Maximum entropy formulation of the Kirkwood superposition approximation

A. Singer[a)]
Department of Applied Mathematics, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel

(Received 11 May 2004; accepted 3 June 2004)

Using a variational formulation, we derive the Kirkwood superposition approximation for systems at equilibrium in the thermodynamic limit. We define the entropy of the triplet correlation function and show that the Kirkwood closure brings the entropy to its maximal value. This approach leads to a different interpretation for the Kirkwood closure relation, usually explained by probabilistic considerations of dependence and independence of particles. The Kirkwood closure is generalized to finite volume systems at equilibrium by computing the pair correlation function in finite domains. Closure relations for high order correlation functions are also found using a variational approach. In particular, maximizing the entropy of quadruplets leads to the high order closure $g_{1234}=g_{123}g_{124}g_{134}g_{234}/[g_{12}g_{13}g_{14}g_{23}g_{24}g_{34}]$ used in the Born-Green-Yvon 2 equations which are a pair of integral equations for the triplet and pair correlation functions. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1776552]

I. INTRODUCTION

The pair correlation function is one of the cornerstones in the theory of simple liquids.[1–6] Many thermodynamic properties of the fluid can be derived from the pair function. There are two main approaches to finding the pair function. The first approach is based on the Ornstein-Zernike integral equation and a closure relation for the direct and indirect correlation functions. Many closure relations fall into this category, such as the Percus-Yevick approximation (PY), the hypernetted chain approximation (HNC), and the mean spherical approximation (MSA). The second approach relies on the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy, which relates the nth correlation function with the $(n+1)$th correlation function, and assumes a closure relation that connects them. The Kirkwood superposition, which approximates the triplet correlation function by the product of the three pair correlation functions $(n=2)$

$$g_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)=g_2(\mathbf{x}_1,\mathbf{x}_2)g_2(\mathbf{x}_1,\mathbf{x}_3)g_2(\mathbf{x}_2,\mathbf{x}_3)$$

[see also Eq. (42)], was the first suggested closure of this kind.[7,8] Approximating the quadruplet correlation function by the triplet correlation function $(n=3)$ using the Fisher-Kopeliovich closure[9] equation (43) turned out to yield a much better approximation for the pair correlation function than the Kirkwood superposition approximation (SA), as noted by Ree *et al.*[10,11] However, truncating the BBGKY hierarchy at a higher level $(n\geqslant 4)$ is computationally impractical at the moment.

Both approaches and the underlying closure relations have their own advantages and disadvantages. Their success is often evaluated in comparison with either molecular dynamics (MD) or Monte Carlo (MC) simulations. All closures succeed in the limit of (very) low density. However, when the density is increased they eventually fail, sooner or later. Choosing the ''best'' closure relation is an art in itself. Obviously, each choice of closure relation results in a different approximate solution for the pair function. The BBGKY equation (with or without the SA) has a great advantage over any other approach. For hard spheres it predicts a point where $dp/d\rho=0$, and hence it predicts solidification. Neither the PY or HNC theories can do this and so one expects the BBGKY approach to be superior at high densities, which is particularly important in applications to protein and channel biology.[12]

Rice *et al.*[13,14] improved the Kirkwood SA for systems of hard spheres and Lennard-Jones 6-12 potential. Meeron[15] and Salpeter[16] proposed a formal expression for the triplet correlation function in the form

$$g_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)=g_2(\mathbf{x}_1,\mathbf{x}_2)g_2(\mathbf{x}_1,\mathbf{x}_3)g_2(\mathbf{x}_2,\mathbf{x}_3)\times\exp[\tau(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\rho)], \quad (1)$$

where $\tau(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\rho)\equiv\Sigma_{n=1}^{\infty}\rho^n\delta_{n+3}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)$. The coefficients $\delta_{n+3}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)$ consist of simple 123-irreducible diagrams. Rowlinson[17] evaluated analytically the term δ_4 for a system of hard spheres. Rice[13,14] evaluated the term δ_5 numerically and showed that the Padé approximation $\tau\approx\rho\delta_4/(1-\rho\delta_5)$ gives a better fit to the computer simulation of the hard-sphere system than the Kirkwood SA. However, Ree proved that this improvement to the Kirkwood SA is inferior to the high order closure relation of Refs. 10 and 11, because the latter takes into account all the diagrams of Refs. 13 and 14 and more. Hu *et al.*[18] showed that the integral closure relations (PY, HNC, and MSA) can be obtained from the Kirkwood SA using another approximation.

In this paper we derive the Kirkwood SA from a variational (Euler-Lagrange) formulation. We define an entropy functional for the triplet correlation function, and show that it produces the Kirkwood closure in the thermodynamic limit of number of particles and volume taken to infinity, while keeping the number density constant, i.e., N, $V\to\infty$, $N/V=\rho$. The triplet entropy functional is different from the physical entropy of the full N-particle system. Maximizing

[a)]Electronic mail: amits@post.tau.ac.il

the triplet entropy functional, given the constraint that the pair correlation function is the marginal of the triplet correlation function, yields the SA.

This maximum entropy formulation leads to a different closure for a finite volume system which we write as an integral equation. In the thermodynamic limit, the solution of this integral equation reduces to the Kirkwood SA. We describe an iterative procedure for solving the BBGKY equation with this generalized entropy closure.

Using this entropy closure instead of the Kirkwood SA produces different pair correlation functions. The entropy closure can be used to calculate the pair function in confined geometries. Specifically, we can deduce the resulting pair function near the domain walls (boundaries), and compare it to MC or MD simulations, and to the results of the original Kirkwood closure.

The present attempt to find the pair correlation function using a variational formulation is not new. Richardson[19] used a maximum entropy (minimum Helmholtz free energy) argument to obtain an equation for the pair correlation function. That variational approach consists in maximizing the entropy while assuming an approximate relation (closure) between the pair and triplet function, and resulted in an integral equation which differs from the Born-Green-Yvon (BGY) equation. On the other hand, the variational approach applied in this paper assumes that the BGY equation is exact, and maximizes the triplet entropy under the constraint that the pair correlation function is the marginal of the triplet function. This approach leads to a closure for the BGY equation. The resulting closure coincides with the Kirkwood SA for the radial function. Mathematically, the approach of Richardson[19] consists in solving a variational problem without imposing constraints, while the current proposed variational formulation includes constraints and is therefore solved by the method of Lagrange multipliers.

The definition of the n-particle entropy ($3 \leqslant n \leqslant N$) is similar to the definition of the triplet entropy functional. The N-particle entropy coincides with the physical entropy and its maximization yields the Boltzmann distribution, as expected. High order closure relations are obtained by maximizing the n-particle entropy. In particular, maximizing the quadruplets entropy leads to the Fisher-Kopeliovich closure[9] and the corresponding BGY2 equation,[10,11] that has been shown to give a very good fit to experimental data.

