様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

# 科学研究費助成事業　　研究成果報告書

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研究課題名（和文）Development of Kirkwood-Buff integral theory for crystalline matter

研究課題名（英文）Development of Kirkwood-Buff integral theory for crystalline matter

研究代表者
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研究成果の概要（和文）：(1) イオン結晶のクーロンエネルギーを新たなアンサンブル平均法を提案した。アンサンブル平均の表面エネルギーは結晶構造に依存しないことを証明した。(2) Kirkwood-Buff積分（KBI）論を固体に適用することに初めて成功した。調和結晶の場合、二体分布関数（PDF)を解析的に求め、圧縮率方程式が固体でも成り立つことを証明した。ArとAr-Xe混合物の場合、シミュレーションで得られたPDFから、圧縮率や部分モル体積など計算した。(3)有限体積の場合、通常な計算で得られたゆらぎから、圧縮率を正確に求められないことがわかった。粒子のサイズを考慮し、新たなPDF定義を提案し、修正できた。

研究成果の学術的意義や社会的意義
本研究はKirkwood-Buff積分(KBI)理論を固体に拡張することを目標をし、その目標を達成した。通常の計算法を用いると固体のKBIが発散し、計算できない。一方、我々が2013年に開発した有限体積KBI理論を使って、固体のKBI理論が収束し、初めて計算することを成功した。そこから、固体の統計力学で使用できる様々の数値法を開発した。

研究成果の概要（英文）：(1) We have proposed the new, ensemble averaged method for the calculation of the Coulomb energy of ionic crystals. We proved that the surface term of the ensemble averaged Madelung energy is independent of crystal structure. (2) We have succeeded in applying Kirkwood-Buff integral (KBI) theory to solids for the first time. In harmonic crystals, we could calculate the pair distribution function (PDF) analytically and proved that the compressibility equation also holds for crystals. In the case of solid argon and a Ar-Xe solid solution, we computed the PDF by simulation and calculated the compressibility, partial molar volumes etc, from the KBI. (3) We discovered that in finite volumes, the compressibility cannot be calculated exactly from the particle number fluctuations, when the usual definition of the PDF is used. We succeeded in correcting the error by a new definition of the PDF which takes account of the excluded volume of the particles.

研究分野：物質科学

キーワード：統計力学　粒子個数ゆらぎ　固体　溶液　圧縮率方程式　マーケティング定数　積分発散

**様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）**

1. Background（研究開始当初の背景）

In gases and liquids, the number of particles contained in a small volume of space fluctuates around the mean value. These density fluctuations are directly linked to the compressibility of the system. In mixtures and solutions, the concentration of some molecular species also fluctuates. From the value of these fluctuations, thermodynamic properties such as partial molar volumes and chemical potential derivatives can be obtained. The most convenient way to compute particle number fluctuations is by using volume integrals over the pair distribution function (PDF), the so-called Kirkwood-Buff (KB) integrals. KB integrals are routinely computed and analyzed for solutions and liquid mixtures, including for biological systems. They provide valuable insights into the local structure around some species as well as thermodynamic information. While KB theory is a powerful tool for the study of liquids, it has never been applied to solids (before we started this project.) This is surprising because KB theory relies only on general statistical mechanics principles, which are valid in all phases of matter. The problem is that in solids, KB integrals cannot be calculated in the usual way, because the integrals diverge when the volume goes to infinity.

2. Aim（研究の目的）

The aim was to extend KB theory, which is much used in the physical chemistry research of liquid mixtures, to solid materials, especially solid solutions. Some time ago, we formulated the finite-volume KB theory [1] which gives a correct physical meaning (in terms of particle number fluctuations) to KB integrals in finite volumes in a liquid. This finite volume KB [1] converges much faster than the standard (“running KB integral”) theory. Therefore we thought that finite volume KB theory may as well solve the divergence problem in solids. As a first step, we used finite volume KB theory to compute the Madelung energy in ionic systems, because this mathematical problem has some similarity with that of KB integrals. Then we wanted to show that KB theory can indeed be used in solids, i.e. that the integrals can be calculated without divergence and that the results are reliable. We started with a perfect crystal of Argon at zero temperature where the PDF is analytical. Then we went to finite temperature where the PDF must be computed numerically using Monte Carlo or molecular dynamics simulations. After the chemically simple case of pure Argon, we tackled solid solutions and we chose the Ar-Xe mixture, which has some interesting applications as a detector material for neutrino experiments as well as in medical imaging.

