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Field theoretical approach to the liquid state. Elements of comprehension of the role of the ideal entropy

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Abstract

In a series of papers we have introduced a field theoretical approach to describe the liquid state. The formalism introduces a simple Hamiltonian which includes the ideal gas free energy and the standard interaction potential between particles coupling the fields. In this paper, we discuss the role and the importance of the ideal term in this formalism. We compare our approach to the standard liquid state theory and another approach based on a field description, the density functional theory where an identical functional appears. The comparison shows that field theory sheds new light on the role of the ideal entropy an aspect which is traditionally discarded in favor of a viewpoint focusing on the interaction potential.

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1. Introduction

Field theory is traditionally used as a heuristic tool and generally considered as a merely qualitative approach. This is due to the fact that most approaches of this kind are based on phenomenological Hamiltonians. The resulting approaches are rather flexible in that they can be used for instance to describe liquid–gas interfaces, polymers or the soft matter in general [1–3]. However, its use in the description of critical phenomena for instance, also shows that it is a robust and powerful tool [4].

In a series of papers [5–9], we have introduced a field theory (FT) to describe the liquid state. The description is based on fields representing the density of the particles. Using these fields, the functional integral, from which one can calculate the partition function, is written in terms of a Hamiltonian. The Hamiltonian includes two contributions, a local functional related to the ideal gas and a non-local quadratic term which includes the two body interaction potential. In this framework the interaction potential describes coupling of the fields rather than interaction between the particles. This approach has been successfully applied to describe ionic solutions in the bulk [5] and at interfaces [7–9] and systems interacting with Yukawa potentials [6]. In [10] we show that this Hamiltonian corresponds to a description of the liquid state equivalent to the standard liquid state theory [11].Well known exact expressions can be derived within this formalism as well as new relations specific to this formalism [12].

The aim of this paper is to discuss important characteristic features of the field theoretical approach — in particular, the core of this formalism which is the ideal gas contribution to the Hamiltonian. In this perspective, we discuss the role of this term in the calculation of the functional integral. It is shown that this term has an important non-trivial role in the theory and that it accounts for the ideal gas contribution to the free energy. In the standard liquid state theory the focus is usually on non-local properties such as the interaction potential or the correlation functions. One consequence of the traditional viewpoint is to give the feeling that once we isolate the ideal gas contribution, we no longer need to discuss the ideal gas properties. In the present paper we show that combinatorics related with the ideal gas properties is present in the field theory at all stages of the calculation just as much as the interactions are. We discuss the physical implications with simple intuitive arguments.

The paper is organized as follows. We first derive an expression of the chemical potential which is a direct consequence

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of the Hamiltonian. Then we discuss the FT in view of the traditional liquid state theory and one specific approach which is the Density Functional Theory (DFT) [13–16]. This approach is also based on a density functional and often involves a term which is identical to the ideal term in our Hamiltonian. We then describe the role of the ideal gas functional in FT in a perturbation expansion. First, we give the expansion theory from the viewpoint of the standard loop expansion of the FT. Second, we provide examples where the physical implications of the ideal gas Hamiltonian are evident.

2. Field theory

2.1. Functional integral

For a one component liquid, with pair interactions, we consider a FT where we fix the external parameters of chemical potential μ and temperature T and V^e stands for the external potential. The generating functional for the theory is written in terms of the generating field J

$$\Xi[\mu,T;J] = \int \mathcal{D}\rho \exp\left\{-\beta\mathcal{H}[\mu,T;\rho] + \int(\beta V^{\mathrm{e}} + J)\rho\right\} \tag{1}$$

where $\mathcal{D}\rho$ is the measure, on a discretized lattice, of lattice spacing ρ. The Hamiltonian $\mathcal{H}[\mu,T;\rho] = \mathcal{H}_{\mathrm{id}}[\mu,T;\rho] + \mathcal{H}_v[T;\rho]$ has two contributions. The first is related to the ideal gas

$$\beta\mathcal{H}_{\mathrm{id}}[\mu,T;\rho] = \sum_i^{V/a^3} \rho(i)a^3\left[\ln(\rho(i)\Lambda^3) - 1 - \beta\mu\right] \tag{2}$$