II. MAXIMUM ENTROPY

We consider a finite domain $\Omega \subset \mathbb{R}^3$. Suppose $p_2(\mathbf{x}_1,\mathbf{x}_2)$ is a known symmetric probability distribution function (pdf)

$$\begin{aligned} &\int_{\Omega\times\Omega} p_2(\mathbf{x}_1,\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2 = 1, \\ &p_2(\mathbf{x}_1,\mathbf{x}_2) = p_2(\mathbf{x}_2,\mathbf{x}_1), \\ &p_2(\mathbf{x}_1,\mathbf{x}_2) \geqslant 0, \end{aligned} \tag{2}$$

where $p_2(\mathbf{x}_1,\mathbf{x}_2)$ represents the joint pdf of finding two particles at locations $\mathbf{x}_1$ and $\mathbf{x}_2$, as usually defined in the statistical mechanics of fluids. This means a relationship between $p_2(\mathbf{x}_1,\mathbf{x}_2)$ and $p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)$ can be expressed in the form of the constraints

$$\begin{aligned} \phi_1(p_3) &= \int_\Omega p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_1 - p_2(\mathbf{x}_2,\mathbf{x}_3) = 0, \\ \phi_2(p_3) &= \int_\Omega p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_2 - p_2(\mathbf{x}_1,\mathbf{x}_3) = 0, \\ \phi_3(p_3) &= \int_\Omega p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_3 - p_2(\mathbf{x}_1,\mathbf{x}_2) = 0. \end{aligned} \tag{3}$$

An approximate closure relation can be found by solving the optimization problem of maximizing the triplet entropy functional

$$\begin{aligned} H(p_3) = &- \int_{\Omega\times\Omega\times\Omega} p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3) \\ &\times \ln p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_3, \end{aligned} \tag{4}$$

under the constraints (3). Note that $H(p_3)$ differs from the physical entropy of the full N-particle system

$$\begin{aligned} H &\equiv H(p_N) \\ &= - \int_\Omega p_N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N) \\ &\quad \times \ln p_N(x_1,x_2,\ldots,x_N)d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N, \end{aligned}$$

where $p_N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)$ is the Boltzmann distribution. The motivation for maximizing the triplet entropy in finding a closure relation is that the Boltzmann distribution brings the physical entropy to a maximum. Thus, maximizing $H(p_3)$ instead of H introduces errors and is expected to be an approximation to the closure problem. This issue will be further discussed in Sec. IV. The notation triplet entropy for $H(p_3)$ of Eq. (4) is in agreement with the definition of the Shannon entropy of three random variables in information theory (see, e.g., Ref. 20).

This variational problem can be solved by the method of Lagrange multipliers. Thus, we define Lagrange multipliers $\lambda_1(\mathbf{x}_2,\mathbf{x}_3)$, $\lambda_2(\mathbf{x}_1,\mathbf{x}_3)$, $\lambda_3(\mathbf{x}_1,\mathbf{x}_2)$ and the functional

$$\begin{aligned} &F(p_3,\lambda_1,\lambda_2,\lambda_3) \\ &= H + \lambda_1\phi_1 + \lambda_2\phi_2 + \lambda_3\phi_3 \\ &= - \int_{\Omega\times\Omega\times\Omega} p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)\ln p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_3 \\ &\quad + \lambda_1(\mathbf{x}_2,\mathbf{x}_3)\left(\int_\Omega p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_1 - p_2(\mathbf{x}_2,\mathbf{x}_3) \right) \\ &\quad + \lambda_2(\mathbf{x}_1,\mathbf{x}_3)\left(\int_\Omega p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_2 - p_2(\mathbf{x}_1,\mathbf{x}_3) \right) \\ &\quad + \lambda_3(\mathbf{x}_1,\mathbf{x}_2)\left(\int_\Omega p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_3 - p_2(\mathbf{x}_1,\mathbf{x}_2) \right). \end{aligned}$$

The Euler-Lagrange equation is

$$-\ln p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)-1+\lambda_1(\mathbf{x}_2,\mathbf{x}_3)+\lambda_2(\mathbf{x}_1,\mathbf{x}_3)+\lambda_3(\mathbf{x}_1,\mathbf{x}_2)=0 \tag{5}$$

or equivalently

$$p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)=\gamma_1(\mathbf{x}_2,\mathbf{x}_3)\,\gamma_2(\mathbf{x}_1,\mathbf{x}_3)\,\gamma_3(\mathbf{x}_1,\mathbf{x}_2), \tag{6}$$

where

$$\gamma_1(\mathbf{x}_2,\mathbf{x}_3)=e^{\lambda_1(\mathbf{x}_2,\mathbf{x}_3)-1/3},$$
$$\gamma_2(\mathbf{x}_1,\mathbf{x}_3)=e^{\lambda_2(\mathbf{x}_1,\mathbf{x}_3)-1/3},$$
$$\gamma_3(\mathbf{x}_1,\mathbf{x}_2)=e^{\lambda_3(\mathbf{x}_1,\mathbf{x}_2)-1/3}.$$

Clearly, $\gamma_i\geqslant 0$ $(i=1,2,3)$, and therefore $p_3\geqslant 0$. Moreover, $\gamma_1=\gamma_2=\gamma_3$ because p_2 is symmetric. Setting $\gamma=\gamma_1=\gamma_2=\gamma_3$ we find that

$$p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)=\gamma(\mathbf{x}_1,\mathbf{x}_2)\,\gamma(\mathbf{x}_2,\mathbf{x}_3)\,\gamma(\mathbf{x}_1,\mathbf{x}_3). \tag{7}$$

The constraint that p_2 is the marginal of p_3 gives an equation for γ,

$$p_2(\mathbf{x}_1,\mathbf{x}_2)=\gamma(\mathbf{x}_1,\mathbf{x}_2)\int_\Omega \gamma(\mathbf{x}_1,\mathbf{x}_3)\,\gamma(\mathbf{x}_2,\mathbf{x}_3)\,d\mathbf{x}_3. \tag{8}$$

The symmetry of p_2 [Eq. (2)] implies that of γ,

$$\gamma(\mathbf{x}_1,\mathbf{x}_2)=\gamma(\mathbf{x}_2,\mathbf{x}_1).$$

If Eq. (8) has a unique solution, then p_2 determines γ. However, the pdf p_2 is unknown. We know that p_2 satisfies the BBGKY equation,

$$0=\mathbf{f}_{\mathrm{ex}}(\mathbf{x}_1)p_2(\mathbf{x}_1,\mathbf{x}_2)+\mathbf{f}(\mathbf{x}_2,\mathbf{x}_1)p_2(\mathbf{x}_1,\mathbf{x}_2)-k_BT\nabla_{\mathbf{x}_1}p_2(\mathbf{x}_1,\mathbf{x}_2)+(N-2)\times\int_\Omega \mathbf{f}(\mathbf{x}_3,\mathbf{x}_1)p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)\,d\mathbf{x}_3,$$

where $\mathbf{f}(\mathbf{x}_2,\mathbf{x}_1)$ is the force exerted on a particle located at $\mathbf{x}_1$ by another particle located at $\mathbf{x}_2$; and $\mathbf{f}_{\mathrm{ex}}(\mathbf{x}_1)$ is an external force field acting on a particle located at $\mathbf{x}_1$. Substituting the maximum entropy closure (7) into the BBGKY equation (9), together with the integral equation (8), produces a system of integral equations for p_2 and γ,

$$0=\mathbf{f}_{\mathrm{ex}}(\mathbf{x}_1)p_2(\mathbf{x}_1,\mathbf{x}_2)+\mathbf{f}(\mathbf{x}_2,\mathbf{x}_1)p_2(\mathbf{x}_1,\mathbf{x}_2)-k_BT\nabla_{\mathbf{x}_1}p_2(\mathbf{x}_1,\mathbf{x}_2)+(N-2)\times\int_\Omega \mathbf{f}(\mathbf{x}_3,\mathbf{x}_1)\,\gamma(\mathbf{x}_1,\mathbf{x}_2)\,\gamma(\mathbf{x}_2,\mathbf{x}_3)\,\gamma(\mathbf{x}_1,\mathbf{x}_3)\,d\mathbf{x}_3,$$

$$p_2(\mathbf{x}_1,\mathbf{x}_2)=\gamma(\mathbf{x}_1,\mathbf{x}_2)\int_\Omega \gamma(\mathbf{x}_1,\mathbf{x}_3)\,\gamma(\mathbf{x}_2,\mathbf{x}_3)\,d\mathbf{x}_3. \tag{9}$$

To determine the pair correlation function p_2, we need to solve the system (9).

