Invariance properties and correlation functions in liquid-state theory: Connection with the Ward-Takahashi identities

D. di Caprio,[1] Q. Zhang,[2] and J. P. Badiali[1]

[1]*Laboratory SRSI, University of Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France*
[2]*Department of Chemistry, State University of New York, Stony Brook, New York 11794-3400*

We derive Ward-Takahashi identities for a scalar field theory in the case of translational invariance. These identities are then generalized to include the case where a linear term in the field breaks this symmetry in the action. Using an analogous procedure, we also derive in the framework of liquid-state theory some well known relations between the direct correlation functions, which are valid also in the presence of an external potential. These relations are therefore basic, in that they are a consequence of an invariance property of the system. The so-called Baxter relations for homogeneous fluids are also derived as a consequence; moreover, we investigate another invariance, which is the rotational invariance.

I. INTRODUCTION

The notion of symmetry is without any doubt an important and basic concept in physics. It has proved a powerful tool in the comprehension of the properties of many phenomena, such as critical phenomena.

In field theory, one of many consequences of the existence of symmetries lies in the so called Ward-Takahashi (WT) identities [1]. It is the aim of this paper to investigate whether similar relations exist in liquid-state theory. We shall in particular consider the simple case of a global symmetry, which is the translational invariance. Basic equations in liquid-state theory will be obtained as a consequence of this symmetry.

Section II will be dedicated to deriving the WT identities for translational invariance. We first study the case of a translational invariant action and then show how these identities still hold when this symmetry is broken by a term which is linear in the field. In Sec. III we shall rederive some equations which exist in liquid-state theory [2,3]. We shall emphasize the necessity to have translational invariance, in order to obtain these relations which bare a profound resemblance with the WT identities. In Sec. IV we shall give an illustration of the importance of these equations by deriving some relations first obtained in [4,5], which are sometimes referred to as Baxter relations for homogeneous fluids, which play a central role in the theory of critical phenomena [6–8], similar to that of the WT identities in renormalization procedures. Finally, we investigate the consequences of another invariance which is the rotational invariance.

II. WARD-TAKAHASHI IDENTITIES

In this section, we derive the WT identities for systems which are translationally invariant. These relations will also be shown to hold when this symmetry is broken by a linear term in the action. Hereafter we shall follow the presentation given in [1].

Let us consider a Euclidian field theory, where $Z[J]$ is the generating functional, defined with a d dimensional Euclidian action $S_{sym}[\phi]$, where ϕ is a scalar field. In addition, we make the hypothesis that this action has a symmetry, that is, $S_{sym}[\phi]$ is invariant under a space translation. The generating functional is written

$$Z_{sym}[J] = \int [d\phi] \exp[-S_{sym}[\phi] + \int J(x)\phi(x)d^dx] .$$

(1)

From now on, if it is not necessary for comprehension, the integral over real space is understood. To study the consequences of the invariance under a space translation, we make an infinitesimal change in field Eq. (2a), which can be interpreted as a infinitesimal translation Eq. (2b),

$$\phi(x) = \phi'(x) + \varepsilon\nabla\phi'(x) \quad (2a)$$

$$= \phi'(x + \varepsilon) . \quad (2b)$$

In terms of this field, ϕ', the value of the partition function $Z[J]$, is not modified, as we have only changed the dummy integration variable ϕ. We can also explicitly write changes occurring by the substitution of ϕ with the variable ϕ', and in Eq. (1) we consider the changes in three terms. (i) The action term is not modified, as by hypothesis it is invariant under a translation: $S_{sym}[\phi'] = S_{sym}[\phi]$; each term in the action is generally a product of fields or derivatives of the field which are integrated over the whole space, and no change occurs if we use Eq. (2b). (ii) The integration measure is formally written using Eq. (2b), $\Pi_x d\phi(x) = \Pi_x d\phi'(x')$ with $x' = x + \varepsilon$. In fact, x' is a dummy index which does not interfere with the space integrations in the action or in the interaction term; therefore, it can be simply renamed x and no change in the measure occurs. (iii) Finally, only the interaction term is modified; we use Eq. (2a) which preserves the locality of the interaction term, and the field ϕ and J are taken for the same point. This is the only term which will yield any contribution if we perform the difference $Z_{sym}[J]_{\phi'} - Z_{sym}[J]_\phi$, calculated respectively with ϕ' and ϕ variables. This difference is zero, as we have simply changed the integration variable; therefore we have

