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

Col.: 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)
Kirkwood-Buff integral

\[ G(V) = \frac{1}{V} \int_V \int_V d\mathbf{r} d\mathbf{r}' \left[ g(|\mathbf{r} - \mathbf{r}'|)_{\mu,V,T} - 1 \right] \], Kirkwood-Buff Integral (KBI)
Kirkwood-Buff integral and number fluctuations

\[ G(V) = \frac{1}{V} \iint d\mathbf{r} d\mathbf{r}' \left[ g(|\mathbf{r} - \mathbf{r}'|)_{\mu,V,T} - 1 \right], \]

\[ \left( \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} \right)_{\mu,V,T} = 1 + \rho \, G(V) \]
Kirkwood-Buff integral and thermodynamics

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

Thermodynamic factor

\[
\Gamma^{-1} = k_B T \left( \frac{\partial \rho}{\partial P} \right)_T = \rho k_B T \beta_T
\]

Isothermal compressibility

Multicomponent mixture => partial molar volume

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)

\[ E_t = TS_t + \mu N_t - \hat{p}V_t \]

\[ E_t = N_r \overline{E} \quad S_t = N_r S \quad N_t = N_r \overline{N} \quad V_t = N_r V \]

\[ \overline{E} = TS + \mu \overline{N} - \hat{p}V \quad (\text{In the thermodynamic limit: } \hat{p} = p) \]

\[ d\overline{E} = TdS + \mu d\overline{N} - pdV \]
T.H. Hill, "Thermodynamics of small systems" (Dover, 1963)

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

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:

\[\hat{p}V = kT \ln \Xi\]

Grand partition function:

\[\Xi = \sum_{N=0}^{\infty} \exp(\beta \mu N) Q_N\]
Open small systems in equilibrium with the surrounding: **grand canonical ensemble \((\mu, V, T)\)**

Sphere of radius \(R\)

Energy: surface + volume contributions

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

\[
\hat{p} = k_B T \Lambda^{-3} \exp(\beta \mu) + 6 k_B T \Lambda^{-2} R^{-1} \exp[\beta (E^s + \mu)] \\
= p^\infty + A / R = p^\infty + A \left( \frac{\text{Surf.}}{\text{Vol.}} \right)
\]

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

Sphere of radius $R$

Energy: surface + volume contributions

\[ \hat{p} = p^\infty + A/R \quad s = s^\infty + B/R \]
\[ p = p^\infty + A'/R \quad \bar{h} = \bar{h}^\infty + C/R \]

For one compound:

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

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

For molecular dynamics and Monte-Carlo simulations

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

Simulation box \((NVT)\) and small embedded boxes

Small System Method: SSM

Linear Extrapolation
Shape effects  

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

\[ L = \sqrt[3]{V} \]

**SPC/E Water 298 K, 10^5 Pa**

\[
\frac{L}{R} = 0.80
\]

\[
\frac{L}{R} = 1.15
\]

\[
\frac{L}{R} = 1.41
\]

\[
\frac{L}{R} = 1.61
\]

\[ R: \text{circumradius} \]

\[ \nu(L) = \langle N \rangle \Gamma^{-1}(L) \]
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 \(\Gamma^{-1}, h_i, v_i, \text{etc}\) by extrapolations

Shape effects?

Not on the thermodynamic limit, scaling like \(S/V\)
Kirkwood-Buff integral, Relation structure-thermodynamics


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

\[
G(V) = \frac{1}{V} \int \int \int \frac{d\mathbf{r} d\mathbf{r}'}{V} \left[ g(|\mathbf{r} - \mathbf{r}'|) - 1 \right], \text{ Kirkwood-Buff Integral}
\]
Kirkwood-Buff integral, Relation structure-thermodynamics


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

\[ G(V) = \frac{1}{V} \int \int_{V \times V} d\mathbf{r} d\mathbf{r}' \left[ g^{\mu VT}(|\mathbf{r} - \mathbf{r}'|) - 1 \right] \], Kirkwood-Buff Integral

2 main challenges:
* g(r) in GC ensemble and
* double integral
Kirkwood-Buff integral

\[ G(V = \infty) = \frac{1}{V} \int \int \frac{d\mathbf{r} d\mathbf{r}'}{V^2} \left[ g^{\mu\nu T} (|\mathbf{r} - \mathbf{r}'|) - 1 \right] \]

\[ = 4\pi \int_0^\infty h(r) r^2 dr \]

\[ h(r) = [g(r) - 1] \]
Kirkwood-Buff integral

\[ G(V = \infty) = 4\pi \int_0^\infty h^{\mu VT}(r)r^2 dr \]
Kirkwood-Buff integral


\[
G(V = \infty) = 4\pi \int_0^\infty \left[ g^{\mu\nu T}(r) - 1 \right] r^2 dr
\]