III. TWO EXAMPLES

The system (9) can be solved or simplified in the case that the particles interact only with the external field and in the thermodynamic limit.

A. Noninteracting particles in an external field

Noninteracting particles in an external field are described by $\mathbf{f}\equiv 0$ and the system (9) is reduced to

$$0=\mathbf{f}_{\mathrm{ex}}(\mathbf{x}_1)p_2(\mathbf{x}_1,\mathbf{x}_2)-k_BT\nabla_{\mathbf{x}_1}p_2(\mathbf{x}_1,\mathbf{x}_2), \tag{10}$$

$$p_2(\mathbf{x}_1,\mathbf{x}_2)=\gamma(\mathbf{x}_1,\mathbf{x}_2)\int_\Omega \gamma(\mathbf{x}_1,\mathbf{x}_3)\,\gamma(\mathbf{x}_2,\mathbf{x}_3)\,d\mathbf{x}_3. \tag{11}$$

Equation (10) can be integrated to yield

$$p_2(\mathbf{x}_1,\mathbf{x}_2)=e^{-U_{\mathrm{ex}}(\mathbf{x}_1)/k_BT}h(\mathbf{x}_2), \tag{12}$$

where $\mathbf{f}_{\mathrm{ex}}(\mathbf{x}_1)=-\nabla_{\mathbf{x}_1}U_{\mathrm{ex}}(\mathbf{x}_1)$, and $h(\mathbf{x}_2)$ is an arbitrary function (the integration constant). The symmetry condition (2) gives

$$p_2(\mathbf{x}_1,\mathbf{x}_2)=C^{-1}e^{-[U_{\mathrm{ex}}(\mathbf{x}_1)+U_{\mathrm{ex}}(\mathbf{x}_2)]/k_BT}, \tag{13}$$

where $C=[\int_\Omega e^{-U_{\mathrm{ex}}(\mathbf{x})/k_BT}d\mathbf{x}]^2$ is a normalization constant. As expected, we find that $\mathbf{x}_1,\mathbf{x}_2$ are independent random variables, $p_2(\mathbf{x}_1,\mathbf{x}_2)=p_1(\mathbf{x}_1)p_1(\mathbf{x}_2)$. In this case, the solution to Eq. (11) is given by

$$\gamma(\mathbf{x}_1,\mathbf{x}_2)=\sqrt{p_2(\mathbf{x}_1,\mathbf{x}_2)}=\sqrt{p_1(\mathbf{x}_1)}\sqrt{p_1(\mathbf{x}_2)}. \tag{14}$$

Indeed,

$$\gamma(\mathbf{x}_1,\mathbf{x}_2)\int_\Omega \gamma(\mathbf{x}_1,\mathbf{x}_3)\,\gamma(\mathbf{x}_2,\mathbf{x}_3)\,d\mathbf{x}_3$$
$$=\sqrt{p_1(\mathbf{x}_1)p_1(\mathbf{x}_2)}\int_\Omega \sqrt{p_1(\mathbf{x}_1)p_1(\mathbf{x}_3)}\sqrt{p_1(\mathbf{x}_2)p_1(\mathbf{x}_3)}\,d\mathbf{x}_3$$
$$=p_1(\mathbf{x}_1)p_1(\mathbf{x}_2)\int_\Omega p_1(\mathbf{x}_3)\,d\mathbf{x}_3=p_2(\mathbf{x}_1,\mathbf{x}_2).$$

B. The thermodynamic limit

The thermodynamic limit is described by the following limiting process in which the domain is gradually enlarged to be all space, $\Omega\to\mathbb{R}^3$, keeping the ratio between the number of particles, N, and the volume of the domain, $V=|\Omega|$, constant. The ratio $N/V=\rho$ is the number density. In this limiting process, all the pdfs tend to zero, because the volume of the domain tends to infinity, and the pdfs are normalized with respect to that volume. It is therefore more convenient to work with number densities, such as ρ, which are normalized with respect to a fixed volume, e.g., 1 cm^3, and do not vanish in the limiting process.

First, we consider a bounded domain $\Omega\subset\mathbb{R}^3$. The previous example of noninteracting particles suggests the definition

$$\delta(\mathbf{x}_1,\mathbf{x}_1)=\frac{\gamma(\mathbf{x}_1,\mathbf{x}_2)}{\sqrt{p_1(\mathbf{x}_1)p_1(\mathbf{x}_2)}}, \tag{15}$$

which transforms Eq. (11) into

$$\frac{p_2(\mathbf{x}_1,\mathbf{x}_2)}{p_1(\mathbf{x}_1)p_1(\mathbf{x}_2)}=\delta(\mathbf{x}_1,\mathbf{x}_2)\int_\Omega p_1(\mathbf{x}_3)\,\delta(\mathbf{x}_1,\mathbf{x}_3)\,\delta(\mathbf{x}_2,\mathbf{x}_3)\,d\mathbf{x}_3. \tag{16}$$

We rewrite Eq. (16) as

$$\frac{p_2^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2)}{p_1^{(\Omega)}(\mathbf{x}_1)p_1^{(\Omega)}(\mathbf{x}_2)} = \delta^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2)\int_\Omega p_1^{(\Omega)}(\mathbf{x}_3)\delta^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_3)\delta^{(\Omega)}(\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_3, \tag{17}$$

where $p_2^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2)=p_2(\mathbf{x}_1,\mathbf{x}_2)$, $\delta^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2)=\delta(\mathbf{x}_1,\mathbf{x}_2)$, $p_1^{(\Omega)}(\mathbf{x}_1)=p_1(\mathbf{x}_1)$, to emphasize their dependency on the specific domain Ω. We set

$$g_2(\mathbf{x}_1,\mathbf{x}_2)=\lim_{\Omega\to\mathbb{R}^3}\frac{p_2^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2)}{p_1^{(\Omega)}(\mathbf{x}_1)p_1^{(\Omega)}(\mathbf{x}_2)}. \tag{18}$$

For example, if the two particles become independent when they are separated,

$$p_2^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2)=p_1^{(\Omega)}(\mathbf{x}_1)p_1^{(\Omega)}(\mathbf{x}_2)[1+o(1)] \quad \text{for } |\mathbf{x}_1-\mathbf{x}_2|\gg 1, \tag{19}$$

then $\lim_{|\mathbf{x}_2|\to\infty} g_2(\mathbf{x}_1,\mathbf{x}_2)=1$.

Next, we show that under the assumption (19)

$$\lim_{\Omega\to\mathbb{R}^3}\delta^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2)=g_2(\mathbf{x}_1,\mathbf{x}_2).$$

Indeed,

$$\int_\Omega p_1(\mathbf{x}_3)\frac{p_2(\mathbf{x}_1,\mathbf{x}_3)}{p_1(\mathbf{x}_1)p_1(\mathbf{x}_3)}\frac{p_2(\mathbf{x}_2,\mathbf{x}_3)}{p_1(\mathbf{x}_2)p_1(\mathbf{x}_3)}d\mathbf{x}_3 = \int_\Omega p_1(\mathbf{x}_3)[1+o(1)]d\mathbf{x}_3 = 1+o(1). \tag{20}$$

Taking the limit $\Omega\to\mathbb{R}^3$, the $o(1)$ term vanishes, and Eq. (17) gives

$$\delta(\mathbf{x}_1,\mathbf{x}_2)=g_2(\mathbf{x}_1,\mathbf{x}_2), \tag{21}$$

as asserted.

