

Kirkwood-Buff Integrals from molecular simulations

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Outline

- I- Kirkwood Buff Integrals and density fluctuations
- II- Nanothermodynamics
- III- Application of nanothermodynamics to molecular simulation
- IV- the integration of the Kirkwood Buff Integral in a finite system
- V- Applications and conclusion

Application of Hill's thermodynamics of small system (nanothermodynamics) and KBI to molecular systems

<u>Col.</u>: S. Kjelstrup, D. Bedeaux and S. Schnell (Trondheim) P. Krüger (University of Chiba), T. Vlugt (T.U.Delft)

 to give validation evidences at a molecular scale of nanothermodynamics
 to explore the use and application of nanothermodynamics for a better understanding and analysing of molecular systems (=> new tools)



$$G(V) = \frac{1}{V} \iint_{V} d\mathbf{r} d\mathbf{r}' \left[g(|\mathbf{r} - \mathbf{r}'|)_{\mu, V, T} - 1 \right], \text{ Kirkwood-Buff Integral (KBI)}$$

Kirkwood-Buff integral and number fluctuations

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J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 19 (1951) 774.



$$G(V) = \frac{1}{V} \iint_{VV} d\mathbf{r} d\mathbf{r} d\mathbf{r}' \Big[g \big(|\mathbf{r} - \mathbf{r}'| \big)_{\mu, V, T} - 1 \Big]$$
$$\left(\frac{\left\langle N^2 \right\rangle - \left\langle N \right\rangle^2}{\left\langle N \right\rangle} \right)_{\mu, V, T} = 1 + \rho \ G(V)$$





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Kirkwood-Buff integral and thermodynamics

J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 19 (1951) 774.

$$\left(\frac{\left\langle N^2 \right\rangle - \left\langle N \right\rangle^2}{\left\langle N \right\rangle} \right)_{\mu, V, T} = 1 + \rho \ G(V) = \frac{k_B T}{\left\langle N \right\rangle} \left(\frac{\partial \left\langle N \right\rangle}{\partial \mu} \right)_{T, V} = \frac{\Gamma_V^{-1}}{\text{Thermodynamic factor}}$$

$$\Gamma^{-1} = k_B T \left(\frac{\partial \rho}{\partial P} \right)_T = \rho k_B T \beta_T \qquad \text{Isothermal compressibility}$$

Multicomponent mixture => partial molar volume

A. Ben-Naim, Molecular Theory of Solutions, Oxford University Press, Oxford, UK, 2006.

molecular systems



Open system: grand canonical ensemble Is there any influence of "smallness" (noise) on thermodynamics ?



Scaling laws?



Shape effects ?

Nanothermodynamics

T.H. Hill,

"Thermodynamics of small systems" (Dover, 1963)





 $E_t = TS_t + \mu N_t - \hat{p}V_t$ $E_t = N_r \overline{E}$ $S_t = N_r S$ $N_t = N_r \overline{N}$ $V_t = N_r V$ $\overline{E}=TS+\mu\overline{N}-\hat{p}V$ (In the thermodynamic limit: $\hat{p}=p$) $d\overline{E} = TdS + \mu d\overline{N} - pdV$

T.H. Hill, "Thermodynamics of small systems" (Dover, 1963)

icas (open systems)

 $d(\hat{p}V) = S\,dT + \overline{N}\,d\mu + p\,dV$

Equivalent to Gibbs- Duhem

$$Vd\hat{p} = (p - \hat{p})dV + SdT + \overline{N}d\mu, \quad p = \hat{p} + \left(\frac{\partial\hat{p}}{\partial\ln V}\right)_{T,\mu}$$

Statistical mechanics:

Grand partition function:

$$\hat{p}V = kT\ln\Xi$$
$$\Xi = \sum_{N=0}^{\infty} \exp(\beta\mu N) Q_N$$

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Open small systems in equilibrium with the surrounding: grand canonical ensemble (μ , V, T)