- Convergence of the integral is poor (i.e. ionic system)
- \(g(r)\) should be known accurately until \(r \Rightarrow \infty\)
Kirkwood-Buff integral

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

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)
Kirkwood-Buff integral

\[ G(V = \infty) = 4\pi \int_0^\infty \left[ g^{\mu VT}(r) - 1 \right] r^2 dr \]

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

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

**Approximation:**

\[ G(V \neq \infty) \approx G^{KB}(R) = 4\pi \int_0^R \left[ g^{\mu VT}(r) - 1 \right] r^2 dr \]
Kirkwood-Buff integral

\[
G(V = \infty) = 4\pi \int_0^\infty \left[ g^{\mu VT}(r) - 1 \right] r^2 dr
\]

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

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

Approximation:

\[
G(V \neq \infty) \text{?}
\]

\[
G(V) \approx \tilde{G}^{KB}(R) = 4\pi \int_0^R \left[ g^{\mu VT}(r) - 1 \right] r^2 dr
\]

Convergence ?
Exact Volume KB Integrals

\[ G(V) = \frac{1}{V} \int \int d\mathbf{r} d\mathbf{r}' \left[ g(|\mathbf{r} - \mathbf{r}'|) - 1 \right] \]

\[ G(V) = G(R) = 4\pi \int_0^{2R} \left[ g^{\mu\nu T}(r) - 1 \right] r^2 w(r, R) \, dr \]

\[ \neq 4\pi \int_0^R \left[ g^{\mu\nu T}(r) - 1 \right] r^2 \, dr \]

The expression of \( w(r, R) \) depends on the shape
Exact Volume KB Integrals

\[ G(V) = \frac{1}{V} \int \int d\mathbf{r} d\mathbf{r}' \left[ g(|\mathbf{r} - \mathbf{r}'|) - 1 \right] \]

\[ G(V) = G(R) = 4\pi \int_0^{2R} \left[ g^{\mu VT}(r) - 1 \right] r^2 w(r, R) dr \]

Exact spherical shape:

\[ w(r, R) = \left( 1 - \frac{3x}{2} + \frac{x^3}{2} \right), \quad x = \frac{r}{2R} \]

\[ G(R) = \frac{V}{N} \left( \Gamma^{-1} - 1 \right)_{\mu, \nu, T} \]

Exact Volume KB Integrals

\[ h(r) = \begin{cases} 
  \frac{3}{2} \exp\left(\frac{1-r/\sigma}{\chi}\right) \cos\left[2\pi\left(\frac{r}{\sigma} - \frac{21}{20}\right)\right], & \frac{r}{\sigma} \geq \frac{19}{20} \\
  -1, & \frac{r}{\sigma} < \frac{19}{20} 
\end{cases} \]

To mimic an atomic liquid of diameter \( \sigma \)
The decaying scale is governed by \( \chi \) (correlation length)
Exact Volume KB Integrals

\[ G(R) = 4\pi \int_0^R \left[ g^{\mu\nu}(r) - 1 \right] r^2 dr \]

\[ \hat{G}^R = 4\pi \int_0^R \left[ g^{\mu\nu}(r) - 1 \right] r^2 dr \]

\[ \hat{G}^R = 4\pi \int_{2R}^R \left[ g^{\mu\nu}(r) - 1 \right] r^2 w(r, R) dr \]
Exact Volume KB Integrals

\[ \tilde{G}^R = 4\pi \int_0^R \left[ g^{\mu\nu} (r) - 1 \right] r^2 dr \]

\[ G^R = 4\pi \int_0^{2R} \left[ g^{\mu\nu} (r) - 1 \right] r^2 w(r, R) dr \]
Correction of the $g(r)$

$g(r)$ should be calculated from open systems

For N constant finite systems:

$$g^{NVT,NPT,NVE}(r) \approx g^{\mu VT}(r)$$  \hspace{1cm} \text{As the system size increases they become identical}

$\Rightarrow$ KBI is very sensitive to the details of $g(r)$

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

$\Rightarrow$ Correction of $g(r)$ N constant $\Rightarrow \mu VT$
**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:

\[
g^{vdV}_{\alpha\beta}(r) = g_{\alpha\beta}(r) \frac{N_\beta \left(1 - \frac{V}{V_{box}}\right)}{N_\beta \left(1 - \frac{V}{V_{box}}\right) - \Delta N_{\alpha\beta}(r) - \delta_{\alpha\beta}} 
\]

\[
\Delta N_{\alpha\beta}(r) = \int_0^r dr' 4\pi r'^2 \rho_\beta \left[g_{\alpha\beta}(r') - 1\right] \quad \text{Excess/depletion number of particle}
\]
Dense non-ideal system (ideal mixture $\Gamma^{-1} = 1$)  
(=> Where grand canonical simulation are difficult to perform)