We interpret Eq. (21) as the Kirkwood SA. Equations (7) and (15) imply that the triplet pdf satisfies

$$\frac{p_3^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)}{p_1^{(\Omega)}(\mathbf{x}_1)p_1^{(\Omega)}(\mathbf{x}_2)p_1^{(\Omega)}(\mathbf{x}_3)} = \delta^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2)\delta^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_3)\delta^{(\Omega)}(\mathbf{x}_2,\mathbf{x}_3). \tag{22}$$

Taking the limit $\Omega\to\mathbb{R}^3$ and using Eq. (21), we obtain

$$g_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)=\lim_{\Omega\to\mathbb{R}^3}\frac{p_3^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)}{p_1^{(\Omega)}(\mathbf{x}_1)p_1^{(\Omega)}(\mathbf{x}_2)p_1^{(\Omega)}(\mathbf{x}_3)} = g_2(\mathbf{x}_1,\mathbf{x}_2)g_2(\mathbf{x}_1,\mathbf{x}_3)g_2(\mathbf{x}_2,\mathbf{x}_3), \tag{23}$$

which is the Kirkwood closure relation for the triplet correlation function. Usually, the motivation for using the Kirkwood SA is a probabilistic consideration of dependency and independency of particles[7] (see also Sec. V). Here we find another interpretation for the Kirkwood closure.

The Kirkwood closure is the (only) closure relation that brings the entropy of triplets of particles to its maximum value. The principle of maximum entropy is a well known principle in statistical mechanics, in testing statistical hypotheses,[21,22] and beyond.[23,24] The maximum entropy principle is also applicable to systems out of equilibrium;[25] therefore, Kirkwood's SA can be generalized to systems out of equilibrium. In the following section we give further motivation for its use.

IV. MINIMUM HELMHOLTZ FREE ENERGY

Elementary textbooks in statistical mechanics mention that the Boltzmann distribution,

$$p_N(\mathbf{x}_1,\ldots,\mathbf{x}_N)=\frac{1}{Z_N}e^{-U(\mathbf{x}_1,\ldots,\mathbf{x}_N)/k_BT}, \tag{24}$$

brings the Helmholtz free energy,

$$F(p)=U(p)-k_BTH(p) = \int_{\Omega^N}U(\mathbf{x}_1,\ldots,\mathbf{x}_N)p(\mathbf{x}_1,\ldots,\mathbf{x}_N)d\mathbf{x}_1\cdots d\mathbf{x}_N + k_BT\int_{\Omega^N}p(\mathbf{x}_1,\ldots,\mathbf{x}_N)\ln p(\mathbf{x}_1,\ldots,\mathbf{x}_N)d\mathbf{x}_1\cdots d\mathbf{x}_N, \tag{25}$$

to its minimum under the normalization constraint

$$\int_{\Omega^N}p(\mathbf{x}_1,\ldots,\mathbf{x}_N)d\mathbf{x}_1\cdots d\mathbf{x}_N=1. \tag{26}$$

For a pairwise additive potential together with an external field force

$$U(\mathbf{x}_1,\ldots,\mathbf{x}_N)=\sum_{1\leqslant i<j\leqslant N}U(\mathbf{x}_i,\mathbf{x}_j)+\sum_{j=1}^{N}U_{\mathrm{ex}}(\mathbf{x}_j), \tag{27}$$

the potential energy term $U(p)$ of the Helmholtz free energy (25) takes the simple form

$$\begin{aligned}U(p)&=\int_{\Omega^N}\left(\sum_{1\leqslant i<j\leqslant N}U(\mathbf{x}_i,\mathbf{x}_j)+\sum_{j=1}^{N}U_{\mathrm{ex}}(\mathbf{x}_j)\right)\\&\quad\times p(\mathbf{x}_1,\ldots,\mathbf{x}_N)d\mathbf{x}_1\cdots d\mathbf{x}_N\\&=\frac{N(N-1)}{2}\int_{\Omega^2}U(\mathbf{x}_1,\mathbf{x}_2)p_2(\mathbf{x}_1,\mathbf{x}_2)d\mathbf{x}_1d\mathbf{x}_2\\&\quad+N\int_\Omega U_{\mathrm{ex}}(\mathbf{x}_1)p_1(\mathbf{x}_1)d\mathbf{x}_1,\end{aligned}$$

where

$$p_2(\mathbf{x}_1,\mathbf{x}_2)=\int_{\Omega^{N-2}}p_N(\mathbf{x}_1,\ldots,\mathbf{x}_N)d\mathbf{x}_1\cdots d\mathbf{x}_N,$$

$$p_1(\mathbf{x}_1)=\int_\Omega p_2(\mathbf{x}_1,\mathbf{x}_2)d\mathbf{x}_2$$

are the marginal densities. If the pdf $p_2(\mathbf{x}_1,\mathbf{x}_2)$ is assumed to be known, as in Sec. II, then the energy term of the Helmholtz free energy $U(p)$ is also known. Therefore, minimizing the Helmholtz free energy, under the assumption that the pdf $p_2(\mathbf{x}_1,\mathbf{x}_2)$ is known, is equivalent to maximizing the entropy, since $U(p)$ is constant during the minimizing process.

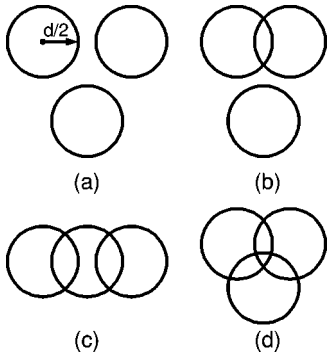

FIG. 1. Four configurations of three particles: (a) no intersections, (b) one intersection, (c) two intersections, (d) three intersections.

V. PROBABILISTIC INTERPRETATION OF THE KIRKWOOD CLOSURE

The Kirkwood SA (23) was the first closure relation to be suggested[7] and tested[8] in the theory of simple liquids. This fact might be explained by its simplicity and its intuitive origin. In this section we give a probabilistic interpretation of the Kirkwood SA, and find its generalization for closure relations of higher orders of the BBGKY hierarchy. The problem at level n $(n\geqslant 2)$ is to find an approximation for the $(n+1)$-particle pdf in terms of the n-particle pdf. For example, the Kirkwood SA (23) closes the hierarchy at level $n=2$. High order closures are much more accurate, fitting better the experimental and simulated (MC or MD) data.[10,11] However, the computational complexity increases drastically with n, making the truncation at level $n\geqslant 4$ impractical at the moment.

