

## Density-functional method for lattice-gas problems

Martina Nieswand and W. Dieterich

*Fakultät für Physik, Universität Konstanz, D-7750 Konstanz, Germany*

A. Majhofer

*Institute of Experimental Physics, Warsaw University, PL-00-681 Warsaw, ul. Hoza 69, Poland*

(Received 17 July 1992)

We formulate a method designed for lattice-gas problems that is analogous to the density-functional theory used to describe equilibrium properties of inhomogeneous classical liquids. After a discussion of the differences between the discrete and the continuous forms of the theory we present a quantitative test for a one-dimensional system. Possible applications of our approach to order-disorder transitions in lattice gases are pointed out.

PACS number(s): 05.50.+q

Lattice gases, i.e., ensembles of interacting particles distributed on discrete lattices, are used as one of the most universal tools in modeling static and dynamic properties of different physical systems. With various interactions, lattice geometries and boundary conditions, such models were successfully used to describe order-disorder transitions in alloys [1–3], general characteristics of phase transitions [4,5], diffusion processes in solids [6–8], and more recently even the Navier-Stokes flows [9]. Due to the simplicity of the underlying physical principle and the inherent discreteness, lattice gases are especially well suited for numerical simulations. A number of approximate methods for computing partition functions [1–3] or diffusion constants [10] have also been developed.

In this work we formulate the lattice analog of density-functional theory (DFT) known for inhomogeneous classical liquids. Lattice sites are allowed to be occupied by at most one particle. In this way a local hardcore repulsion is taken into account from the outset. Thus, apart from the discreteness, the main difference to conventional density-functional theory for continuous classical systems lies in the fact that average occupation numbers are based on Fermi statistics. Following the method presented, e.g., by Evans [11] we describe the system by the grand potential depending on the average occupation numbers, and define a hierarchy of many-particle direct correlation functions. With the help of the lattice analog of the Ornstein-Zernike equation (cf. also [12]) and discrete forms of the closure relation between the direct correlation function and the interactions potential we present an approximate scheme to calculate average occupation numbers for inhomogeneous lattice gases. As a working example we apply our method to a one-dimensional system of interacting particles subject to a site-dependent external potential. Using a closure relation given by the discrete form of the mean spherical ap-

proximation [13] we obtain results which agree very well with those computed by the exact transfer-matrix method.

Let us consider a regular lattice of sites  $l$ , which are occupied by at most one particle. We assume the following lattice-gas Hamiltonian:

$$H = \frac{1}{2} \sum_{l,l'} V(l-l') n_l n_{l'} + \sum_l \epsilon_l n_l - \mu \sum_l n_l, \quad (1)$$

where  $n_l = 0$  or 1. The first part describes a pair interaction,  $\epsilon_l$  denotes the site-dependent external potential, and  $\mu$  the chemical potential. It is easily shown that Mermin's theorem [14] also holds for lattice gases. In that case it states the uniqueness of the set of site energies  $\epsilon_l$ , which result in a given set of mean occupation numbers  $\langle n_l \rangle$ . That enables us to introduce the function [11]

$$\Omega_\epsilon(\{\langle n_l \rangle\}) = \sum_l \langle n_l \rangle \epsilon_l + F(\{\langle n_l \rangle\}) - \mu \sum_l \langle n_l \rangle \quad (2)$$

which is minimized by the equilibrium density  $\langle n_l \rangle_0$ ,

$$\left. \frac{\partial \Omega_\epsilon}{\partial \langle n_l \rangle} \right|_{\langle n_l \rangle_0} = 0. \quad (3)$$

Its minimum value is equal to the grand potential  $\Omega$  for the system [15],

$$\Omega_\epsilon(\langle n_l \rangle_0) = \Omega. \quad (4)$$

The free energy  $F(\{\langle n_l \rangle\})$  can be written as a sum of the ideal-gas free energy  $F_{\text{id}}$  and the excess part  $F_{\text{exc}}$  which contains all corrections due to the interaction

$$F = F_{\text{id}} + F_{\text{exc}}. \quad (5)$$

In the present context,

$$F_{\text{id}} = -TS_{\text{id}} = kT \sum_l [\langle n_l \rangle \ln \langle n_l \rangle + (1 - \langle n_l \rangle) \ln(1 - \langle n_l \rangle)], \quad (6)$$

where  $S_{\text{id}}$  represents the ideal-gas entropy and  $T$  is the temperature.