Sphere of radius R

Energy: surface + volume contributions

$$\hat{p}V = kT\ln\Xi$$
$$\Xi = \sum_{N=0}^{\infty} \exp(\beta\mu N) Q_N$$

$$\hat{p} = k_B T \Lambda^{-3} \exp(\beta \mu) + 6k_B T \Lambda^{-2} R^{-1} \exp\left[\beta \left(E^s + \mu\right)\right]$$
$$= p^{\infty} + A / R = p^{\infty} + A' \left(\frac{Surf}{Vol}\right)$$

S. K. Schnell, et al. Chem. Phys. Let. 504, 199 (2011) S. K. Schnell, et al. Mol. Phys, 110, 1069 (2012) Open small systems in equilibrium with the surrounding: grand canonical ensemble (μ , V, T)



Sphere of radius R

Energy: surface + volume contributions

$$\hat{p} = p^{\infty} + A/R \qquad s = s^{\infty} + B/R$$
$$p = p^{\infty} + A'/R \qquad \overline{h} = \overline{h}^{\infty} + C/R$$

For one compound:

$$\Gamma^{-1}(L) = \frac{1}{\beta} \left(\frac{\partial \ln \bar{N}}{\partial \mu} \right)_{T,V} = \left(\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} \right)_{\mu,V(L),T} = \Gamma^{-1}(L = \infty) + D/R$$

S. K. Schnell, et al. Chem. Phys. Let. 504, 199 (2011) S. K. Schnell, et al. Mol. Phys, 110, 1069 (2012)

For molecular dynamics and Monte-Carlo simulations



A small system embedded in a large one obeys the rules of grand canonical ensemble

The fluctuation approach in small systems

$$\Gamma^{-1}(L) = \left(\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}\right)_{\mu, V(L), T}$$

Simulation box (*NVT*) and small embedded boxes

S. K. Schnell, et al. Chem. Phys. Let. 504, 199 (2011) S. K. Schnell, et al. J. Phys. Chem. B, 115, 10911 (2011)

For molecular dynamics and Monte-Carlo simulations



Simulation box (*NVT*) and small embedded boxes

$$\Gamma^{-1}(L) = \left(\frac{\left\langle N^2 \right\rangle - \left\langle N \right\rangle^2}{\left\langle N \right\rangle}\right)_{\mu, V(L), T} = \left(\Gamma^{\infty}\right)^{-1} + D/L$$



Linear Extrapolation

Shape effects ???

- Size and shape effects on thermodynamic properties of nanoscale volumes of water, B. Strøm et al., PCCP, **19**, 9016 (2017).



Effect on smallness on thermodynamics ?

Yes => predicted by the thermodynamics of small systems (Hill)

Scaling Laws ?

Yes => linear in 1/R or S/V => New efficient tool to compute Γ^{-1} h_i, v_i, etc by extrapolations

Shape effects ?

Not on the thermodynamic limit, scaling like S/V

Kirkwood-Buff integral, Relation structure-thermodynamics



Kirkwood-Buff integral, Relation structure-thermodynamics

J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 19 (1951) 774.



* g(r) in GC ensemble and * double integral

$$G(V = \infty) = \frac{1}{V} \iint_{V} d\mathbf{r} d\mathbf{r}' \left[g^{\mu VT} \left(|\mathbf{r} - \mathbf{r}'| \right) - 1 \right]$$
$$= 4\pi \iint_{0}^{\infty} h(r) r^{2} dr$$
$$h(r) = \left[g(r) - 1 \right]$$



$$G(V=\infty)=4\pi\int_{0}^{\infty}h^{\mu VT}(r)r^{2}dr$$



$$G(V=\infty) = 4\pi \int_{0}^{\infty} \left[g^{\mu VT}(r) - 1\right] r^{2} dr$$

- Convergence of the integral is poor (i.e. ionic system)
- g(r) should be known accurately until r
 ⇒∞

J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 19 (1951) 774.