$$\int [d\phi'] \exp[-S_{\text{sym}}[\phi'] + \int J(x)\phi'(x)d^dx] - \int [d\phi] \exp[-S_{\text{sym}}[\phi] + \int J(x)\phi(x)d^dx]$$

$$= \int [d\phi] \exp[-S_{\text{sym}}[\phi] + \int J(x)\{\phi(x) - \varepsilon \cdot \nabla_x \phi(x)\}d^dx] - \int [d\phi] \exp[-S_{\text{sym}}[\phi] + \int J(x)\phi(x)d^dx] = 0 . \quad (3)$$

We thus have

$$\varepsilon \cdot \left\{ \int [d\phi] \left[\int J(x)\nabla_x \phi(x)d^dx \right] \right.$$

$$\left. \times \exp \left[-S_{\text{sym}}[\phi] + \int J(x)\phi(x)d^dx \right] \right\} = 0 , \quad (4)$$

where we have dropped higher orders in ε. Using the fact that ε is arbitrary, the term in brackets is zero,

$$\int [d\phi] \left[\int J(x)\nabla_x \phi(x)d^dx \right]$$

$$\times \exp \left[-S_{\text{sym}}[\phi] + \int J\phi \right] = 0 . \quad (5)$$

Now if we use the identity

$$\int [d\phi]\phi(x) \exp \left[-S_{\text{sym}}[\phi] + \int J\phi \right]$$

$$= [\delta Z_{\text{sym}}[J]/\delta J(x)] , \quad (6)$$

we obtain

$$\int d^dx \, J(x)\nabla_x[\delta Z_{\text{sym}}[J]/\delta J(x)] = 0 . \quad (7a)$$

This is one formulation of the WT identities in the case of translational invariance; it is straightforward to derive the identities for the generating functional of the connected Green's functions, $W_{\text{sym}}[J] \equiv \ln Z_{\text{sym}}[J]$,

$$\int d^dx \, J(x)\nabla_x[\delta W_{\text{sym}}[J]/\delta J(x)] = 0 , \quad (7b)$$

and for its Legendre transform, which is the one particle irreducible generating functional $\Gamma_{\text{sym}}[\varphi]$, such that

$$\Gamma_{\text{sym}}[\varphi] + W_{\text{sym}}[J] = \int d^dx \, J(x)\varphi(x)$$

$$\text{with } \varphi(x) = \delta W_{\text{sym}}[J]/\delta J(x) . \quad (8)$$

Notice that we use the notation $\varphi = \langle \phi \rangle$. We have

$$\int d^dx \, \nabla_x \varphi(x)[\delta \Gamma_{\text{sym}}[\varphi]/\delta \varphi(x)] = 0 , \quad (9)$$

$$\int d^dx \, \varphi(x)\nabla_x[\delta \Gamma_{\text{sym}}[\varphi]/\delta \varphi(x)] = 0 , \quad (10)$$

where the second expression is obtained by partial integration, under the assumption that the test function $\varphi(x)$ is such that the surface term vanishes.

Generating functionals are usually computed at $J = 0$; in this case Eqs. (7) are trivial, as we consider the gradient of quantities which are homogeneous for this translational invariant action. However, these equations have been derived whatever the value of J, and therefore also for a nonhomogeneous field. It is then possible to extend the use of Eqs. (7) to actions with a linear term in the field which breaks the translational invariance.