As usual, we introduce a hierarchy of derivatives of the excess free energy, with the first two members

$$-\beta \frac{\partial F_{\text{exc}}}{\partial \langle n_l \rangle} = c_1(l, \{ \langle n_l \rangle \}) , \quad (7)$$

$$\frac{\partial c_1(l, \{ \langle n_l \rangle \})}{\partial \langle n_{l'} \rangle} = c_2(l, l', \{ \langle n_l \rangle \}) . \quad (8)$$

The first member of the hierarchy  $c_1(l, \{ \langle n_l \rangle \})$  is the effective one-body potential and  $c_2(l, l', \{ \langle n_l \rangle \})$  the direct correlation function. Combining Eqs. (3)–(7) we get a self-consistency condition for the mean occupation numbers,

$$\langle n_l \rangle = \frac{1}{1 + \exp[\beta(\epsilon_l - \mu) - c_1(l, \{ \langle n_l \rangle \})]} . \quad (9)$$

In contrast to the theory of continuous liquids [11] we obtain here an expression in the form of the Fermi distribution, which is a natural consequence of the assumption that no more than one particle can occupy a site.

If  $c_2(l, l', \{ \langle n_{l'} \rangle \})$  were known, one could integrate Eq. (8) to obtain  $c_1(l, \{ \langle n_l \rangle \})$  and then calculate  $\langle n_l \rangle$  from Eq. (9). Following the standard procedure [11] we first find the exact relation between  $c_2(l, l', \{ \langle n_{l'} \rangle \})$  and the pair-correlation function. Solving Eq. (9) for  $c_1(l, \{ \langle n_l \rangle \})$  and differentiating with respect to  $\langle n_{l'} \rangle$  we obtain

$$\frac{\partial(-\beta\epsilon_l)}{\partial \langle n_{l'} \rangle} = \frac{\delta_{l,l'}}{\langle n_l \rangle (1 - \langle n_l \rangle)} - c_2(l, l', \{ \langle n_l \rangle \}) . \quad (10)$$

On the other hand it is easy to show that

$$\begin{aligned} \frac{\partial \langle n_{l'} \rangle}{\partial(-\beta\epsilon_l)} &= \delta_{l,l'} \langle n_l \rangle (1 - \langle n_l \rangle) \\ &+ (1 - \delta_{l,l'}) [g(l, l') - 1] \langle n_l \rangle \langle n_{l'} \rangle , \end{aligned} \quad (11)$$

where the pair-correlation function  $g(l, l')$  is defined by

$$g(l, l') = \begin{cases} \langle n_l n_{l'} \rangle / \langle n_l \rangle \langle n_{l'} \rangle , & l \neq l' , \\ 0 , & l = l' . \end{cases} \quad (12)$$

In deriving Eq. (11) we used the identity  $n_l^2 = n_l$ . Combining Eqs. (10) and (11) we obtain the lattice-gas analog of the Ornstein-Zernike equation:

$$g(l, l') - 1 = C(l, l') + \sum_{l''} C(l, l'') \langle n_{l''} \rangle [g(l'', l') - 1] , \quad (13)$$

with

$$C(l, l') = c_2(l, l') - \frac{\delta_{l,l'}}{(1 - \langle n_l \rangle)} , \quad (14)$$

where, for simplicity, we dropped the  $\{ \langle n_l \rangle \}$  dependence in our notation. Note that the kernel  $C(l, l')$  in Eq. (13) differs from Eq. (8) by a local term, which ultimately is a consequence of the discreteness of the underlying lattice together with the constraint  $n_l^2 = n_l$ .