$$G(V=\infty) = 4\pi \int_{0}^{\infty} \left[g^{\mu VT}(r) - 1\right] r^{2} dr$$

In general in molecular simulation g(r) is not known accurately until $r \Rightarrow \infty$

And g(r) is often not computed in GC ensemble but in closed system (N constant)

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$$\left[G(V \neq \infty) ? \right]$$

Approximation:

$$G(V) \approx \tilde{G}^{KB}(R) = 4\pi \int_{0}^{R} \left[g^{\mu VT}(r) - 1\right] r^{2} dr$$

J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 19 (1951) 774.

$$G(V=\infty) = 4\pi \int_{0}^{\infty} \left[g^{\mu VT}(r) - 1\right] r^{2} dr$$

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And g(r) is often not computed in GC ensemble but in closed system (N constant)

Approximation:

$$G(V \neq \infty)?$$
Convergence?

$$G(V) \approx \tilde{G}^{KB}(R) = 4\pi \int_{0}^{R} \left[g^{\mu VT}(r) - 1 \right] r^{2} dr$$
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P. Kruger, et al. J. Phys. Chem. Letter, 4, 235 (2013)

$$G(V) = \frac{1}{V} \iint_{VV} d\mathbf{r} d\mathbf{r} d\mathbf{r}' \Big[g \big(|\mathbf{r} - \mathbf{r}'| \big) - 1 \Big]$$

$$G(V) = G(R) = 4\pi \iint_{0}^{2R} \Big[g^{\mu VT}(r) - 1 \Big] r^2 w(r, R) dr$$

$$\neq 4\pi \iint_{0}^{R} \Big[g^{\mu VT}(r) - 1 \Big] r^2 dr$$

The expression of w(r, R) depends on the shape

P. Kruger, et al. J. Phys. Chem. Letter, 4, 235 (2013)

$$G(V) = \frac{1}{V} \iint_{VV} d\mathbf{r} d\mathbf{r} d\mathbf{r}' \Big[g \big(|\mathbf{r} - \mathbf{r}'| \big) - 1 \Big]$$
$$G(V) = G(R) = 4\pi \iint_{0}^{2R} \Big[g^{\mu VT}(r) - 1 \Big] r^2 w(r, R) dr$$

Exact spherical shape:

$$w(r,R) = \left(1 - \frac{3x}{2} + \frac{x^3}{2}\right), \quad x = \frac{r}{2R}$$
$$G(R) = \frac{V}{N} \left(\Gamma^{-1} - 1\right)_{\mu,V,T}$$

Other shapes: see N.Dawas et al, Mol. Phys 2018, P. Kruger Phys. Rev. E 97 (2018), 051301

P. Kruger, et al. J. Phys. Chem. Letter, 4, 235 (2013)

$$h(r) = \left\{ \begin{array}{c} \frac{3/2}{r/\sigma} \exp\left(\frac{1-r/\sigma}{\chi}\right) \cos\left[2\pi\left(\frac{r}{\sigma} - \frac{21}{20}\right)\right], \frac{r}{\sigma} \ge \frac{19}{20} \\ -1, \frac{r}{\sigma} < \frac{19}{20} \end{array} \right.$$

To mimic an atomic liquid of diameter σ The decaying scale is governed by χ (correlation length)

P. Kruger, et al. J. Phys. Chem. Letter, 4, 235 (2013)



P. Kruger, et al. J. Phys. Chem. Letter, 4, 235 (2013)





Correction of the g(r)

N. Dawass, et al., Fluid Phase Equilibria, 486 (2019) 21

g(r) should be calculated from open systems

For N constant finite systems :

 $g^{NVT,NPT,NVE}(r) \approx g^{\mu VT}(r)$ As the system size increases they become identical

=> KBI is very sensitive to the details of g(r)

 $G^{NVT,NPT}(R) \approx G^{\mu VT}(R)$

=> Correction of g(r) N constant => μ VT

Correction of the g(r)