3. Methods（研究の方法）

For the integral calculations, we used our finite volume KB integral method [1] and extrapolations to infinite volume that we developed previously [2]. The PDF of argon and that of the Ar-Xe mixture were calculated with Monte-Carlo simulations (DL Monte-code) as well as molecular dynamics simulations (LAMMPS

code). For theory development we used well-known statistical mechanical results such as the equipartition theorem and the central limit theorem and the Debye approximation for the phonon dispersion.

4. Results（研究結果）

(1) A new method for computing the Coulomb (Madelung) energy in ionic systems [3]

By adapting our finite volume KB integral method to the Coulomb interaction energy problem, we have derived exact expressions for the ensemble averaged Madelung energy in a finite sub-volume of an infinite ionic solid. The averaging is done over all possible positions and orientations of the finite volume, which corresponds to the ensemble of a powder sample. This ensemble is homogeneous and isotropic, as a fluid, and thus KB theory can be applied. In the thermodynamic limit, i.e. for infinitely large sub-volumes, the ensemble averaged Madelung energy converges unconditionally. This is in sharp contrast to all other real-space summation methods of the Madelung constant, which require a particular summation order and/or compensating charges. We found that the ensemble averaged Madelung constant approaches the infinite volume limit in the same way, completely independent of the crystal structure (Fig.1) As a consequence, in the large volume limit, the surface term of the ensemble averaged Madelung energy has a universal form, independent of the crystal structure. By using this surprising fact, we derived a condition for the relative stability of different structural phases in ionic clusters of finite size. From this we could give a simple explanation for the fact that cesium halides (CsCl, CsBr, CsI) which crystallize in the cesium-chloride structure in the bulk, transform to the rock-salt structure for small clusters of a few hundred atoms.

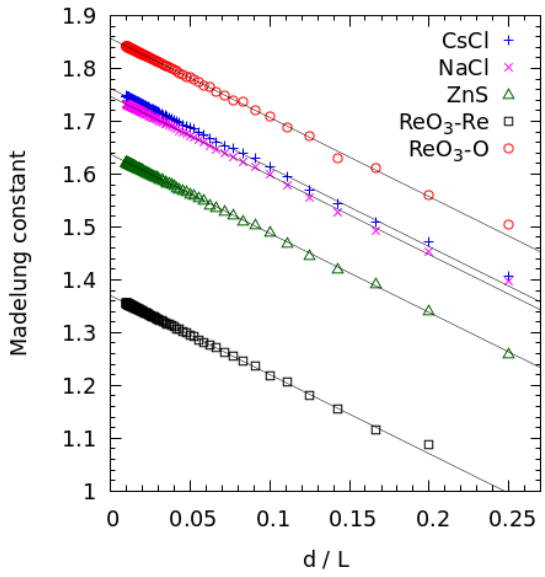


*Fig.1 Ensemble averaged Madelung constant of spherical clusters of diameter L for different ionic crystals with nearest neighbor distance d.*

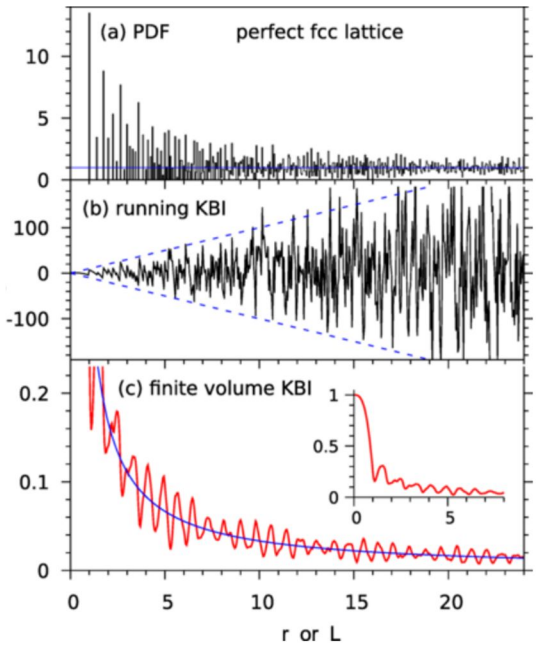


*Fig.2. Fcc lattice at T=0. PDF (a) and KBI (b,c) as a function of distance (r) or diameter (L). (b) running KBI diverges (c) new finite volume KBI converges*

(2) Extension of Kirkwood-Buff integral theory to solids and solid solutions [4,5,6]

This has been our main goal and we fully succeeded in achieving it.