First, consider the case $n=2$. We assume that particles become independent as they are separated (19), although we are certainly aware that long range forces such as the electric field can produce strong correlations over all of even a very large domain, as already noted by Kirkwood in his original paper.[7] In order to make the exact equality (19) into an approximation, we assume that there exists a distance $d>0$ such that

$$p_2(\mathbf{x}_1,\mathbf{x}_2)=p_1(\mathbf{x}_1)p_1(\mathbf{x}_2) \tag{28}$$

for $|\mathbf{x}_1-\mathbf{x}_2|>d$. Three interchangeable particles can be in four different configurations with respect to the distance d, depending on the number of intersections (see Fig. 1). In all configurations but configuration (d), where all three particles intersect, there are at least two particles that do not intersect. Since the particles are interchangeable we may assume that $|\mathbf{x}_1-\mathbf{x}_3|>d$. Applying Bayes' law we have

$$p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)=p_3(\mathbf{x}_3|\mathbf{x}_1,\mathbf{x}_2)p_2(\mathbf{x}_1,\mathbf{x}_2). \tag{29}$$

By the independence assumption (28) we have

$$p_3(\mathbf{x}_3|\mathbf{x}_1,\mathbf{x}_2)=p_2(\mathbf{x}_3|\mathbf{x}_2). \tag{30}$$

Therefore,

$$\begin{aligned} p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)&=p_2(\mathbf{x}_3|\mathbf{x}_2)p_2(\mathbf{x}_1,\mathbf{x}_2)\\ &=\frac{p_2(\mathbf{x}_2,\mathbf{x}_3)}{p_1(\mathbf{x}_2)}p_2(\mathbf{x}_1,\mathbf{x}_2). \end{aligned} \tag{31}$$

Multiplying by $1=p_2(\mathbf{x}_1,\mathbf{x}_3)/p_1(\mathbf{x}_1)p_1(\mathbf{x}_3)$ we obtain

$$p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)=\frac{p_2(\mathbf{x}_1,\mathbf{x}_2)p_2(\mathbf{x}_2,\mathbf{x}_3)p_2(\mathbf{x}_1,\mathbf{x}_3)}{p_1(\mathbf{x}_1)p_1(\mathbf{x}_2)p_1(\mathbf{x}_3)}, \tag{32}$$

which is the Kirkwood SA. We see that the Kirkwood closure is a good approximation when at least two particles are sufficiently far apart and independent. However, it fails when all three particles are close to each other.

Next, we find the n-level Kirkwood closure relation for the $(n+1)$-particle pdf in terms of the n-particle pdf using probabilistic considerations.

Proposition. The n-level Kirkwood closure relation is given by

$$\begin{aligned} &p_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)\\ &\quad=\prod_{k=1}^{n-1}\prod_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n}p_k(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_k})^{(-1)^{n-1-k}}. \end{aligned} \tag{33}$$

Proof. We have already seen that the approximation holds for $n=2,3$. Assuming, by induction, that at least two particles are sufficiently far apart and independent, we can assume without loss of generality that particles 1 and n are far apart, and independent, $|\mathbf{x}_1-\mathbf{x}_n|>d$. Using Bayes' law, we find that

$$\begin{aligned} &p_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)\\ &\quad=p_{n-1}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_{n-1})p_n(\mathbf{x}_n|\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_{n-1}). \end{aligned}$$

Because particles 1 and n are sufficiently far apart it follows that

$$\begin{aligned} p_n(\mathbf{x}_n|\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_{n-1})&=p_{n-1}(\mathbf{x}_n|\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_{n-1})\\ &=\frac{p_{n-1}(\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_n)}{p_{n-2}(\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_{n-1})}. \end{aligned}$$

Hence,

$$\begin{aligned} &p_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)\\ &\quad=\frac{p_{n-1}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_{n-1})p_{n-1}(\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_n)}{p_{n-2}(\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_{n-1})}. \end{aligned} \tag{34}$$

It follows from the induction assumption that for every $j=2,3,\ldots,n-1$, with particles 1 and n far apart, we have

$$\begin{aligned} 1=&p_{n-1}(\mathbf{x}_1,\ldots,\mathbf{x}_{j-1},\mathbf{x}_{j+1},\ldots,\mathbf{x}_n)\\ &\times\prod_{k=1}^{n-2}\prod_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n,\ i_l\neq j}p_k(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_k})^{(-1)^{n-1-k}}. \end{aligned} \tag{35}$$

Multiplying Eqs. (34) and (35) (for all $j=2,3,\ldots,n-1$) ends the proof. ■

Corollary. For $n=4$ Kirkwood's formula becomes

$$p_4(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\mathbf{x}_4)=\frac{p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_4)p_3(\mathbf{x}_1,\mathbf{x}_3,\mathbf{x}_4)p_3(\mathbf{x}_2,\mathbf{x}_3,\mathbf{x}_4)p_1(\mathbf{x}_1)p_1(\mathbf{x}_2)p_1(\mathbf{x}_3)p_1(\mathbf{x}_4)}{p_2(\mathbf{x}_1,\mathbf{x}_2)p_2(\mathbf{x}_1,\mathbf{x}_3)p_2(\mathbf{x}_1,\mathbf{x}_4)p_2(\mathbf{x}_2,\mathbf{x}_3)p_2(\mathbf{x}_2,\mathbf{x}_4)p_2(\mathbf{x}_3,\mathbf{x}_4)}. \tag{36}$$

In the case $\Omega=\mathbb{R}^3$, we define

$$g_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)=\lim_{\Omega\to\mathbb{R}^3}\frac{p_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)}{\Pi_{j=1}^n p_1(\mathbf{x}_j)}. \tag{37}$$

Dividing Eq. (33) by $\Pi_{j=1}^n p_1(\mathbf{x}_j)$ gives

$$\frac{p_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)}{\Pi_{j=1}^n p_1(\mathbf{x}_j)}=\prod_{k=1}^{n-1}\prod_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n}\left(\frac{p_k(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_k})}{\Pi_{j=1}^k p_1(\mathbf{x}_{i_j})}\right)^{(-1)^{n-1-k}}, \tag{38}$$

where we used the combinatorial identity

$$\sum_{k=1}^{n-1}\binom{n-1}{k-1}(-1)^{n-1-k}=1. \tag{39}$$

Note that the $k=1$ terms in the product of Eq. (38) cancel out, so the product may begin from $k=2$,

$$\frac{p_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)}{\Pi_{j=1}^n p_1(\mathbf{x}_j)}=\prod_{k=2}^{n-1}\prod_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n}\left(\frac{p_k(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_k})}{\Pi_{j=1}^k p_1(\mathbf{x}_{i_j})}\right)^{(-1)^{n-1-k}}. \tag{40}$$

Taking the limit $\Omega\to\mathbb{R}^3$ we obtain the n-level Kirkwood closure relation,

$$g_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)=\prod_{k=2}^{n-1}\prod_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n} g_k(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_k})^{(-1)^{n-1-k}}. \tag{41}$$

Examples are as follows:

(a) $n=3$ (Kirkwood SA)

$$g_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)=g_2(\mathbf{x}_1,\mathbf{x}_2)g_2(\mathbf{x}_1,\mathbf{x}_3)g_2(\mathbf{x}_2,\mathbf{x}_3). \tag{42}$$

(b) $n=4$ (Fisher-Kopeliovich[9])

$$g_4(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\mathbf{x}_4)=\frac{g_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)g_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_4)g_3(\mathbf{x}_1,\mathbf{x}_3,\mathbf{x}_4)g_3(\mathbf{x}_2,\mathbf{x}_3,\mathbf{x}_4)}{g_2(\mathbf{x}_1,\mathbf{x}_2)g_2(\mathbf{x}_1,\mathbf{x}_3)g_2(\mathbf{x}_1,\mathbf{x}_4)g_2(\mathbf{x}_2,\mathbf{x}_3)g_2(\mathbf{x}_2,\mathbf{x}_4)g_2(\mathbf{x}_3,\mathbf{x}_4)}. \tag{43}$$

