On Stable Pair Potentials with an Attractive Tail, Remarks on Two Papers by A. G. Basuev

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Received: 17 March 2015 / Accepted: 12 October 2015
Published online: 14 December 2015 – © Springer-Verlag Berlin Heidelberg 2015

Abstract: We revisit two old and apparently little known papers by Basuev (Teoret Mat Fiz 37(1):130–134, 1978, Teoret Mat Fiz 39(1):94–105, 1979) and show that the results contained there yield strong improvements on current lower bounds of the convergence radius of the Mayer series for continuous particle systems interacting via a very large class of stable and tempered potentials, which includes the Lennard-Jones type potentials. In particular we analyze the case of the classical Lennard-Jones gas under the light of the Basuev scheme and, using also some new results (Yuhjtman in J Stat Phys 160(6):1684–1695, 2015) on this model recently obtained by one of us, we provide a new lower bound for the Mayer series convergence radius of the classical Lennard-Jones gas, which improves by a factor of the order $10^5$ on the current best lower bound recently obtained in de Lima and Procacci (J Stat Phys 157(3):422–435, 2014).

1. Introduction

The possibility to obtain the equation of state for a non-ideal gas only from first principles, i.e., once given the microscopic interaction between its molecules, has been a subject of intense investigation by the mathematical physics community and several rigorous results on this issue have been obtained, especially in the decade of the Sixties, concerning mainly systems of classical particles interacting via a pair potential.

In this context, Mayer \cite{21,22} and Mayer and Mayer \cite{23}, in their seminal works in the Forties, were able to obtain an explicit representation of the pressure of a non ideal gas whose particles interact via a pair potential. Such an expression, known nowadays by the name of Mayer series, is a formal power series in terms of the activity (a quantity trivially related to the chemical potential) whose coefficients (called the Ursell coefficients) can be computed once given the microscopic pair potential.

The Mayer series represents an explicit expression of the equation of the state of a non ideal gas deduced from first principles (i.e., only from the microscopic pair interaction between particles). However, the series was at that time only formal, in the sense that
nothing could be said about its convergence due to the intricate combinatorial structure of the Ursell coefficients. Even so, the Mayer series (truncated at some order) has been successfully used since then by chemists and physicists to extract useful information about the behavior of real gases. This was a strong motivation to prove its convergence, at least in the region of low density or high temperature, where every classical system of particles is supposed to be in the gas state. Such an achievement would provide a firm ground to the interpretation of the Mayer series as the rigorous and exact equation of state for any non-ideal gas.

It took more than twenty years after Mayer’s results to obtain the first rigorous results on the convergence of the Mayer series. The first breakthrough, due to Groeneveld [17], was a proof of the convergence of the Mayer series in the low-density/high-temperature phase for gases of particles that interact via a purely repulsive pair potential. The latter was a quite dramatic restriction, which ruled out most, if not all, pair potentials modeling realistic continuous particle systems in physics. However, just one year later, Penrose [25,26] and, independently, Ruelle [34,35] obtained the astonishing result that the Mayer series of continuous systems of particles was actually an analytic function of the temperature and activity in the low density/high temperature phase. The result holds for an enormous class of pair interactions (the so-called stable and tempered pair potentials, see ahead for the definitions), which included practically all known examples of pair potentials for realistic gases. More than this, Penrose and Ruelle were able to provide a lower bound for the convergence radius of the Mayer series, which stands among the best available in the literature until today.

The mathematical methods developed by Penrose and Ruelle to get their results were based on the so called Kirkwood–Salzburg equations (see e.g. Sec. 4.2.1 in [33] and references therein). Such techniques do not face directly the structure of the general nth order Ursell coefficient of the Mayer series (a well behaved upper bound for it, e.g., such as $C^n$ for some constant $C$, would provide immediately the analyticity of the series for low densities). Rather, these methods are based on the analysis of an infinite set of relations relating the n-point correlation function of the system (which can also be expressed as a series similar to the Mayer series) to the m-point correlation functions with $m < n$.

Despite the undoubting success of the methods based on Kirkwood–Salzburg equations, the apparently great difficulty to obtain a direct bound for the Mayer coefficients starting from their explicit expression in terms of sum over connected graphs remained an intriguing open question.

The first result in this direction was obtained in 1967 by Penrose [27], who was able to obtain bounds on the Mayer coefficients, as powerful as those of Penrose–Ruelle in 1963 [26,34], directly via a resummation of the connected graphs appearing in the Ursell coefficients in terms of trees: it was the first example of tree graph identity. This very nice result, however, was restricted to pair potentials that had not only to be stable and tempered but also possess a hard-core. The Penrose tree-graph identity, somehow forgotten for thirty years, was recently rescued in [11,30] and [12], where it has been utilized to improve the convergence region of the abstract polymer gas and the gas of hard spheres in the continuum respectively.

In 1978, Brydges and Federbush [5] developed a new tree-graph identity (different from that of Penrose) through which they were able to obtain bounds stronger than those of Penrose–Ruelle for a subclass of the stable and tempered potentials. Pair potentials in this subclass needed to be absolutely summable. This was a quite severe restriction since it left out the important class of the Lennard-Jones type potentials. However a quite popular potential among chemists was included: the so called Morse Potential, and in this case the improvement was really consistent (see e.g. [24]).