We now suppose that a term linear in the field is included in the action [1], for instance a nonuniform potential $V(x)$. The new action is

$$S[\phi] = S_{\text{sym}}[\phi] - \int d^dx \, V(x)\phi(x) . \quad (11)$$

The WT identities should *a priori* not hold, as the action is no longer invariant in a space translation. However, it is easy to see that the generating functionals satisfy

$$Z[J] = Z_{\text{sym}}[J + V] \quad \text{and} \quad W[J] = W_{\text{sym}}[J + V] , \quad (12)$$

where the subscript sym indicates that the functions are relative to the previous symmetric action. What Eq. (12) states is that we can reinterpret the nonsymmetric functions as functionals of J, in terms of the previous symmetric functions as functionals of a field $K = J + V$. Expanding the nonsymmetric functions around $J = 0$ is equivalent to expanding the symmetric functions with $K = V$. The equivalent Ward identities for the nonsymmetric action are obtained from Eq. (7b) for $K = J + V$

$$\int d^dx \, K(x)\nabla_x[\delta W_{\text{sym}}[K]/\delta J(x)]$$

$$= \int d^dx [J + V](x)\nabla_x[\delta W_{\text{sym}}[J + V]/\delta J(x)] = 0 .$$

Using Eq. (12), we have

$$\int d^dx [J + V](x)\nabla_x[\delta W[J]/\delta J(x)] = 0 . \quad (13a)$$

Equation (13a) shows that we still have a WT identity for the nonsymmetric action, with an additional term related to V. When J is zero, we now have a nontrivial relation which is

$$\int d^dx \, V(x)\nabla_x[\delta W[J = 0]/\delta J(x)] = 0 . \quad (13b)$$

We can also study the behavior of the $\Gamma[\rho]$ functions. To obtain a relation between $\Gamma[\rho]$ and $\Gamma_{\text{sym}}[\rho]$, we compare the Legendre transforms, for both the symmetric and nonsymmetric action,

$$\Gamma[\varphi] + W[J] = \int d^dx \, J(x)\varphi(x)$$

$$\text{with } \varphi(x) = \delta W[J]/\delta J(x) , \quad (14a)$$

$$\Gamma_{\text{sym}}[\varphi] + W_{\text{sym}}[J + V] = \int d^dx [J + V](x)\varphi(x)$$

$$\text{with } \varphi(x) = \delta W_{\text{sym}}[J + V]/\delta J(x) . \quad (14b)$$

Using Eq. (12) we have the equation relating $\Gamma[\varphi]$ to $\Gamma_{\text{sym}}[\varphi]$,

$$\Gamma[\varphi] = \Gamma_{\text{sym}}[\varphi] - \int d^dx \, V(x)\varphi(x) . \quad (15)$$

The Γ n-body functions are usually considered as an expansion around the mean value φ_0 of the field obtained for $J = 0$. This mean value φ_0 for the nonsymmetric function is

$$\varphi_0(x) \equiv [\delta W[J = 0]/\delta J(x)]$$

$$= [\delta W_{\text{sym}}[K = V]/\delta K(x)] , \quad (16)$$

which in terms of the $\Gamma[\rho]$ functions satisfies

$$[\delta\Gamma[\varphi_0]/\delta\varphi(x)]\equiv\Gamma^{(1)}(x)=0 \tag{17a}$$

or the equivalent,

$$[\delta\Gamma_{\text{sym}}[\varphi_0]/\delta\varphi(x)]\equiv\Gamma_{\text{sym}}^{(1)}(x)=V(x) \ . \tag{17b}$$

The WT identity Eq. (7c) of the symmetrical case can be written for this mean value φ_0 which is nontrivial, and *a priori* different from zero and nonuniform in space,

$$\int d^dx\ \varphi_0(x)\nabla_x[\delta\Gamma_{\text{sym}}[\varphi=\varphi_0]/\delta\varphi(x)]=0 \ . \tag{18}$$

In conclusion, we see that the WT identities (7) can be transposed to the nonsymmetric action Eq. (11) simply using relations (12) and (15).