$$= \sum_i^{V/a^3} \rho(i)a^3\left[\ln(\rho(i)/\bar{\rho}) - 1\right] \tag{3}$$

where β is the inverse temperature, Λ the de Broglie wavelength and in the second line we have introduced the notation $\bar{\rho}=(1/\Lambda^3)\exp(\beta\mu)$, which is simply the density of an ideal gas of the same given temperature and chemical potential. The second contribution to the Hamiltonian is related to the interactions

$$\beta\mathcal{H}_v[T;\rho] = \frac{1}{2}\sum_{i\neq j}^{V/a^3} \rho(i)a^3(\beta v(i,j))\rho(j)a^3 \tag{4}$$

where $v(i,j)$ is the pair potential between sites i and j.

The thermodynamic grand partition function of the system $\hat{\Xi}=\Xi[\mu,T;0]$ is then simply the generating functional for $J=0$. The density correlation functions are obtained differentiating the generating functional

$$<\rho(i_1)\ldots\rho(i_n)> = \left.\frac{\delta^n \Xi[\mu,T;J]}{\delta J(i_1)\ldots\delta J(i_n)}\right|_{J=0} \tag{5}$$

2.2. Exact relation in field theory

If we express the partition function as a functional integral, the Dyson relation [4,17] follows as a direct consequence of ρ being the dummy variable. In the quantum field theory it is known as the equation of movement. In the transformation $\rho\rightarrow\rho+\Delta\rho$ of the stochastic variable, where $\Delta\rho$ is a given function the partition function remains unchanged. Starting from expression (1) and taking $J=0$, we have at each site i the general expression

$$\beta<\frac{\delta\mathcal{H}}{\delta\rho(i)}> + \beta V^{\mathrm{e}}(i) = 0. \tag{6}$$

Using the Hamiltonian given by Eqs. (2) and (4), at a given lattice site i, the relation above becomes [8]

$$<\ln\rho(i)\Lambda^3> + \sum_{j\neq i}\beta v(i,j)<\rho_j>a^3 + \beta V^{\mathrm{e}}(i) = \beta\mu. \tag{7}$$

This relation shows that the chemical potential is the sum of the external potential, the derivative of the ideal gas free energy with respect to the density at a given point and the sum over all other points of the interaction potential with the weighting of the density.

This expression is similar to the traditional expression of the one-particle density $\tilde{\rho}\,(i)$ (i.e. $<p(i)>$ in FT) in the liquid state theory [18–20] which can be written

$$\ln(\tilde{\rho}(i)\Lambda^3) - c^{(1)}(T,[\rho];i) + \beta V^{\mathrm{e}}(i) = \beta\mu \tag{8}$$

where $c^{(1)}(T,[\rho];i)$ is the single-particle direct correlation function [11,18,19]. And it can also be compared with another expression of the chemical potential [21] based on a charging process of the interaction potential

$$v(n;\xi) = \sum_{n1}\xi v(n,n_1) + \sum_{n_1,n_2\neq n} v(n_1,n_2) \tag{9}$$

where the potential of all particles with particle n is progressively turned on by increasing ξ from 0 to 1. We thus have

$$\ln(\tilde{\rho}(i)\Lambda^3) + \tilde{\rho}(i)a^3\int_0^1 \mathrm{d}\xi \sum_j \beta v(i,j)g^{(2)}(i,j;\xi) + \beta V^{\mathrm{e}}(i) = \beta\mu \tag{10}$$

where $g^{(2)}\,(i,\,j;\,\xi)$ is the pair distribution function [11] as a function of the charging parameter ξ.

If we compare the first two expressions of the chemical potentia1, Eqs. (7) and (8), we have that the two quantities

$$<\ln\rho(i)\Lambda^3> + \sum_{j\neq i}\beta v(i,j)<\rho_j>a^3 \text{ and } \ln(\tilde{\rho}(i)\Lambda^3) - c^{(1)}(T,[\rho];i) \tag{11}$$

must be identical. The comparison shows that it would be deceptive to identify logarithmic terms in both theories. In the case of the FT, the term which involves explicitly the potential is simple, it is just multiplied and summed with the average density. The complexity of the system sits in the average of the logarithmic term, where the average has to be calculated with the full Hamiltonian which includes the interactions. In contrast