N. Dawass, et al., Fluid Phase Equilibria, 486 (2019) 21

Ben Naim :
$$g^N(r) = g^{\infty}(r) + \frac{c(r)}{N} + O\left(\frac{1}{N^2}\right)$$

Ganguly and V.d. Vegt :

$$g_{\alpha\beta}^{\nu dV}(r) = g_{\alpha\beta}(r) \frac{N_{\beta} \left(1 - \frac{V}{V_{box}}\right)}{N_{\beta} \left(1 - \frac{V}{V_{box}}\right) - \Delta N_{\alpha\beta}(r) - \delta_{\alpha\beta}}$$

$$\Delta N_{\alpha\beta}(r) = \int_{0}^{r} dr' 4\pi r'^{2} \rho_{\beta} \left[g_{\alpha\beta}(r') - 1\right] \qquad \text{Excess/depletion number of particle}$$

Dense non-ideal system (ideal mixture ^{Γ-1}=1)

(=> Where grand canonical simulation are difficult to perform)



X. Liu, et al. J. Phys. Chem. B, 115, 12921 (2011), Ind. Eng. Chem. Res, 51, 10247 (2012), Int. J. Thermophys., 34, 1169 (2013)

Dense non-ideal system (ideal mixture Γ⁻¹=1)

(=> Where grand canonical simulation are difficult to perform)

Acetone-methanol (300K, 1bar)

Acetone-CCl₄ (300K, 1 bar)



X. Liu, et al. J. Phys. Chem. B, 115, 12921 (2011), Ind. Eng. Chem. Res, 51, 10247 (2012), Int. J. Thermophys., 34, 1169 (2013)

Kirkwood-Buff Integrals and partial molar volume

Simulation of ionic (long range interaction) system NaCl solution

J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 19 (1951) 774.

P. Kruger, et al. J. Phys. Chem. Letter, 4, 235 (2013)

Kirkwood-Buff Integrals =>
$$G_{ij} = \frac{V}{\langle N_j \rangle} (\Gamma_{ij}^{-1} - \delta_{ij}), \quad \Gamma_{ij}^{-1} = \left(\frac{\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle}{\langle N_i \rangle} \right)$$

Partial molar volume (binary) => $v_1 = \left[\frac{1 + (G_{22} - G_{12})N_2}{N_1 + N_2 + N_1 N_2 (G_{11} + G_{22} - 2G_{12})} \right]$

System : NaCl 2 mol/l in water (SPCE) at 350 K, 1 bar, electroneutrality constraints S.K. Schnell, et al. Chem. Phys. Letter, 582, p154 (2013)

Partial n	nolar v	olume (ml/mol.)	
water:	sim.	18.5	exp.	17.6
Na+:	sim.	-19.6		
Cl⁻:	sim.	45.4		
NaCI:	sim.	25.8	exp.	25.0

Conclusions

A- Open subsystems of larger one can give access to these partial molar quantities by looking at fluctuations around equilibrium values or KBI

B- Small systems can be analyzed within the framework of thermodynamic of small systems (nanothermodynamics)

=> "intensive" properties (partial molar quantities) are no longer intensive at small scales

=> scale like 1/R (surface /volume) independent on the shape

C- => new tools for molecular simulation (avoid to use grand canonical ensemble)

Application to liquid mixtures, 2D adsorption, solids, ... => Kirkwood-Buff Integrals, partial molar enthalpy, volume,...

P. Kruger, et al. J. Phys. Chem. Letter, 4, 235 (2013)

1- Kirkwood buff Integrals predict the size dependence of thermodynamic properties

2- In agreement with thermodynamics of small systems of Hill (nanothermodynamics) and Gibbs surface thermodynamics.

- Finite-size effects of Kirkwood–Buff integrals from molecular simulations, N Dawass, et al., Mol. Sim., **44**, 599 (2018).