We shall now derive the WT identities for higher order correlation functions. According to the previous statement, we shall only treat the case of the symmetric action, the generalization of which is trivial and we choose more specifically the case of the $\Gamma[\varphi]$ functions. Starting from Eq. (7d), we can differentiate with respect to $\delta\varphi(y)$, and we obtain

$$\nabla_y\Gamma_{\text{sym}}^{(1)}(y)+\int d^dx\ \varphi_0(x)\nabla_x\Gamma_{\text{sym}}^{(2)}(x,y)=0 \ , \tag{19a}$$

where we have used the notation

$$\Gamma_{\text{sym}}^{(n)}(x_1,x_2,\ldots,x_n)\equiv\left[\frac{\delta^n\Gamma_{\text{sym}}[\varphi]}{\delta\varphi(x_1)\cdots\delta\varphi(x_n)}\right]_{\varphi=\varphi_0} .$$

With further differentiation with respect to the fields, and possibly some adequate change in the labels, we obtain

$$\sum_{i=1,n}\nabla_{x_i}\Gamma_{\text{sym}}^{(n)}(x_1,\ldots,x_n)+\int d\mathbf{x}_{n+1}\varphi(n+1)\nabla_{x_{n+1}}\Gamma_{\text{sym}}^{(n+1)}(x_1,\ldots,x_n,x_{n+1})=0 \ . \tag{19b}$$

Let us insist on the fact that when used the nonsymmetric action these equations have to be computed for the field φ_0 defined by Eqs. (17), which takes into account the nonuniform field $V(x)$.

III. CONSEQUENCES OF TRANSLATIONAL INVARIANCE IN LIQUIDS AND WT IDENTITIES

In this section, we study the consequences of translation invariance on the grand partition function, under the hypothesis that the interparticle potential is invariant under a space translation. Some relations between the correlation functions, previously obtained [2,3], will be rederived; the emphasis will be put on showing the close relation and similarities with the WT identities obtained in Sec. II. In the following we restrict our study to two-body interparticle interactions, without any loss in generality.

For the description of liquids, we can start from the grand partition function

$$\Xi=\sum_{N=0}^{\infty}(1/N!)\int\Pi_{l=1}^N d\mathbf{x}_l\exp[-\beta\Sigma_{1\le i<j\le N}V(\mathbf{x}_j-\mathbf{x}_i)+\Sigma_{1\le i\le N}\gamma(\mathbf{x}_i-\mathbf{x}_0)] \ , \tag{20}$$

where the $\mathbf{x}_i$ are vectors, $\beta=(kT)^{-1}$,

$$\gamma(\mathbf{x}_i-\mathbf{x}_0)=\lambda+\beta\mu-\beta\int d\mathbf{x}\ \delta(\mathbf{x}_i-\mathbf{x})V_{\text{ext}}(\mathbf{x}-\mathbf{x}_0)=\lambda+\beta\mu-\beta V_{\text{ext}}(\mathbf{x}_i-\mathbf{x}_0) \tag{21}$$

is the logarithm of the activity, μ is the chemical potential, and $\lambda=\frac{3}{2}\ln(2\pi mkT/h^2)$. V_{ext} is some external potential which can also include the finite size of the system. The $\mathbf{x}_0$ notation specifies some absolute origin and direction, and this notation is introduced in what follows to indicate a change in coordinates that is not to be understood as a displacement of the real physical system. In the following, the specifications for the index summations will be dropped unless some change occurs.

To investigate the consequences of a translation, we perform the following change in the integration variables: $\mathbf{x}_i=\mathbf{x}_i'-\varepsilon$, for the N particles. This is a change of coordinates, like the one performed on the fields in Sec. II, and as it corresponds to a change in the dummy integration variable it does not modify the value of the partition function Ξ.

As in Sec. II three different changes occur in Eq. (20) if we explicitly replace $\mathbf{x}_i$ with $\mathbf{x}_i'-\varepsilon$. (i) For the interparticle term we have $V(\mathbf{x}_j'-\mathbf{x}_i')=V(\mathbf{x}_j-\mathbf{x}_i)$, which shows the covariance of this term with respect to the translation, as a consequence of the translation invariance. (ii) The change in the measure is simply a change in the origin of the spatial integration of the N particles, which is trivial. (iii) Finally, according to Eq. (21) the interaction term becomes $\gamma(\mathbf{x}_i'-\mathbf{x}_0)=\gamma(\mathbf{x}_i-\varepsilon-\mathbf{x}_0)$, where $\mathbf{x}_0$ is as expected not modified for the real physical field is the same.