① For perfect crystals at zero temperature we showed that the KB integrals strongly diverge when the integrals are computed in the usual way (so-called running KB integral) and that they converge to the exact value if we use our finite volume KB method (Fig.2) [1]. Then we considered a harmonic crystal at finite temperature. Within the Debye approximation, we derived an exact, analytic expression for the PDF. From this we computed the KB integral and showed that the compressibility equation holds exactly [4]. This has never been done before, because the usual KB integrals diverge in crystals, even at finite temperature, as we showed.

② We applied our new theory to a realistic material, namely solid argon and computed the compressibility from the KB integrals. We used a Lennard-Jones potential with parameters suitable for solid argon. The PDF was obtained from Monte-Carlo simulations in the canonical ensemble in the temperature range 15-75 K (the melting temperature is 88 K). As a check we also computed the PDF from molecular dynamics simulations which gave virtually identical results. The KB integrals converge when using the finite volume KB method [1], but the convergence is slow and in solids, with a wildly oscillating PDF, the extrapolation to infinite volume is tricky. To solve this problem, we introduced a convolution of the PDF (Fig.3) which makes the PDF very smooth but does not alter the infinite volume integral. With these numerical inventions, we succeeded in obtaining converged compressibility values for solid argon from KB theory. The temperature dependence agrees very well with experiment, but the absolute value is underestimated by a few tens of percent. This problem could be fixed with a simple scaling up from zero temperature, but the origin of the problem remains unclear and will require further studies.

③ We applied KB theory for the first time to a solid solution, namely to a Xe rich Ar-Xe mixture [5].

We computed the PDF using Monte-Carlo simulations with a Mie-potential. All the numerical techniques developed for solid argon were used again.

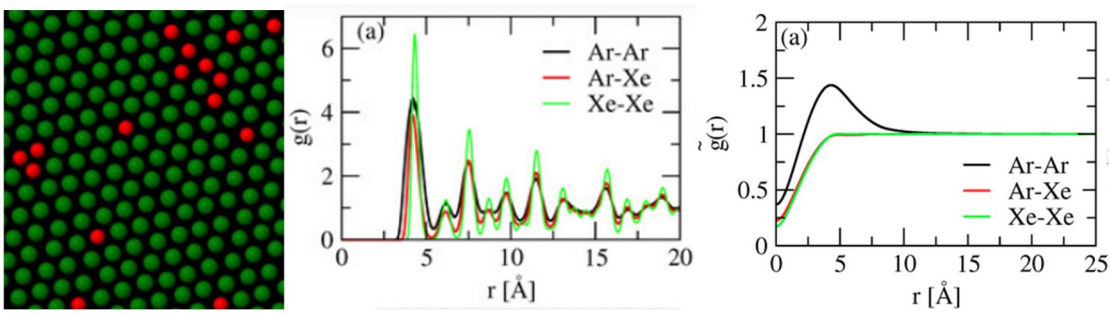


*Fig.3 Left: snapshot of the Monte Carlo simulation of AsXe solid solution (Ar: red, Xe: green). The Ar*

*atoms tend to cluster. Middle: PDFs at T=45 K. Right: Same PDFs after convolution. The graphs are much smoother which improves tremendeously the convergence of the KB integrals (not shown).*

We showed that correcting the PDF for the ensemble error (canonical vs grand-canonical) is crucial in the case of a solid solutions. From the KBI we computed the compressibility, the partial molar volumes of Ar and Xe and the chemical potentials. While this is quite common in liquid solutions, this was never achieved before in solid solutions. The obtained results agree well with those obtained with other theoretical methods (and the scarce experimental data).

(3) Correction method for obtaining local compressibility from density fluctuations in finite volumes

When computing particle number fluctuations, the particles are commonly counted as point-like objects. This is also reflected in the definition of the PDF. Recently, we discovered that when fluctuations are computed in this usual way in an (open) volume of finite size, the fluctuations do not give the correct compressibility. The neglect of the particle volume leads to a spurious term in the fluctuations. We have shown that this error can be corrected by a redefinition of the PDF where the excluded volume is explicitly taken into account. We have presented this result at a conference [7] and a publication is in preparation. We think that this finding has important implications for the interpretation of local intrinsic quantities.

Finally we note that the project was very successful. Indeed, we achieved our main goals, published six peer-reviewed papers and organized an international workshop [8] where we brought together the leading researchers in the field.


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[3] Peter Krüger, Ensemble averaged Madelung energies of finite volumes and surfaces, Phys. Rev. B 101, 205423 (2020).