- *Kirkwood-Buff integrals from molecular simulation,* N. Dawass et al., Fluid Phase Equilibria **486**, 21-36 (2019)
- *Kirkwood–Buff integrals of finite systems: shape effects*, N. Dawass, et al., Mol.phys. **116**, 15573 (2018)
- Size and shape effects on thermodynamic properties of nanoscale volumes of water, B. Strøm et al., PCCP, **19**, 9016 (2017).

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Happy birthday Signe !!! And Thank You



The 1/R (S/V) dependence of G(V)

We show now that G^R varies asymptotically with the inverse size of any system having a finite correlation length ξ . Consider the quantity $F \equiv \int_V d\mathbf{r}_1 \int_{\Omega-V} d\mathbf{r}_2 h(r_{12})$, where V is a closed volume with surface S, Ω is the whole space, and $\Omega - V$ is the space outside V. For sufficiently large V, only particles in a layer of thickness ξ on either side of the surface contribute to F. Therefore, when V increases, F scales as the surface S. We can write $F = \int_{V} d\mathbf{r}_{1} / \Omega d\mathbf{r}_{2} h(r_{12}) - \int_{V} d\mathbf{r}_{1} / \int_{V} d\mathbf{r}_{2} h(r_{12})$. In the integral over Ω , using $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ for any \mathbf{r}_1 , we obtain $F = \int_V$ $\mathbf{dr}_1 \int_{\Omega} \mathbf{dr} h(r) - \int_V \mathbf{dr}_1 \int_V \mathbf{dr}_2 h(r_{12}) = V G^{\infty} - V G^V$. As $F \sim S$ for large V, we have $G^V - G^\infty \sim S/V \sim 1/R$ for volumes of any shape and dimension that are large compared to $(2\xi)^d$. The only assumption is the existence of a finite correlation length, which solely breaks down in the critical point. The

Number fluctuations and Kirkwood-Buff integral, Relation structure-thermodynamics

J. G. Kirkwood and F. P. Buff, J. Chem. Phys. 19 (1951) 774.





$$\Gamma^{-1}(V) = \left(\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}\right)_{\mu,V,T} = 1 + \rho G(V)$$

 $G(V) = \frac{1}{V} \iint_{V} d\mathbf{r} d\mathbf{r} d\mathbf{r}' \Big[g(|\mathbf{r} - \mathbf{r}'|) - 1 \Big], \text{ Kirkwood-Buff Integral (KBI)}$

Partial molar enthalpy from small system method

(mixtures) S. Schnell et al. J. Chem. Phys. 141, 144501 (2014)

Partial molar enthalpy =>
$$\left(\frac{\partial H}{\partial N_i}\right)_{N_{j\neq i},P,T} = h_i$$

Calorimetry

Grand canonical ensemble

$$\left(\frac{\partial H}{\partial N_{i}}\right)_{\mu_{j\neq i},V,T} = -\frac{\left\langle UN_{i}\right\rangle - \left\langle U\right\rangle \left\langle N_{i}\right\rangle + k_{B}T\left\langle N_{i}\right\rangle}{\left\langle N_{i}^{2}\right\rangle - \left\langle N_{i}\right\rangle^{2}}$$

U: internal energy

PT ensemble

$$\left(\frac{\partial H}{\partial N_{i}}\right)_{\mu_{j\neq i},V,T} \Longrightarrow \left(\frac{\partial H}{\partial N_{i}}\right)_{N_{j\neq i},P,T} = h_{i} \qquad \text{knowing, } \Gamma^{-1} \text{ and } V_{i}$$

Partial molar enthalpy from small system method

(mixtures) S. Schnell et al. J. Chem. Phys. 141, 144501 (2014)

Grand canonical ensemble

$$\left(\frac{\partial H}{\partial N_{i}}\right)_{\mu_{j\neq i},V,T} = -\frac{\left\langle UN_{i}\right\rangle - \left\langle U\right\rangle \left\langle N_{i}\right\rangle + k_{B}T\left\langle N_{i}\right\rangle}{\left\langle N_{i}^{2}\right\rangle - \left\langle N_{i}\right\rangle^{2}}$$