As in Sec. II we now take the difference between Ξ expressed, respectively, in terms of the two integration variables $\mathbf{x}'$ and $\mathbf{x}$. Having changed some dummy integration variable the difference is zero; we therefore have

$$\sum_N(1/N!)\int\Pi_{l=1}^N d\mathbf{x}_l'\exp[-\beta\Sigma V(\mathbf{x}_j'-\mathbf{x}_i')+\Sigma\gamma(\mathbf{x}_i'-\mathbf{x}_0)]-\sum_N(1/N!)\int\Pi_{l=1}^N d\mathbf{x}_l\exp[-\beta\Sigma V(\mathbf{x}_j-\mathbf{x}_i)+\Sigma\gamma(\mathbf{x}_i-\mathbf{x}_0)]$$

$$=\sum_N(1/N!)\int\Pi_{l=1}^N d\mathbf{x}_l\exp[-\beta\Sigma V(\mathbf{x}_j-\mathbf{x}_i)+\Sigma\gamma(\mathbf{x}_i-\varepsilon-\mathbf{x}_0)]$$

$$-\sum_N(1/N!)\int\Pi_{l=1}^N d\mathbf{x}_l\exp[-\beta\Sigma V(\mathbf{x}_j-\mathbf{x}_i)+\Sigma\gamma(\mathbf{x}_i-\mathbf{x}_0)]=0 \ .$$

We thus have

$$\sum_N (1/N!) \sum_{k=1}^{N} \int d\mathbf{x}_k \boldsymbol{\varepsilon}\cdot\nabla_k \gamma_k \left\{ \int \Pi_{l\neq k} d\mathbf{x}_l \exp[-\beta\Sigma V(i,j)+\Sigma\gamma(i)] \right\} = 0 , \tag{22}$$

where $\mathbf{V}(i,j) \equiv V(\mathbf{x}_j - \mathbf{x}_i)$, $\gamma(i) \equiv \gamma(\mathbf{x}_i - \mathbf{x}_0)$, and we have used $\gamma(\mathbf{x}_k - \boldsymbol{\varepsilon} - \mathbf{x}_0) - \gamma(\mathbf{x}_k - \mathbf{x}_0) \approx -\boldsymbol{\varepsilon}\cdot\nabla_k \gamma_k$. The indiscernibility of the particles shows that the sum over k gives N times the same contribution, and dividing by Ξ, Eq. (22) becomes

$$\sum_{N=1} ((N-1)!\Xi)^{-1} \int d\mathbf{x}_1 \nabla_1 \gamma_1 \left\{ \int \Pi_{2\leq i} d\mathbf{x}_i \exp[-\beta\Sigma_{1\leq i<j\leq N} V(i,j)+\Sigma_{i=1}^{N}\gamma(i)] \right\} = 0 .$$

Inverting the summation over N and integrating over $d\mathbf{x}_1$, we have

$$\int d\mathbf{x}_1 \nabla_1 \gamma_1 \left\{ \sum_{N=1} [(N-1)!\Xi]^{-1} \int \Pi_{2\leq i} d\mathbf{x}_i \exp[-\beta\Sigma_{1\leq i<j\leq N} V(i,j)+\Sigma_{i=1}^{N}\gamma(i)] \right\} = 0 . \tag{23}$$

The term in brackets is simply $\delta\Xi/\delta\gamma(1)$; if we divide by Ξ, we have

$$\int d\mathbf{x}_1 \nabla_1 \gamma(1)[\delta \ln\Xi/\delta\gamma(1)] = 0 , \tag{24a}$$

or the equivalent

$$\int d\mathbf{x}_1 \gamma(1)\nabla_1[\delta \ln\Xi/\delta\gamma(1)] = 0 , \tag{24b}$$

which is obtained from partial integration and neglecting a surface term. Equation (24b) is the equivalent of the formulation of the WT identities given in Eq. (7b). In this formalism [4,6], we know that the conjugated variable to $\gamma(1)$ is the density $\rho(1)$. We can define the Legendre transform of $\ln\Xi$,