VI. HIGH LEVEL ENTROPY CLOSURE

In this section we use the maximum entropy principle to derive the n-level closure relation, and compare the resulting closure relation with the n-level probabilistic Kirkwood closure of Sec. V. The problem at level n ($n\geqslant 2$) is to find an approximation for the $(n+1)$-particle pdf in terms of the n-particle pdf. For example, the Kirkwood SA (23) closes the hierarchy at level $n=2$. We use the principle of maximum entropy to obtain the closure relation. As in the derivations of Sec. II, we assume that the n-particle pdf $p_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)$ is known, and we search for the $(n+1)$-particle pdf $p_{n+1}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_{n+1})$ that maximizes the entropy

$$H=-\int_{\Omega^{n+1}}p_{n+1}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_{n+1})\times\ln p_{n+1}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_{n+1})d\mathbf{x}_1d\mathbf{x}_2\cdots d\mathbf{x}_{n+1},$$

with the $n+1$ constraints that the p_n are the marginals of p_{n+1},

$$p_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)=\int_\Omega p_{n+1}(\mathbf{x}_1,\ldots,\mathbf{x}_j,\ldots,\mathbf{x}_{n+1})d\mathbf{x}_j,\quad j=1,2,\ldots,n+1.$$

Since p_2 is the marginal of p_n ($n\geqslant 2$), it follows that p_2 is also known. Therefore, for a pairwise additive potential, maximizing the Helmholtz free energy of the $(n+1)$-particle system is equivalent to minimizing the entropy of the $(n+1)$-particle system. Introducing the Lagrange multipliers $\lambda_j(\mathbf{x}_1,\ldots,\mathbf{x}_{j-1},\mathbf{x}_{j+1},\ldots,\mathbf{x}_{n+1})$, $j=1,2,\ldots,n+1$, the Euler-Lagrange equation gives

$$-\ln p_{n+1}-1+\sum_{j=1}^{n+1}\lambda_j=0. \tag{44}$$

Since the n particles are interchangeable,

$$p_{n+1}(\mathbf{x}_1,\ldots,\mathbf{x}_{n+1})=\prod_{j=1}^{n+1}\gamma(\mathbf{x}_1,\ldots,\mathbf{x}_{j-1},\mathbf{x}_{j+1},\ldots,\mathbf{x}_{n+1}). \tag{45}$$

Integration with respect to $\mathbf{x}_{n+1}$ yields

$$p_n(\mathbf{x}_1,\ldots,\mathbf{x}_n)=\gamma(\mathbf{x}_1,\ldots,\mathbf{x}_n)\int_\Omega\prod_{j=1}^{n}\gamma(\mathbf{x}_1,\ldots,\mathbf{x}_{j-1},\mathbf{x}_{j+1},\ldots,\mathbf{x}_{n+1})d\mathbf{x}_{n+1}. \tag{46}$$

Solving the nonlinear integral equation (46) for γ and substituting in Eq. (45) gives the n-level closure relation of the n-level BBGKY hierarchy equation for p_n,

$$0=\mathbf{f}_{\mathrm{ex}}(\mathbf{x}_1)p_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)+\sum_{j=2}^{n}\mathbf{f}(\mathbf{x}_j,\mathbf{x}_1)p_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)-k_BT\nabla_{\mathbf{x}_1}p_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)+(N-n)$$
$$\times\int_\Omega\mathbf{f}(\mathbf{x}_{n+1},\mathbf{x}_1)p_{n+1}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_{n+1})d\mathbf{x}_{n+1}. \tag{47}$$

A. The thermodynamic limit

We have seen in Sec. III that the maximum entropy principle yields the Kirkwood SA ($n=2$) in the thermodynamic limit. In this section we show that in the thermodynamic limit, the maximum entropy principle results in the probabilistic Kirkwood closure (33) for all levels $n\geqslant 2$.

First, we consider a bounded domain $\Omega\subset\mathbb{R}^3$. We set

$$h_n^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)=\frac{p_n^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)}{\prod_{k=1}^{n-1}\prod_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n}p_k^{(\Omega)}(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_k})^{(-1)^{n-1-k}}} \tag{48}$$

and

$$\delta^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)=\frac{\gamma^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)}{\prod_{k=1}^{n-1}\prod_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n}p_k^{(\Omega)}(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_k})^{(-1)^{n-1-k}(n-k)/(n-k+1)}}. \tag{49}$$

Dividing Eq. (46) by $\prod_{k=1}^{n-1}\prod_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n}p_k^{(\Omega)}(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_k})^{(-1)^{n-1-k}}$ we obtain

$$h_n^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)=\delta^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)\int_\Omega F(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n,\mathbf{x}_{n+1})\prod_{j=1}^{n}\delta^{(\Omega)}(\mathbf{x}_1,\ldots,\mathbf{x}_{j-1},\mathbf{x}_{j+1},\ldots,\mathbf{x}_{n+1})d\mathbf{x}_{n+1}, \tag{50}$$

where

$$F(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n,\mathbf{x}_{n+1})=\prod_{k=1}^{n-2}\prod_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n}p_k^{(\Omega)}(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_k})^{(-1)^{n-1-k}(n-k-1)}$$
$$\times\prod_{k=1}^{n-1}\prod_{1\leqslant i_1<i_2<\cdots<i_{k-1}\leqslant n}p_k^{(\Omega)}(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_{k-1}},\mathbf{x}_{n+1})^{(-1)^{n-1-k}(n-k)}. \tag{51}$$

For $\min_{1\leqslant j\leqslant n}|\mathbf{x}_{n+1}-\mathbf{x}_j|\gg 1$, the $(n+1)$-th particle becomes independent of particles 1,2,…,n, and we have

$$p_k^{(\Omega)}(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_{k-1}},\mathbf{x}_{n+1})=p_1^{(\Omega)}(\mathbf{x}_{n+1})p_{k-1}^{(\Omega)}(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_{k-1}})[1+o(1)],$$

for all $k=1,2,\ldots,n$ and all sets of indices $1\leqslant i_1<i_2<\cdots<i_{k-1}\leqslant n$. Therefore, to leading order in $(\min_{1\leqslant j\leqslant n}|\mathbf{x}_{n+1}-\mathbf{x}_j|)^{-1}$

$$\begin{aligned}F(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n,\mathbf{x}_{n+1})&=\prod_{k=1}^{n-2}\prod_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n}p_k^{(\Omega)}(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_k})^{(-1)^{n-1-k}(n-k-1)}\\&\times\prod_{k=1}^{n-1}\prod_{1\leqslant i_1<i_2<\cdots<i_{k-1}\leqslant n}p_{k-1}^{(\Omega)}(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_{k-1}})^{(-1)^{n-1-k}(n-k)}\\&\times\prod_{k=1}^{n-1}\prod_{1\leqslant i_1<i_2<\cdots<i_{k-1}\leqslant n}p_1^{(\Omega)}(\mathbf{x}_{n+1})^{(-1)^{n-1-k}(n-k)}\\&=\prod_{k=1}^{n-1}\prod_{1\leqslant i_1<i_2<\cdots<i_{k-1}\leqslant n}p_1^{(\Omega)}(\mathbf{x}_{n+1})^{(-1)^{n-1-k}(n-k)}\\&=[p_1^{(\Omega)}(\mathbf{x}_{n+1})]^{\{\sum_{k=1}^{n-1}(-1)^{n-1-k}(n-k)\binom{n}{k-1}\}}=p_1^{(\Omega)}(\mathbf{x}_{n+1}),\end{aligned} \tag{52}$$

where we have used the combinatorial identity

$$\sum_{k=1}^{n-1}(-1)^{n-1-k}(n-k)\binom{n}{k-1}=1. \tag{53}$$

We conclude that

$$h_n^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)$$
$$=\delta^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)\int_\Omega p_1^{(\Omega)}(\mathbf{x}_{n+1})[1+o(1)]$$
$$\times\prod_{j=1}^{n}\delta^{(\Omega)}(\mathbf{x}_1,\ldots,\mathbf{x}_{j-1},\mathbf{x}_{j+1},\ldots,\mathbf{x}_{n+1})d\mathbf{x}_{n+1}.$$