Partial molar enthalpy from small system method (binary mixture MD, dense LJ liquid)



- ND : Numerical differentiation (exact method, very time consuming, not for chemically constrained systems)DM : Difference method (Frenkel et al., standard in molecular simulation)
- **SSM** : Small System Method

Chemically constrained systems in mixtures => Reduced degree of freedom (Gibb's phase rule)

=> Equilibrium chemical reaction

$$H_{2} \rightleftharpoons 2H$$
$$K_{T} = \left[\frac{\left(a_{H}\right)^{2}}{a_{H_{2}}}\right]_{eq}$$

=> Charge neutrality NaCl solution in water Number of Na⁺=Number of Cl⁻

Partial molar enthalpy and reaction enthalpy from small system method R. Skorpa et al. PCCP 16, 19681 (2014)

$${
m H}_{2}$$

 ⇒ 2H (ЗОООК-20,000К)
 ${
m \Delta}_{r}H = 2h_{{
m H}} - h_{{
m H}_{2}}$







$$\rho^* = 0.004 \Rightarrow 0.0695 \text{ g/cm}^3$$

Reactive force field $H_2 \rightleftharpoons 2H$

$$N_{P} = N_{H} + 2N_{H_{2}} = 1000$$

$$\rho = 17.38 \ \rho^{*} \qquad T = 52000 \ T^{*}$$

$$10^{-5} \le \rho^{*} \le 0.004 \qquad 2.68 \ 10^{-4} \le T^{*} \le 0.4$$

$$1.7110^{-4} \text{ g/cm}^{3} \le \rho \le 0.0695 \ \text{g/cm}^{3} \qquad 14\text{K} \le T \le 20800 \ \text{K}$$

=> Bellow 200K quantum effects, not taken into account

Atomic model interacting through 2 and 3 bodies



Composition (Bulk) $K_{th} = \frac{(x_{\rm H}\gamma_{\rm H})^2}{x_{{\rm H}_2}\gamma_{{\rm H}_2}} = K_x \frac{\gamma_{\rm H}^2}{\gamma_{{\rm H}_2}}, \quad K_x = \frac{x_{\rm H}^2}{x_{{\rm H}_2}}$ $H_{2} = 2 H$ 2 comp. gas \odot $\rho = 0.0695 \text{ g/cm}^3$ 0 $\sim \rho = 0.0191 \text{ g/cm}^3$ liquid • 0.8 -2 $\ln(K_{\chi})$ 6.0 X -4 -6 0.4 -8 -10 0.2^L 5000 10000 15000 20000 25000 30000 0.0001 0.00015 0.0002 5e-05 Temperature / K $1/T [K^{-1}]$ van't Hoff : $\rho^* = 0.0011 \Longrightarrow 0.0191 \text{ g/cm}^3$, $\left[\frac{d\ln K_{th}}{d(1/T)}\right]_{R} = -\frac{\Delta_{r}H^{0}}{R},$ gas like $\rho^* = 0.004 \Rightarrow 0.0695 \text{ g/cm}^3$, $\rho^* = 0.0011, \ \Delta_r H^0 = 380 \text{ kJ/mol},$ liquid like $\rho^* = 0.004, \ \Delta_r H^0 = 430 \text{ kJ/mol},$ $\Delta_r H_{exp}^0 = 436 \text{ kJ/mol}$

Partial molar enthalpy and reaction enthalpy from small system method

$$\Delta_r H = 2h_{\rm H} - h_{\rm H_2}$$



$$\rho^* = 0.004 \Rightarrow 0.0695 \text{ g/cm}^3$$

$$\rho^* = 0.0011 \Rightarrow 0.0191 \text{ g/cm}^3$$

Temperature 156K



Partial molar enthalpy and reaction enthalpy from small system method