$$\Gamma[\rho] = \ln\Xi - \int d\mathbf{x}_1 \rho(1)\gamma(1) . \tag{25}$$

We have used the definition given in [4,6], which differs in sign, with the definition of the Legendre transform given in Eq. (8). In this context the functions are defined as follows [4]:

$$\delta\Gamma[\rho]/\delta\rho(1) \equiv \mathbf{c}(1) \equiv c(1) - \ln\rho(1) \tag{26a}$$

$$= -\gamma(1) \tag{26b}$$

and, for $n \geq 2$,

$$\delta^n\Gamma[\rho]/\delta\rho(1)\cdots\delta\rho(n) \equiv \mathbf{c}(1,\ldots,n) \equiv c(1,\ldots,n) + (-1)^{n-1}\Pi_{2\leq i\leq n}\delta(\mathbf{x}_i - \mathbf{x}_1)/\rho^{n-1}(1) , \tag{27}$$

where the $c(1,\ldots,n)$ are the direct correlation functions defined in the liquid-state theory [10], and $\mathbf{c}(1,\ldots,n)$ are defined in [4]. Note that Eq. (26b) is simply a consequence of the Legendre transform. We can now rewrite Eq. (24a) using $\rho(1) = \delta \ln\Xi/\delta\gamma(1)$ and Eq. (26b)

$$\int d\mathbf{x}_1 \rho(1)\nabla_1[\delta\Gamma[\rho]/\delta\rho(1)] = \int d\mathbf{x}_1 \rho(1)\nabla_1 \mathbf{c}(1) = 0 . \tag{28}$$

Differentiating with respect to $\delta\rho(2)$ and interchanging labels 1 and 2, we obtain

$$\nabla_1\{\delta\Gamma[\rho]/\delta\rho(1)\}$$
$$+ \int d\mathbf{x}_2 \rho(2)\nabla_2\{\delta^2\Gamma[\rho]/\delta\rho(1)\delta\rho(2)\} = 0 , \tag{29a}$$

or the equivalent

$$\nabla_1\mathbf{c}(1) + \int d\mathbf{x}_2 \rho(2)\nabla_2\mathbf{c}(1,2) = 0 . \tag{29b}$$

Equation (29a) is the equivalent of Eq. (19a) for the field theory, the excess free energy $\Gamma[\rho]$ defined as Eq. (25) is independent of any external potential and is therefore equivalent to $\Gamma_{\text{sym}}[\varphi]$ in the field theory.

It is more common in liquid-state theory to use the $c(1,\ldots,n)$ functions which do not include the dirac function term. Equation (29b) can also be written

$$\nabla_1 c(1) + \int d\mathbf{x}_2 \rho(2)\nabla_2 c(1,2) = 0 . \tag{29c}$$

Taking the gradient of Eq. (26b) with $\nabla_1\gamma(1) = -\beta\nabla_1 V_{\text{ext}}(1)$, we have

$$\nabla_1 \ln\rho(1) + \beta\nabla_1 V_{\text{ext}}(1) = \nabla_1 c(1) . \tag{30}$$

Using Eq. (30), we finally obtain a more standard form [2,3] of Eq. (29c), where a partial integration has been performed:

$$\nabla_1 \ln\rho(1) + \beta\nabla_1 V_{\text{ext}}(1) = \int d\mathbf{x}_2 \nabla\rho(2) c(1,2) . \tag{31}$$

We also give the general form of Eq. (31) for higher order correlation functions $c(1,\ldots,n)$, which is obtained by further functional differentiation from Eq. (31):

$$\sum_{i=1,n} \nabla_i c(1,\ldots,n)$$
$$+ \int d\mathbf{x}_{n+1}\rho(n+1)\nabla_{n+1}c(1,\ldots,n,n+1) = 0 . \tag{32}$$

This set of relations can be considered as the equivalent of the WT identities Eq. (19b), in the case of liquids, for the translational invariance.

IV. BAXTER RELATIONS AND THE STUDY OF ROTATIONAL INVARIANCE

Related to fundamental properties of the system like symmetries, the WT identities are crucial relations, and are constraints that the system must verify, for instance, in renormalization procedures. In a similar way, the so-called Baxter relations first obtained in [4] have been shown to play an essential part in the approach of critical phenomena [7,8]. Here we will present a derivation of these relations starting from Eq. (32).