Therefore,

$$\lim_{\Omega\to\mathbb{R}^3}\delta^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)=\lim_{\Omega\to\mathbb{R}^3}h_n^{(\Omega)}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n). \tag{54}$$

Substituting Eq. (49) in Eq. (45), using the relations (48) and (54), and the definition (37), we find that

$$g_{n+1}(\mathbf{x}_1,\ldots,\mathbf{x}_{n+1})$$
$$=\prod_{k=2}^{n}\prod_{1\leqslant i_1<i_2<\cdots<i_k\leqslant n+1}g_k(\mathbf{x}_{i_1},\mathbf{x}_{i_2},\ldots,\mathbf{x}_{i_k})^{(-1)^{n-k}}. \tag{55}$$

We observe that for systems in the entire space, the probabilistic Kirkwood closure (41) agrees with the maximum entropy closure (55) for all orders n.

B. Closure at the highest level $n=N-1$

Although the probabilistic Kirkwood closure and the maximum entropy closure agree in the case of systems in the entire space, they differ in the case of confined systems with a finite number of particles N. It appears that the maximum entropy closure (45) is exact in a confined system when applied at the highest level $n=N-1$, whereas the probabilistic Kirkwood closure (33) is not exact. In other words, the maximum entropy closure relation yields the Boltzmann distribution (24). What appeared at first to be an approximation turns out to be the exact result. Indeed, setting

$$\gamma(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_{N-1})$$
$$=\left(\frac{1}{Z_N}\right)^{1/N}\exp\left\{-\left[\frac{1}{N-2}\sum_{1\leqslant i<j\leqslant N-1}U(\mathbf{x}_i,\mathbf{x}_j)\right.\right.$$
$$\left.\left.+\frac{1}{N-1}\sum_{j=1}^{N-1}U_{\mathrm{ex}}(\mathbf{x}_j)\right]\Big/\ k_BT\right\}, \tag{56}$$

we see that clearly,

$$\prod_{j=1}^{N}\gamma(\mathbf{x}_1,\ldots,\mathbf{x}_{j-1},\mathbf{x}_j,\ldots,\mathbf{x}_N)=\frac{1}{Z_N}e^{-U(\mathbf{x}_1,\ldots,\mathbf{x}_N)/k_BT}, \tag{57}$$

which is the Boltzmann distribution. The Boltzmann distribution obviously satisfies the BBGKY equation (47). Therefore, we have found a solution to BBGKY equation which satisfies the closure relation (45). This solution coincides with the Boltzmann distribution, and so we conclude that it is the exact solution. For the $(N-1)$-particle pdf p_{N-1} we have

$$p_{N-1}(\mathbf{x}_1,\ldots,\mathbf{x}_{N-1})=\frac{1}{Z_N}\int_\Omega e^{-U(\mathbf{x}_1,\ldots,\mathbf{x}_N)/k_BT}d\mathbf{x}_N, \tag{58}$$

which is both the exact and ''approximate'' result.

The probabilistic Kirkwood approximation (33) gives, however, a different result. If it were to be exact, then the resulting $(N-1)$-particle pdf would have been given by Eq. (58). Therefore, all lower level pdf's p_n $(n\leqslant N-1)$ would be (multiple) integrals of the Boltzmann distribution. Therefore, by the closure (33), p_N should be a product of integrals of the Boltzmann distribution, which is a contradiction to the known form of the Boltzmann distribution (24).

Although the maximum entropy closure is exact at the highest order $n=N-1$, it is not exact at lower orders. The observation that the maximum entropy closure is exact at the highest level, while the probabilistic Kirkwood closure is not, may indicate that the maximum entropy closure may fit the experimental data better than the probabilistic Kirkwood closure does in confined systems, even when used at lower levels $(n=2,3)$.

VII. CONFINED SYSTEMS

Systems in bounded domains are particularly important because only bounded domains can include the spatially nonuniform boundary conditions needed to describe devices, with spatially distinct inputs, outputs, and (sometimes) power supplies. A large fraction of electrochemistry involves such devices as batteries or concentration cells. A large fraction of molecular biology involves such devices as transport proteins that move ions across otherwise impermeable membranes.[26,27]

In the general case, where $\Omega\subset\mathbb{R}^3$ is a bounded domain, there is no known analytic solution to the system (9). We propose to solve this system by the following iterative scheme:

(1) Initial guess $\gamma^{(0)}(\mathbf{x}_1,\mathbf{x}_2)$. Set $i=0$.
(2) Solve the nonhomogeneous linear equation for $p_2^{(i)}(\mathbf{x}_1,\mathbf{x}_2)$

$$k_BT\nabla_{\mathbf{x}_1}p_2^{(i)}(\mathbf{x}_1,\mathbf{x}_2)-\mathbf{f}(\mathbf{x}_2,\mathbf{x}_1)p_2^{(i)}(\mathbf{x}_1,\mathbf{x}_2)-\mathbf{f}_{\mathrm{ex}}(\mathbf{x}_1)p_2^{(i)}(\mathbf{x}_1,\mathbf{x}_2)$$
$$=(N-2)\int_\Omega\mathbf{f}(\mathbf{x}_3,\mathbf{x}_1)\gamma^{(i)}(\mathbf{x}_1,\mathbf{x}_2)\gamma^{(i)}(\mathbf{x}_2,\mathbf{x}_3)$$
$$\times\gamma^{(i)}(\mathbf{x}_1,\mathbf{x}_3)d\mathbf{x}_3.$$

(3) Solve the nonlinear system for $\gamma^{(i+1)}$

$$p_2^{(i)}(\mathbf{x}_1,\mathbf{x}_2)=\gamma^{(i+1)}(\mathbf{x}_1,\mathbf{x}_2)$$
$$\times\int_\Omega\gamma^{(i+1)}(\mathbf{x}_2,\mathbf{x}_3)\gamma^{(i+1)}(\mathbf{x}_1,\mathbf{x}_3)d\mathbf{x}_3. \tag{59}$$

(4) $i\leftarrow i+1$. Return to step 2, until convergence is achieved.

The analysis of the preceding section indicates that a good initial guess might be

$$\gamma^{(0)}(\mathbf{x}_1,\mathbf{x}_2)=\sqrt{p_1(\mathbf{x}_1)p_1(\mathbf{x}_2)}g_2(\mathbf{x}_1,\mathbf{x}_2), \tag{60}$$

where $g_2(\mathbf{x}_1,\mathbf{x}_2)$ is the solution to the BBGKY equation with the Kirkwood SA in the entire space $\mathbb{R}^3$. This solution can be found rather easily using the inherited symmetries of the problem. For example, it is well known that if $\mathbf{f}_{\text{ex}}=0$, then $g_2(\mathbf{x}_1,\mathbf{x}_2)=g_2(|\mathbf{x}_1-\mathbf{x}_2|)$, and the problem for g_2 becomes one dimensional.

