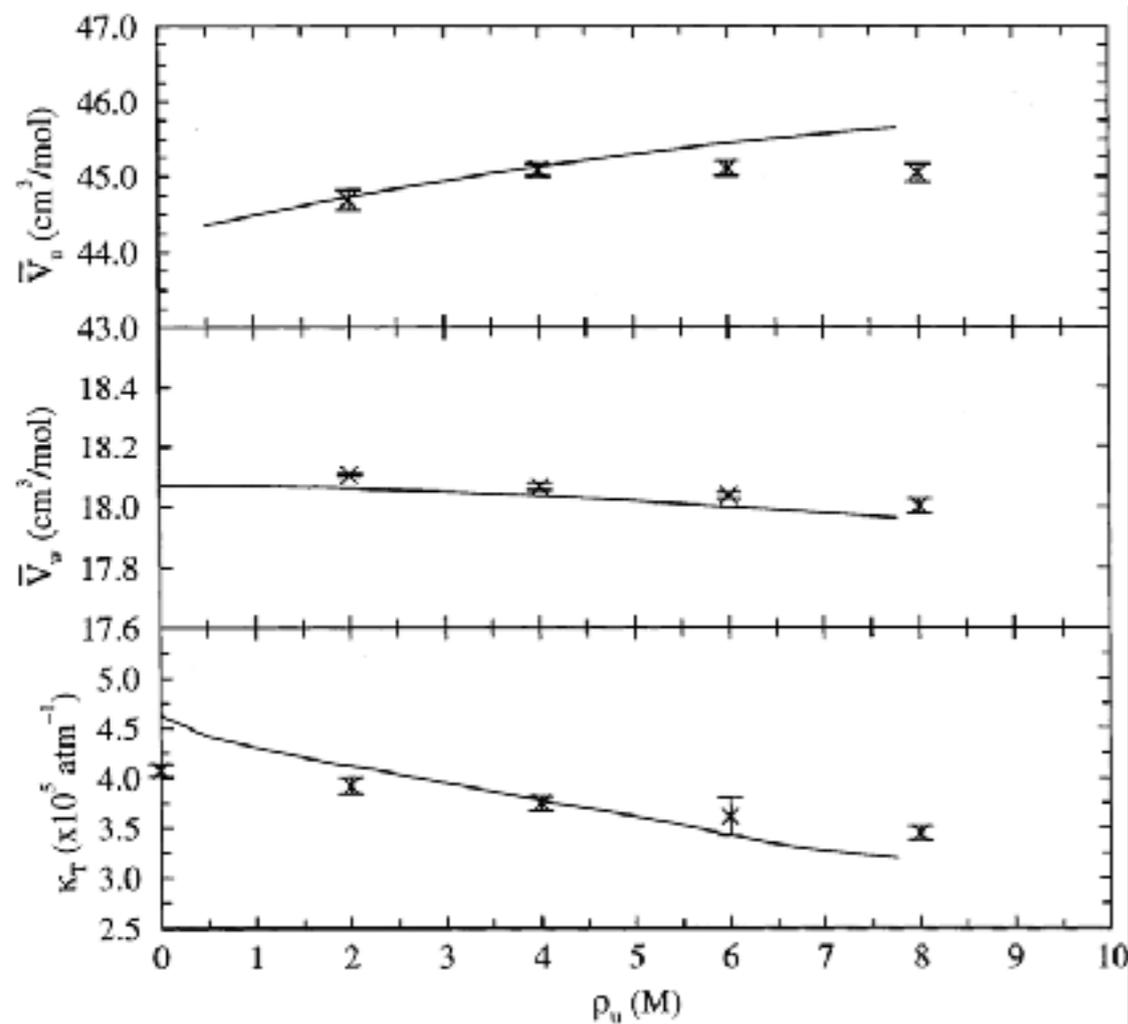
J. Phys. Chem. B 2003, 107, 3891-3898

A Kirkwood-Buff Derived Force Field for Mixtures of Urea and Water

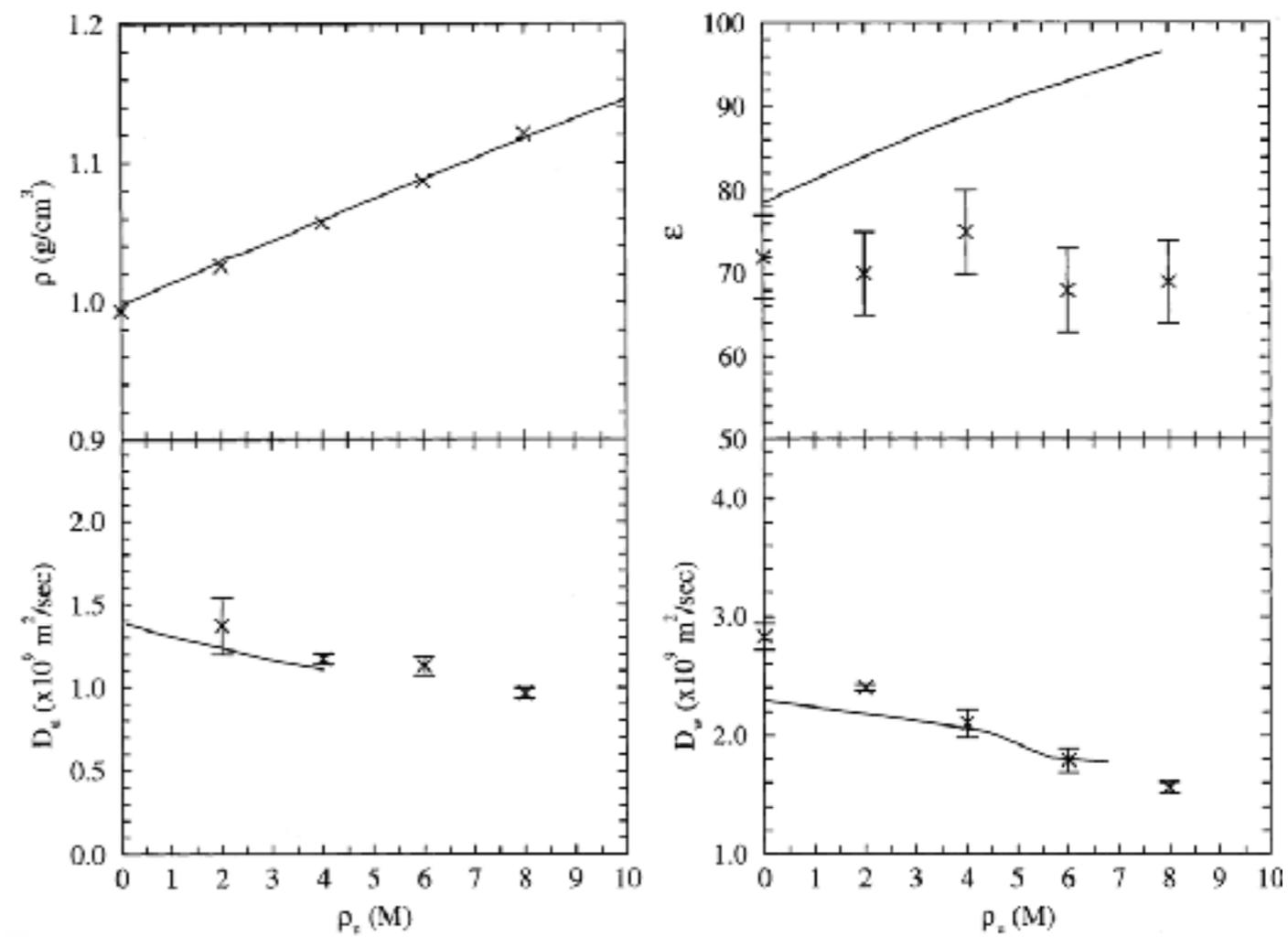
Samantha Weerasinghe and Paul E. Smith

Application: Water urea mixture

molar volumes and compressibility



density, relative permittivity, and diffusion constants



lines: experimental data
crosses: Kirkwood-Buff theory

Application: Water urea mixture

Comparison of OPLS with KBFF models for Urea with various water models

property	KBFF			OPLS		exp ^b	units
	SPC/E	SPC	TIP3P	SPC/E	TIP3P		
ρ	1.121	1.104	1.108	1.130	1.118	1.119	g/cm ³
D_u	1.0	1.5	1.9	1.1	1.8		$\times 10^{-9}$ m ² /s
D_w	1.5	2.4	3.3	2.2	3.8		$\times 10^{-9}$ m ² /s
ϵ	69	62	78	63	61	95	
G_{uu}	-39	-51	-29	391	142	-53/-42	cm ³ /mol
G_{uw}	-48	-41	-53	-282	-134	-40/-44	cm ³ /mol
G_{ww}	-1	-5	1	128	41	-4/-1	cm ³ /mol
a_{uu}	0.93	1.08	0.84	0.16	0.32	1.11/0.96	
f_{uu}	-0.30	-0.14	-0.33	-0.88	-0.78	-0.13/-0.25	

^a See text for definitions; Typical errors are shown in Figures 3 to 5. ^b Two sets of experimental data exist for the activity of urea solutions, leading to two sets of KB integrals. Experimental data was taken from refs 17, 48–51.

Conclusions (by Weerasinghe & Smith):

- Kirkwood-Buff theory allows for realistic model of solvent
- convergence requires large systems and long simulations

J. Phys. Chem. B 2003, 107, 3891-3898

A Kirkwood-Buff Derived Force Field for Mixtures of Urea and Water

Samantha Weerasinghe and Paul E. Smith

Summary

- Kirkwood-Buff theory, or the **theory of liquid fluctuations**, allows for calculation of (non-entropic) thermodynamic properties from **density fluctuations** or from **pair-correlation functions** (RDFs).
- By **inversion of Kirkwood-Buff theory**, by Ben-Naim, the KB integrals can be computed from a series of (experimentally determined) thermodynamic material properties.
- **Convergence of the Kirkwood-Buff integrals** is sometimes problematic, and several approaches have been developed to improve convergence.
- Kirkwood-Buff integrals have been used with good success to parameterise accurate atomistic and coarse-grain **forcefields** for simulation of complex solvent mixtures.