To study the properties of homogeneous fluid, it is possible to investigate the response of the system for a very smooth external field to lowest order in this field. The one-body direct correlation function $c[1,\rho]$ is generally a function of point 1, and a functional of the density $\rho(x)$ over the whole space. In the linear-response framework, any quantity is reasonably estimated in the homogeneous system. The spatial dependence of the function then occurs via the density at the point taken into consideration, which is simply the density; that is, $c[1,\rho] = c(\rho(1)) = c(1)$ where $c(\ )$ are simply functions and no longer functional. In this case Eq. (31) is changed into

$$\nabla_1 c[1,\rho] = [dc(\rho(1))/d\rho(1)]\nabla\rho(1) \tag{33a}$$

$$= \int d\mathbf{x}_2 c(1,2)\nabla\rho(2) , \tag{33b}$$

where $dc(\rho(1))/d\rho(1)$ and $c(1,2)$ are computed for the homogeneous system. Finally, we can choose the external potential in such a way that it gives a uniform density gradient $\nabla\rho(1) = \nabla\rho$ over the whole system. This is possible because there is one-to-one correspondence between the density and the external potential [9]. We therefore have

$$dc/d\rho = \int d\mathbf{x}_2 c(1,2) . \tag{34}$$

This is in fact the first of the so-called Baxter relations;

from Eq. (32) we can obtain the rest of hierarchy. The sum of gradients which appears in Eq. (32) can be interpreted as a global translation. If one performs the difference $c[1',\ldots,n';\rho] - c[1,\ldots,n;\rho]$, where the points i' are the points i after an infinitesimal translation of vector ε, we have

$$c[1',\ldots,n';\rho] - c[1,\ldots,n;\rho]$$
$$= [\Sigma_{i=1,n}\nabla_i c[1,\ldots,n;\rho]]\cdot\varepsilon + O(\varepsilon^2) . \tag{35}$$

The left hand side in the linear-response framework is also $[dc(1,\ldots,n)/d\rho]\nabla\rho\cdot\varepsilon$, where $c(1,\ldots,n)$ is the n-body direct correlation function in a homogeneous system, and $\nabla\rho$ is the homogeneous gradient in density. Equation (32) is now, to first order in ε,

$$[dc(1,\ldots,n)/d\rho]\nabla\rho$$
$$+ \int d\mathbf{x}_{n+1}\rho(n+1)\nabla_{n+1}c(1,\ldots,n,n+1) = 0 . \tag{36}$$

Performing a partial integration on the second term in Eq. (31) yields

$$[dc(1,\ldots,n)/d\rho]\nabla\rho$$
$$- \int d\mathbf{x}_{n+1}\nabla\rho(n+1)c(1,\ldots,n,n+1) = 0 . \tag{37}$$

Once more using the fact that we have an homogeneous gradient in the density, we finally obtain

$$dc(1,\ldots,n)/d\rho = \int d\mathbf{x}_{n+1}c(1,\ldots,n+1) . \tag{38}$$

Equation (38) is one of the so called Baxter relations. These have been shown to be a consequence of Eq. (32) for homogeneous fluids; this implies that they are also a consequence of the translational invariance.

We have focused, so far, only on the example of translational invariance. We shall now briefly investigate the consequences of rotational invariance, which is another possible symmetry.

The displacement ε used in Eq. (22) for a rotation is $\varepsilon(\mathbf{x}) = \delta\alpha\mathbf{n}\times\mathbf{x}$, where $\delta\alpha$ is an infinitesimal angle and $\mathbf{n}$ a unitary vector along the rotation axis. Replacing this ε in Eq. (22),

$$\sum_N (1/N!\Xi)\Sigma_{k=1}^N \int d\mathbf{x}_k \delta\alpha(\mathbf{n}\times\mathbf{x})\cdot\nabla_k\gamma_k \int \Pi_{i\neq k}d\mathbf{x}_i \exp[-\beta\Sigma V(i,j) + \Sigma\gamma(i)] = 0 , \tag{39}$$