As already mentioned, to find  $c_2(l, l', \{ \langle n_{l'} \rangle \})$  we need a relation between this quantity and the two-body inter-

action (the so-called closure relation), which will complete our set of equations for the direct correlation function. This is easily done for homogeneous systems with average occupation  $\bar{n}$ . As in the theory of homogeneous liquids there are several possibilities. The simplest approach is the mean spherical approximation (MSA):

$$c_{\text{MSA}}(l-l') = -\beta V(l-l') , \quad |l-l'| \geq R , \quad (15)$$

$$g_{\text{MSA}}(l-l') = 0 , \quad |l-l'| < R , \quad (16)$$

where  $R$  denotes the hard-core radius or the radius of an effective hard core [16]. Another possibility would be the Percus-Yevick approximation (PY) whose discrete form has been discussed for example in relationship with the Ising model [12]:

$$c_{\text{PY}}(l-l') = g(l-l') (1 - e^{\beta V(l-l')}) . \quad (17)$$

Combining one of the above closure relations with Eq. (13) we can calculate  $c_2(l-l', \bar{n})$  as a function of the mean density  $\bar{n}$ , and Eq. (8) in turn determines  $c_1(l, \bar{n}) \equiv c_1(\bar{n})$ .

For inhomogeneous systems, instead of integrating Eq. (8), we introduce a simple approximation,

$$c_1(l, \{ \langle n_l \rangle \}) \simeq c_1(\bar{n}) + \sum_{l'} c_2(l-l', \bar{n}) (\langle n_{l'} \rangle - \bar{n}) , \quad (18)$$

where we have linearized  $c_1(l, \{ \langle n_l \rangle \})$  with respect to  $\langle n_l \rangle - \bar{n}$ . Clearly, the expression (18) could be improved in various ways [17]. For the present purpose, however, we confine ourselves to the linear approximation, which allows us to compute the mean occupation  $\langle n_l \rangle$  in a rather straightforward way.

Let us now apply our formalism to an exactly solvable problem in order to test the quality of the approximations made. As our example we take a one-dimensional model with two inequivalent sites, described by

$$H = \sum_l V n_l n_{l+1} + \sum_l n_l \epsilon_l - \mu \sum_l n_l , \quad (19)$$

where

$$\epsilon_l = \begin{cases} \epsilon_1 , & l \text{ even} , \\ \epsilon_2 , & l \text{ odd} , \end{cases} \quad (20)$$

and  $V > 0$ . In particular we are interested in the mean occupation number  $\langle n_1 \rangle$  of sites with energy  $\epsilon_1$  as a function of the energy difference  $\Delta\epsilon = \epsilon_1 - \epsilon_2$  in the case of a half-filled lattice ( $\bar{n} = 0.5$ ). Using the simplest MSA-closure relation Eq. (15) with  $R = 1$ , we calculate the direct correlation function and evaluate Eq. (18). Finally, Eq. (9) is solved for  $\langle n_l \rangle$ . Let us compare our results with exact results obtained by evaluating the four-dimensional transfer matrix which corresponds to the Hamiltonian equation (19). In Fig. 1 we have plotted  $\langle n_1 \rangle$  as a function of  $\Delta\epsilon$  at a given temperature corresponding to  $\beta V = 1.5$ . The noninteracting case as derived from the Fermi function is also shown for comparison. Generally, the repulsive interaction enhances occupation of the lower-energy sites. As seen in the figure, the deviation from (ideal) Fermi statistics due to interparticle

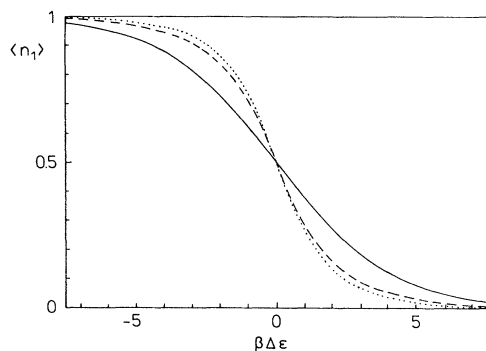


FIG. 1. Mean occupation  $\langle n_1 \rangle$  of sites with energy  $\epsilon_1$  as a function of the energy difference  $\Delta\epsilon = \epsilon_1 - \epsilon_2$ . The DFT (dashed line), exact results (dotted line) corresponding to the interaction strength  $\beta V = 1.5$ , and, as a reference, the noninteracting case (solid line) are compared with each other.

correlations is well accounted for by the DFT with MSA closure. Our approximation, however, slightly underestimates this effect, although the difference between the approximate and the exact solution is small in comparison with the full effect of interaction. This discrepancy decreases with growing temperature, see Fig. 2. But even at the rather low temperature  $\beta V = 2.5$  the error does not exceed 5% for the least favorable energy difference  $\Delta\epsilon$  displayed in the figure.

