# Multispecies Virial Expansion 

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## Outline

(1) Background and Motivation
(2) The Problem
(3) Main Results and Ideas
(4) Conclusions, Open Questions/Further Problems

## Single Species Expansions

- Context of a Classical Interacting Gas


## Single Species Expansions

- Context of a Classical Interacting Gas
- We have the pair potential $\phi\left(x_{i}-x_{j}\right)$
- The Grand Canonical Partition Function
$\equiv(z):=\sum_{n=0}^{\infty} \frac{z^{n}}{n!} \int_{\Lambda} \cdots \int_{\Lambda} \exp \left(-\beta \sum_{1 \leq i<j \leq n} \phi\left(x_{i}-x_{j}\right)\right) \mathrm{d} x_{1} \cdots \mathrm{~d} x_{n}$, where
$z$ is the fugacity parameter
- In the Thermodynamic Limit $|\Lambda| \rightarrow \infty$, we have the pressure $\beta P=\lim _{|\wedge| \rightarrow \infty} \frac{1}{|\lambda|} \log \equiv(z)$
- Expansion for pressure $P$ in terms of fugacity $z$ is the cluster expansion
- We have $\rho=z \frac{\partial}{\partial z} P$, the density
- The virial development of the Equation of State is the power series $P=\sum_{n=1}^{\infty} c_{n} \rho^{n}$ called the virial expansion.


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## Single Species Expansions

- Context of a Classical Interacting Gas
- Cluster and Virial Expansions are reasonably well understood
- Represent cluster coefficients as weighted connected graphs ...
- ... and virial coefficients as weighted 2-connected graphs or irreducible integrals
- Main work done in the 1930's and 40's by Mayer J. E. Mayer, M. G. Mayer, Statistical Mechanics New York, John Wiley and Sons Inc. (1940)
- But what happens if we have a mixture of different particles?


## Finitely Many Species - Early Ideas/Formulae

- Imagining why we would want to generalise to many different types of particles is easy


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- Initial difficulty: going from a single type particle to two different types gives 3 degrees of freedom (one for each of the 'single types' and one for the mixture)
- Paper implicitly uses Lagrange-Good Inversion and Tree-like relationships
- Notion of generalised Radii of convergence (Borel)


## Combinatorial Tools

Approaching the Multispecies Cluster Expansion, we come armed with tools developed in Combinatorics:

- The Lagrange-Good Inversion
I. J. Good, The generalisation of Lagrange's expansion and the enumeration of trees, Proc. Cambridge Philos. Soc., 61, 499-517 (1965) provides the way in which we can invert power series of form:

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\begin{equation*}
\rho(z)=z+\sum_{n \geq 2} n b_{n} z^{n} \tag{1}
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- The Dissymmetry Theorem for Connected Graphs (and also trees) F. Bergeron, G. Labelle, P. Leroux, Combinatorial Species and Tree-like Structures, Encyclopaedia of Mathematics and its Applications, Vol. 67, Cambridge University Press, Cambridge, U.K. (1998)


## Combinatorial Tools

- The notion of coloured graphs and an extension of the Dissymmetry Theorem - Application of this to the multivariate virial expansion W. G. Faris, Biconnected graphs and the multivariate virial expansion, Markov Proc. Rel. Fields 18, 357-386 (2012)


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- The notion of coloured graphs and an extension of the Dissymmetry Theorem - Application of this to the multivariate virial expansion W. G. Faris, Biconnected graphs and the multivariate virial expansion, Markov Proc. Rel. Fields 18, 357-386 (2012)
- There is a lack of attention on the convergence of such expansions only as formal power series


## Statistical Mechanics

- The context of the work is on the multispecies generalisation of the paper by Poghosyan and Ueltschi
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- We begin with a collection of fugacity parameters $\left\{z_{i}\right\}_{i \in \mathbb{N}}$ with $z_{i}$ being the activity of the species $i$
- We assume the achievement of a 'cluster expansion' for the pressure and understand conditions to achieve a convergent virial expansion
- We start from the 'formal' power series representation (Cluster Expansion):