Using the properties of the vector product, the fact that the relation holds for any direction $\mathbf{n}$ and finally the fact that the particles are identical. Therefore the sum over k gives N times the same contribution, and we have

$$\int d\mathbf{x}_1\mathbf{x}_1\times\nabla_1\gamma_1\rho(1) = 0 . \tag{40}$$

Using Eq. (26), we can express the relation in terms of c or $\mathbf{c}$ functions

$$\int d\mathbf{x}_1\rho(1)\mathbf{x}_1\times\nabla_1\mathbf{c}(1)$$

$$= \int d\mathbf{x}_1\rho(1)\mathbf{x}_1\times\nabla_1[c(1) - \ln\rho(1)]$$

$$= 0 . \tag{41}$$

Equation (41) is equivalent to Eq. (31) for the rotational invariance.

In the specific case of an homogeneous and isotropic liquid, Eq. (41) also gives the Baxter relations. Taking the derivative of Eq. (41) with respect to $\delta\rho(2)$, we can see that the term obtained from $\ln\rho(1)$ does not yield any contribution, and interchanging labels 1 and 2, we have

$$\mathbf{x}_1\times\nabla_1 c(1) + \int d\mathbf{x}_2\rho(2)\mathbf{x}_2\times\nabla_2 c(1,2) = 0 . \tag{42}$$

Using the same external field, which yields a constant gradient in density, we obtain

$$x_1 dc/d\rho = \int d\mathbf{x}_2 \mathbf{x}_2 \rho(2)c(1,2) \ . \tag{43}$$

The right hand side can be transformed as

$$\int d\mathbf{x}_2 \mathbf{x}_2 \rho(2)c(1,2) = \int d\mathbf{x}_2 (\mathbf{x}_2 - \mathbf{x}_1)\rho(2)c(1,2)$$
$$+ \mathbf{x}_1 \int d\mathbf{x}_2 \rho(2)c(1,2) \ . \tag{44}$$

Using the isotropy of the system, $c(1,2)$ is only a function of the distance $|\mathbf{x}_2 - \mathbf{x}_1|$, therefore the first term on the right-hand side is zero. Comparison of the second term in Eq. (44) with the left-hand side of Eq. (43) is simply one of the Baxter relations given in Eq. (34).

V. CONCLUSION

Given the importance of symmetry in physics, we have found it interesting to rederive some basic relations in liquid-state theory, placing the emphasis on invariance properties. In this paper, we thus find that, also for liquids, symmetries of the system have consequences which are fundamental constraints. These relations must have the same status as the one of the WT identities in field theory [1]. For instance, the so-called Baxter relations must play an important part in the study of critical phenomena, as indicated in some approaches [6–8].

Field theory and statistical mechanics have naturally been presented in parallel. Although the purpose is not to investigate relations between these two subjects, it is interesting to note an example illustrating the existence of some profound analogies.

[1] J. Zinn-Justin, *Quantum Field Theory and Critical Phenomena* (Clarendon, Oxford, 1989).

[2] M. S. Wertheim, J. Chem. Phys. **65**, 2377 (1976).

[3] R. A. Lovett, C. Y. Mou, and F. P. Buff, J. Chem. Phys. **65**, 570 (1976).

[4] J. L. Lebowitz and J. K. Percus, Phys. Rev. **122**, 1675 (1961); J. L. Lebowitz and J. K. Percus, J. Math. Phys. **4**, 117 (1963).

[5] R. J. Baxter, J. Chem. Phys. **41**, 553 (1964).

[6] G. Stell, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1975) Vol. 5B; G. Stell, Phys. Rev. Lett. **20**, 533 (1968); Phys. Rev. B **1**, 2265 (1970).

[7] Q. Zhang and J. P. Badiali, Phys. Rev. Lett. **67**, 1598 (1991); Phys. Rev. A **45**, 8666 (1992).

[8] D. Di Caprio, Ph. D. thesis, Paris, 1993; D. Di Caprio, J. P. Badiali, and V. Russier, J. Stat. Phys. **80**, 1241 (1995).

[9] R. Evans, Adv. Phys. **28**, 143 (1979).

[10] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1986).