[4] Peter Krüger, Validity of the compressibility equation and Kirkwood-Buff theory for crystalline matter, Phys. Rev. E 103, L061301 (2021)

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https://www.cecam.org/workshop-details/1064

５．主な発表論文等

〔雑誌論文〕　計5件（うち査読付論文　5件／うち国際共著　3件／うちオープンアクセス　1件）

| | |
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| １．著者名<br>Peter Krueger | ４．巻<br>103 |
| ２．論文標題<br>Validity of compressibility equation and Kirkwood-Buff theory for crystalline matter | ５．発行年<br>2021年 |
| ３．雑誌名<br>Physical Review E | ６．最初と最後の頁<br>L061301 |
| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.1103/PhysRevE.103.L061301 | 査読の有無<br>有 |
| オープンアクセス<br>オープンアクセスではない、又はオープンアクセスが困難 | 国際共著<br>該当する |

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| １．著者名<br>Masafumi Miyaji, Bastien Radola, Jean-Marc Simon, Peter Krueger | ４．巻<br>154 |
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| ３．雑誌名<br>Journal of Chemical Physics | ６．最初と最後の頁<br>164506 |
| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.1063/5.0049673 | 査読の有無<br>有 |
| オープンアクセス<br>オープンアクセスではない、又はオープンアクセスが困難 | 国際共著<br>該当する |

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| １．著者名<br>Krueger Peter | ４．巻<br>101 |
| ２．論文標題<br>Ensemble averaged Madelung energies of finite volumes and surfaces | ５．発行年<br>2020年 |
| ３．雑誌名<br>Physical Review B | ６．最初と最後の頁<br>1～6 |
| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.1103/PhysRevB.101.205423 | 査読の有無<br>有 |
| オープンアクセス<br>オープンアクセスではない、又はオープンアクセスが困難 | 国際共著<br>－ |

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| １．著者名<br>Dawass Noura、Krueger Peter、Schnell Sondre K.、Moultos Othonas A.、Economou Ioannis G.、Vlugt Thijs J. H.、Simon Jean-Marc | ４．巻<br>10 |
| ２．論文標題<br>Kirkwood-Buff Integrals Using Molecular Simulation: Estimation of Surface Effects | ５．発行年<br>2020年 |
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| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.3390/nano10040771 | 査読の有無<br>有 |
| オープンアクセス<br>オープンアクセスとしている（また、その予定である） | 国際共著<br>－ |

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| 1．著者名<br>N. Dawass, P. Krueger, J.-M. Simon and T. J. H. Vlugt, | 4．巻<br>486 |
| 2．論文標題<br>Kirkwood-Buff integrals from molecular simulation, | 5．発行年<br>2019年 |
| 3．雑誌名<br>Fluid Phase Equilibria | 6．最初と最後の頁<br>21-36 |
| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.1016/j.fluid.2018.12.027 | 査読の有無<br>有 |
| オープンアクセス<br>オープンアクセスではない、又はオープンアクセスが困難 | 国際共著<br>該当する |

〔学会発表〕　計10件（うち招待講演　0件／うち国際学会　1件）

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| 1．発表者名<br>Peter Krueger |
| 2．発表標題<br>Madelung Energy and Bragg Peak Function from Finite Volume Kirkwood-Buff Integrals |
| 3．学会等名<br>Twenty-first Symposium on Thermophysical Properties |
| 4．発表年<br>2021年 |

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| 1．発表者名<br>Peter Krueger |
| 2．発表標題<br>From exact finite volume integrals to KBI for the solid state |
| 3．学会等名<br>Recent progress in the statistical mechanics of solutions through Kirkwood-Buff integrals and related approaches |
| 4．発表年<br>2021年 |

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| 1．発表者名<br>Masafumi Miyaji, Bastien Radola, Jean-Marc Simon and Peter Krueger |
| 2．発表標題<br>Extension of Kirkwood-Buff Integral Theory to Solids |
| 3．学会等名<br>Twenty-first Symposium on Thermophysical Properties |
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３．学会等名
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４．発表年
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Masafumi Miyaji, Peter Krueger

２．発表標題
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３．学会等名
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３．学会等名
日本物理学会第76回年次大会

４．発表年
2021年

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２．発表標題
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３．学会等名
日本物理学会第76回年次大会

４．発表年
2021年

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２．発表標題
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2020年

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３．学会等名
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Peter Krueger

２．発表標題
System Size Scaling of the Statistical Distribution Function of the Diffusion Coefficient in Porous Matter

３．学会等名
The International Symposium on Adsorption 2019 (Japan Adsorption 2019), Makuhari, 21-23 May 2019.（国際学会）

４．発表年
2019年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

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６．研究組織

| | 氏名<br>（ローマ字氏名）<br>（研究者番号） | 所属研究機関・部局・職<br>（機関番号） | 備考 |
|---|---|---|---|

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

８．本研究に関連して実施した国際共同研究の実施状況

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