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\begin{equation*}
P(\mathbf{z})=\sum_{\mathbf{n}} b(\mathbf{n}) \mathbf{z}^{\mathbf{n}} \tag{CE}
\end{equation*}
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- We may formally define:

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\begin{equation*}
\rho_{k}:=z_{k} \frac{\partial}{\partial z_{k}} P \tag{R1}
\end{equation*}
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or via the power series:

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\rho_{k}:=\sum_{\mathbf{n}} n_{k} b(\mathbf{n}) \mathbf{z}^{\mathbf{n}} \tag{R2}
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- We wish to invert (R2), substitute for $z$ in (CE) to obtain:

$$
\begin{equation*}
P(\rho)=\sum_{\mathbf{n}} c(\mathbf{n}) \rho^{\mathbf{n}} \tag{VE}
\end{equation*}
$$

## Convergence Conditions

## Theorem (Jansen, T., Tsagkarogiannis, Ueltschi)

Assume that there exist $0<r_{i}<R_{i}$ and $a_{i} \geq 0, i \in \mathbb{N}$, such that

- $p(\mathbf{z})$ converges absolutely in the polydisc

$$
D=\left\{\mathbf{z} \in \mathbb{C}^{\mathbb{N}}\left|\forall i \in \mathbb{N}:\left|z_{i}\right|<R_{i}\right\}\right.
$$

- $\left|\log \frac{\partial p}{\partial z_{i}}(\mathbf{z})\right|<a_{i}$ for all $i \geq 1$ and all $\mathbf{z} \in D$.
- $\sum_{i \geq 1} \sqrt{\frac{r_{i}}{R_{i}}}<\infty$ and $\sum_{i \geq 1} \frac{r_{i} a_{i}^{2}}{R_{i}}<\infty$.

Then there exists a constant $C<\infty$ (which depends on the $r_{i}, R_{i}, a_{i}$, but not on $\mathbf{n}$ ) such that

$$
\begin{equation*}
|c(\mathbf{n})| \leq C \sup _{\mathbf{z} \in D}|p(\mathbf{z})| \prod_{i \geq 1}\left(\frac{e^{a_{i}}}{r_{i}}\right)^{n_{i}} . \tag{C1}
\end{equation*}
$$

## Convergence Conditions

The estimate for $c(\mathbf{n})$ guarantees convergence of the series $\sum_{\mathbf{n}} c(\mathbf{n}) \boldsymbol{\rho}^{\mathbf{n}}$ for all $\rho$ in the polydisc

$$
D^{\prime}=\left\{\rho \in \mathbb{C}^{\mathbb{N}}\left|\forall i \in \mathbb{N}:\left|\rho_{i}\right|<r_{i} e^{-a_{i}}, \sum_{i \in \mathbb{N}}\right| \rho_{i} \left\lvert\, \frac{e^{a_{i}}}{r_{i}}<\infty\right.\right\} .
$$

## Lagrange-Good Inversion

## Theorem

Let $\mathbf{z}(\rho)$ be a summable collection of power series and $\mathbf{G}(\rho)$ be a collection of formal power series, such that $\forall i \in \mathbb{N}$

$$
\begin{equation*}
z_{i}(\boldsymbol{\rho})=\rho_{i} G_{i}(\mathbf{z}(\boldsymbol{\rho})) \tag{LI1}
\end{equation*}
$$

Let $J=\left\{i \in \mathbf{N} \mid n_{i} \neq 0\right\}$ and $\mathbf{n} \geq \mathbf{k}$, then we have that:

$$
\begin{equation*}
\left[\rho^{\mathrm{n}}\right] \mathbf{z}(\rho)^{\mathbf{k}}=\left[\mathbf{z}^{\mathbf{n}-\mathbf{k}}\right]\left|\delta_{i, j} G_{i}(\mathbf{z})^{n_{i}}-z_{j} \frac{\partial G_{i}}{\partial z_{j}} G_{i}(\mathbf{z})^{n_{i}-1}\right|_{i, j \in J} \tag{2}
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Recall that:

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\begin{equation*}
\rho_{i}(\mathbf{z}):=z_{i} \frac{\partial P}{\partial z_{i}} \tag{R}
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So we have that $G_{i}=\frac{1}{\frac{\partial P}{\partial z_{i}}}$

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This gives us the Lagrange Inversion Formula:

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\left[\rho^{\mathbf{n}}\right] P(\boldsymbol{\rho})=\left[\mathbf{z}^{\mathbf{n}}\right] P(\mathbf{z})\left|\delta_{i, j}\left(\frac{1}{\frac{\partial P}{\partial z_{i}}}\right)^{n_{i}}-z_{j} \frac{\partial}{\partial z_{j}}\left(\frac{1}{\frac{\partial P}{\partial z_{i}}}\right)\left(\frac{1}{\frac{\partial P}{\partial z_{i}}}\right)^{n_{i}-1}\right|
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We rearrange this to:

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\begin{equation*}
\left[\rho^{\mathbf{n}}\right] P(\rho)=\left[\mathbf{z}^{\mathbf{n}}\right] P(\mathbf{z}) \frac{1}{\left(\frac{\partial P}{\partial \mathbf{z}}\right)^{\mathbf{n}}}\left|\delta_{i, j}+z_{j} \frac{\partial}{\partial z_{j}} \ln \frac{\partial P}{\partial z_{i}}\right|_{i, j \in J} \tag{LI4}
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We can therefore see where the bound comes from - the $C$ as uniform bound on determinant, the final product from bounds on the derivative in the assumption

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- The dissymmetry theorem can be generalised to this case, but we still have issues in considering block-multiplicative weight-functions
- The dissymmetry theorem gives us a relationship between connected and two-connected graphs via rooted connected graphs


## The Dissymmetry Theorem

The dissymmetry theorem for connected graphs gives us the relation:

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\begin{equation*}
\mathcal{C}+\mathcal{B}^{\bullet}\left(\mathcal{C}^{\bullet}\right)=\mathcal{C}^{\bullet}+\mathcal{B}\left(\mathcal{C}^{\bullet}\right) \tag{D1}
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There is a combinatorial interpretation of what each term means:

- The superscript - denotes a rooted structure
- The composition of structures eg $\mathcal{B}^{\prime}(\mathcal{C})$ indicates a $\mathcal{B}^{\prime}$ assembly of $\mathcal{C}^{\bullet}$-structures


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- $\mathcal{B}\left(\mathcal{C}^{\bullet}\right)$ is a connected graph rooted at a particular block


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- The Dissymmetry theorem relies on the connection with $\mathcal{B}^{\prime}$-enriched trees
- The idea is to view connected graphs as being made up of 'trees of 2-connected graphs'
- This extra structure adds more to the interpretation of what we get from Lagrange Inversion


## Conclusions and Open Questions

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- The explanation of the virial coefficients representing 2-connected coloured graphs is possible in some circumstances


## Conclusions and Open Questions

- We have obtained convergence conditions for infinitely many species in the virial expansion
- Lagrange-Good inversion generalises precisely what one needs to do to get a virial expansion from the cluster expansion in the multispecies case
- The explanation of the virial coefficients representing 2-connected coloured graphs is possible in some circumstances
- There are some difficulties in applying some of the conditions and the dissymmetry theorem to particular examples. The issue relies on understanding how to gain appropriate lower bounds on the derivative.


## Further Work/Open Questions

- Langrange Inversion and the Dissymmetry Theorem run in parallel to provide in the former case a method of computing coefficients exactly and in the latter case an interpretation of the coefficients in terms of combinatorial structures


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- Further work could be done in understanding what models can precisely fit the requirements of our paper


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- Further work could be done in understanding what models can precisely fit the requirements of our paper
- There are notable difficulties in considering such a problem from an implicit-function theorem point of view