Dense non-ideal system (ideal mixture $\Gamma^{-1}=1$)
(=> Where grand canonical simulation are difficult to perform)

Acetone-methanol (300K, 1bar)

Acetone-CCl₄ (300K, 1 bar)

\[ J = -D^{Fick} \nabla C = -D^{MS} \frac{C}{RT} (\nabla \mu)_T \]

\[ D^{Fick} = D^{MS} / \Gamma^{-1} \]

\[ D^{Fick} \Rightarrow \text{experiments} \]

\[ D^{MS} \Rightarrow \text{molecular dynamics} \]

Kirkwood-Buff Integrals and partial molar volume
Simulation of ionic (long range interaction) system NaCl solution


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

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

System: NaCl 2 mol/l in water (SPCE) at 350 K, 1 bar, electroneutrality constraints

Partial molar volume (ml/mol.)
water: sim. 18.5 exp. 17.6
Na⁺: sim. -19.6
Cl⁻: sim. 45.4

NaCl: 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,...
**Exact Volume KB Integrals**

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

- *Kirkwood-Buff integrals from molecular simulation*, N. Dawass et al., Fluid

- *Kirkwood–Buff integrals of finite systems: shape effects*, N. Dawass, et al.,

- *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 \( \xi \). Consider the quantity \( F \equiv \int_V dr_1 \int_{\Omega-V} dr_2 h(r_{12}) \), where \( V \) is a closed volume with surface \( S \), \( \Omega \) is the whole space, and \( \Omega - V \) is the space outside \( V \). For sufficiently large \( V \), only particles in a layer of thickness \( \xi \) on either side of the surface contribute to \( F \). Therefore, when \( V \) increases, \( F \) scales as the surface \( S \). We can write \( F = \int_V dr_1 \int_{\Omega} dr_2 h(r_{12}) - \int_V dr_1 \int_V dr_2 h(r_{12}) \). In the integral over \( \Omega \), using \( r = r_1 - r_2 \) for any \( r_1 \), we obtain \( F = \int_V dr_1 \int_{\Omega} dr h(r) - \int_V dr_1 \int_V dr_2 h(r_{12}) = VG^\infty - VG^V \). 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

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

\[
G(V) = \frac{1}{V} \int_{V} \int_{V} d\mathbf{r} d\mathbf{r}' \left[ g(|\mathbf{r} - \mathbf{r}'|) - 1 \right], \text{Kirkwood-Buff Integral (KBI)}
\]
Partial molar enthalpy from small system method (mixtures)  

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

Calorimetry

Grand canonical ensemble

$$\left( \frac{\partial H}{\partial N_i} \right)_{\mu_{j \neq i}, V, T} = - \frac{\langle UN_i \rangle - \langle U \rangle \langle N_i \rangle + k_B T \langle N_i \rangle}{\langle N_i^2 \rangle - \langle N_i \rangle^2}$$

U: internal energy

PT ensemble

$$\Rightarrow \left( \frac{\partial H}{\partial N_i} \right)_{\mu_{j \neq i}, V, T} = h_i \quad \text{knowing, } \Gamma^{-1} \text{ and } V_i$$
**Partial molar enthalpy from small system method (mixtures)**  

Grand canonical ensemble

\[
\left( \frac{\partial H}{\partial N_i} \right)_{\mu_j, \nu, T} = - \frac{\langle UN_i \rangle - \langle U \rangle \langle N_i \rangle + k_B T \langle N_i \rangle}{\langle N_i^2 \rangle - \langle N_i \rangle^2}
\]

**FIG. 1.** Double-well spring potential (Eq. 52) used for the model reaction \(A \rightleftharpoons B\). The distance between the potential wells is \(2w\), and \(h_{\text{min}, 2}\) is the height of the second well. The height of the barrier between the two wells changes with \(h_{\text{min}, 2}\).

**FIG. 2.** \(\langle \frac{\partial N_i}{\partial \hat{H}} \rangle_{T, V, \mu_j}\) as a function of the small system size \(1/L\) for \(x_1 = 0.2\). In agreement with Eq. (21), the trend is linear until it deviates for small \(1/L\) when the small system size is close to the simulation box size. The thermodynamic limit was obtained from a linear extrapolation (black lines and red points) between the two dashed lines.