In summary we adapted the density-functional theory to lattice-gas systems. Our formalism, when applied to the one-dimensional system of interacting particles, gives results which are quantitatively very similar to the exact

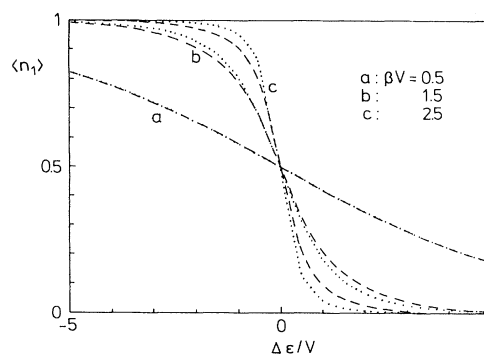


FIG. 2. Mean occupation  $\langle n_1 \rangle$  of sites with energy  $\epsilon_1$  as a function of energy difference  $\Delta\epsilon = \epsilon_1 - \epsilon_2$ . Exact (transfer matrix) results (dotted lines) are compared with DFT results (dashed lines) for three different temperatures.

solution. This encourages us to apply our method to more realistic cases in three dimensions. Of particular interest are order-disorder transitions in three-dimensional lattice gases, which can be treated within the present scheme in analogy to the freezing theory of simple liquids based on density functionals [18]. A comparison of our method with Monte Carlo simulations in cases of an order-disorder phase transition and two-phase coexistence will be the subject of forthcoming work.

The authors are grateful to the Deutsche Forschungsgemeinschaft, Sonderforschungsbereich 306, and the Bundesministerium für Forschung und Technologie, Project No. X083.6, for financial support for this work.

- [1] H. Bethe, Proc. R. Soc. London, Ser. A **150**, 552 (1935).
- [2] R. Kikuchi, J. Chem. Phys. **60**, 1071 (1974).
- [3] K. Binder, Adv. Solid State Phys. **26**, 133 (1986).
- [4] T. D. Lee and C. N. Yang, Phys. Rev. **87**, 410 (1952).
- [5] K. Binder, Rep. Prog. Phys. **50**, 783 (1987).
- [6] K. W. Kehr and K. Binder, in *Applications of the Monte Carlo Method*, edited by K. Binder (Springer, Berlin, 1987), pp. 181–222.
- [7] M. Kolb, J. F. Gouyet, and B. Sapoval, Europhys. Lett. **3**, 33 (1987).
- [8] P. Maass, J. Petersen, A. Bunde, W. Dieterich, and H. E. Roman, Phys. Rev. Lett. **66**, 52 (1991).
- [9] U. Frisch, B. Hasslacher, and Y. Pomeau, Phys. Rev. Lett. **56**, 1505 (1985).
- [10] H. Sato and R. Kikuchi, J. Chem. Phys. **55**, 677 (1971); **55**, 702 (1971); T. Ishii, H. Sato, and R. Kikuchi, Phys. Rev. B **34**, 8335 (1986).
- [11] R. Evans, Adv. Phys. **28**, 143 (1979).
- [12] J. K. Percus, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).
- [13] J. L. Lebowitz and J. K. Percus, Phys. Rev. **144**, 251 (1966); A. Bunde, D. K. Chaturvedi, and W. Dieterich, Z. Phys. B **87**, 209 (1982).
- [14] N. D. Mermin, Phys. Rev. **137**, 1441 (1965).
- [15] Since we are dealing with a set of countable variables we prefer to write partial derivatives instead of functional derivatives.
- [16] M. J. Gillan, J. Phys. C **7**, L1 (1974).
- [17] M. Baus, J. Stat. Phys. **48**, 1129 (1987); E. Johnson, J. Chem. Phys. **86**, 5739 (1987).
- [18] D. W. Oxtoby, Nature (London) **347**, 725 (1990), and references therein.