**FIG. 3.** Partial enthalpies in the grand-canonical ensemble. Data were sampled for small systems embedded in a larger simulation box, maintained in the canonical ensemble. These values were extrapolated to the thermodynamic limit (see also Fig. 2). For comparison, partial enthalpies were computed directly in grand-canonical simulations. The chemical potential was adjusted to approximate the density and composition used in the canonical ensemble. Clearly both approaches yield identical results.

**FIG. 4.** Partial enthalpies in the \(NVT\) ensemble. A series of \(NVT\) simulations with different particle numbers were carried out (method (i)). The red line is obtained by converting the molar enthalpies from Fig. 3, using the Kirkwood-Buff coefficients needed to calculate \(A\) and \(B\).
Partial molar enthalpy from small system method (binary mixture MD, dense LJ liquid)

\[ \frac{\partial H}{\partial N_1} \]

\[ x_1 \]

\[ h_1 \]

\[ h_2 \]

**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

\[ H_2 \rightleftarrows 2H \]

\[ K_T = \left[ \frac{(a_H)^2}{a_{H_2}} \right]_{eq.} \]

=> 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)

\[ \Delta_r H = 2h_H - h_{H_2} \]

\[ H_2 \leftrightarrow 2H \quad (3000K-20,000K) \]

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

\[ \rho^* = 0.004 \Rightarrow 0.0695 \text{ g/cm}^3 \]
Reactive force field \[ \ce{H_2 \rightleftharpoons 2H} \]

\[
N_P = N_H + 2N_{H_2} = 1000
\]

\[
\rho = 17.38 \rho^* \\
10^{-5} \leq \rho^* \leq 0.004 \\
1.71 \times 10^{-4} \text{g/cm}^3 \leq \rho \leq 0.0695 \text{g/cm}^3
\]

\[
T = 52000 T^* \\
2.68 \times 10^{-4} \leq T^* \leq 0.4 \\
14K \leq T \leq 20800 \text{K}
\]

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

Atomic model interacting through 2 and 3 bodies

\[
U(r_1, \ldots, r_N) = \sum_{i<j} u(2)(r_{ij}) + \sum_{i<j<k} u(3)(r_{ij}, r_{jk}, r_{ik})
\]

\[
u(3) = h_{i,j,k}(r_{ij}, r_{jk}, \theta_{ij,k}) + h_{j,i,k}(r_{ji}, r_{ik}, \theta_{j,i,k}) + h_{i,k,j}(r_{ik}, r_{jk}, \theta_{i,k,j})
\]

Composition (Bulk)

\[ 
\text{H}_2 = 2 \text{H} 
\]

\[ 
K_{th} = \frac{(x_H \gamma_H)^2}{x_{H_2} \gamma_{H_2}^2} = K_x \frac{\gamma_H^2}{\gamma_{H_2}}, \quad K_x = \frac{x_H^2}{x_{H_2}} 
\]

\[ 
\begin{align*}
\rho^* &= 0.0011 \Rightarrow 0.0191 \text{ g/cm}^3, \\
\text{gas like} \\
\rho^* &= 0.004 \Rightarrow 0.0695 \text{ g/cm}^3, \\
\text{liquid like} \\
\end{align*}
\]

van't Hoff:

\[ 
\left[ \frac{d \ln K_{th}}{d(1/T)} \right]_P = -\frac{\Delta_r H^0}{R}, 
\]

\[ 
\begin{align*}
\rho^* &= 0.0011, \quad \Delta_r H^0 = 380 \text{ kJ/mol}, \\
\rho^* &= 0.004, \quad \Delta_r H^0 = 430 \text{ kJ/mol}, \\
\Delta_r H^0_{\text{exp}} &= 436 \text{ kJ/mol} 
\end{align*}
\]
Partial molar enthalpy and reaction enthalpy from small system method

Grand canonical ensemble

\[
\left( \frac{\partial H}{\partial N_i} \right)_{\mu_j, V, T} = -\frac{\langle UN_i \rangle - \langle U \rangle \langle N_i \rangle + k_B T \langle N_i \rangle}{\langle N_i^2 \rangle - \langle N_i \rangle^2}
\]

PT ensemble

\[
\left( \frac{\partial H}{\partial N_i} \right)_{\mu_j, V, T} \Rightarrow \left( \frac{\partial H}{\partial N_i} \right)_{N_j, P, T} = h_i
\]

\[
\Delta_r H = 2h_H - h_{H_2}
\]

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

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

Temperature 156K
Partial molar enthalpy and reaction enthalpy from small system method

\[ \Delta_r H = 2h_H - h_{H_2} \]
\[ \Delta_r H(T) / \Delta_r H^0 (\text{exp}, 298 \text{ K}) \]

\[ \Delta_r H^0 (\text{exp}, 298 \text{ K}) = 436 \text{ kJ/mol} \]