Step 2 requires the solution of a linear partial differential equation in a bounded region. This equation can be written in a gradient form as

$$\nabla_{\mathbf{x}_1}[e^{[U(\mathbf{x}_1,\mathbf{x}_2)+U_{\text{ex}}(\mathbf{x}_1)]/k_BT}p_2(\mathbf{x}_1,\mathbf{x}_2)]$$
$$=-\frac{N-2}{k_BT}e^{[U(\mathbf{x}_1,\mathbf{x}_2)+U_{\text{ex}}(\mathbf{x}_1)]/k_BT}$$
$$\times\int_\Omega \nabla_{\mathbf{x}_1}U(\mathbf{x}_1,\mathbf{x}_3)p_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_3.$$

The identity $\nabla_{\mathbf{x}_1}\times\nabla_{\mathbf{x}_1}u(\mathbf{x}_1)=0$, for all u, imposes a solvability condition for γ. Indeed, taking the curl of the last equation, together with the closure (7) results in

$$0=\nabla_{\mathbf{x}_1}\times\Bigg[e^{[U(\mathbf{x}_1,\mathbf{x}_2)+U_{\text{ex}}(\mathbf{x}_1)]/k_BT}$$
$$\times\int_\Omega \nabla_{\mathbf{x}_1}U(\mathbf{x}_1,\mathbf{x}_3)\gamma(\mathbf{x}_1,\mathbf{x}_2)\gamma(\mathbf{x}_1,\mathbf{x}_3)\gamma(\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_3\Bigg].$$

In step 3 we solve a nonlinear integral equation. We suggest solving the nonlinear Eq. (8) by a Newton-Raphson iterative scheme. Let $\gamma^{(n)}(\mathbf{x}_1,\mathbf{x}_2)$ be the nth iteration. Define the operator $\Gamma^{(n)}:\Omega^2\to\Omega^2$ as follows:

$$\Gamma^{(n)}u(\mathbf{x},\mathbf{z})=\int_\Omega \gamma^{(n)}(\mathbf{x},\mathbf{y})u(\mathbf{z},\mathbf{y})d\mathbf{y}. \tag{61}$$

Let the operator $S:\Omega^2\to\Omega^2$ be the symmetrization operator,

$$Su(\mathbf{x},\mathbf{y})=u(\mathbf{y},\mathbf{x}). \tag{62}$$

The Newton-Raphson iteration scheme suggests

$$\gamma^{(n+1)}=\gamma^{(n)}+\Delta(\mathbf{x}_1,\mathbf{x}_2), \tag{63}$$

where $\Delta(\mathbf{x}_1,\mathbf{x}_2)$ satisfies the linear integral equation

$$p_2(\mathbf{x}_1,\mathbf{x}_2)-p_2^{(n)}(\mathbf{x}_1,\mathbf{x}_2)$$
$$=\frac{p_2^{(n)}(\mathbf{x}_1,\mathbf{x}_2)}{\gamma^{(n)}(\mathbf{x}_1,\mathbf{x}_2)}\Delta(\mathbf{x}_1,\mathbf{x}_2)+\gamma^{(n)}(\mathbf{x}_1,\mathbf{x}_2)\Gamma^{(n)}\Delta(\mathbf{x}_1,\mathbf{x}_2)$$
$$+\gamma^{(n)}(\mathbf{x}_1,\mathbf{x}_2)S\Gamma^{(n)}\Delta(\mathbf{x}_1,\mathbf{x}_2),$$

where

$$p_2^{(n)}(\mathbf{x}_1,\mathbf{x}_2)=\gamma^{(n)}(\mathbf{x}_1,\mathbf{x}_2)\int_\Omega \gamma^{(n)}(\mathbf{x}_1,\mathbf{x}_3)\gamma^{(n)}(\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_3. \tag{64}$$

We may write the iteration equivalently as

$$\gamma^{(n+1)}=\gamma^{(n)}+\left(\frac{p_2^{(n)}}{\gamma^{(n)}}+\gamma^{(n)}\Gamma^{(n)}+\gamma^{(n)}S\Gamma^{(n)}\right)^{-1}$$
$$\times(p_2-p_2^{(n)}). \tag{65}$$

The steps in the algorithm are iterated until convergence is achieved.

We have yet to test our generalized Kirkwood closure in practice. The resulting pair correlation function should be compared with MD or MC simulations of particles in a confined region. The observation of Sec. VI B and the generality of the maximum entropy principle (minimum Helmholtz free energy) may indicate that it will outperform the regular Kirkwood SA in bounded domains. The difference between the results of the two closure methods should be seen near the boundary walls of the domain.

VIII. MIXTURES

The maximum entropy principle can also be used to find closure relations of mixtures, both in confined domains and in the entire space. Suppose a mixture of $S\geqslant 2$ species, with N_α $(\alpha=1,2,\ldots,S)$ particles of each species. Let $N=\sum_{\alpha=1}^S N_\alpha$ be the total number of particles of all species. There are S^2 two-particle pdfs,

$$p_2^{\alpha\beta}(\mathbf{x}_1,\mathbf{x}_2),\quad \alpha,\beta\in\{1,2,\ldots,S\},$$

that exhibit the symmetry $p_2^{\alpha\beta}(\mathbf{x}_1,\mathbf{x}_2)=p_2^{\beta\alpha}(\mathbf{x}_2,\mathbf{x}_1)$. In this section we briefly discuss how to find the closure relation in the mixture problem.

In the maximum entropy approach, one is searching for S^3 three-particle pdfs $p_3^{\alpha\beta\gamma}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)$, $\alpha,\beta,\gamma\in\{1,2,\ldots,S\}$, that bring the entropy

$$H=-\sum_{\alpha,\beta,\gamma=0}^{S}\frac{N_\alpha}{N}\frac{N_\beta}{N}\frac{N_\gamma}{N}$$
$$\times\int_\Omega p_3^{\alpha\beta\gamma}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)\ln p_3^{\alpha\beta\gamma}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_1d\mathbf{x}_2d\mathbf{x}_3 \tag{66}$$

to maximum, with the $3S^3$ marginal constraints

$$p_2^{\alpha\beta}(\mathbf{x}_1,\mathbf{x}_2)=\int_\Omega p_3^{\alpha\beta\gamma}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_3,$$
$$p_2^{\alpha\gamma}(\mathbf{x}_1,\mathbf{x}_3)=\int_\Omega p_3^{\alpha\beta\gamma}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_2, \tag{67}$$
$$p_2^{\beta\gamma}(\mathbf{x}_2,\mathbf{x}_3)=\int_\Omega p_3^{\alpha\beta\gamma}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)d\mathbf{x}_1.$$

This variational problem is solved using the Euler-Lagrange formulation similar to the derivation done in Sec. II.

In the case of a system in the entire space, the methods of Secs. III B and VI A show that the mixture entropy closure coincides with the probabilistic Kirkwood closure. Both sections suggest that the triplets correlation functions are related to the pair correlation function through

$$g_3^{\alpha\beta\gamma}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)=g_2^{\alpha\beta}(\mathbf{x}_1,\mathbf{x}_2)g_2^{\alpha\gamma}(\mathbf{x}_1,\mathbf{x}_3)g_2^{\beta\gamma}(\mathbf{x}_2,\mathbf{x}_3) \tag{68}$$

for $\alpha,\beta,\gamma\in\{1,2,\ldots,S\}$. Closures of higher orders can be obtained in a similar manner.

In confined systems, the Euler-Lagrange formulation leads to integral equations of the form (8). Note that since

the entropy (66) depends on the particle fraction N_α/N, we expect the resulting confined system pair correlation will also depend on the particle fraction.

IX. DISCUSSION AND SUMMARY

We have used the maximum entropy principle to derive a closure relation for the BBGKY hierarchy. It is possible to consider functionals over distributions other than the entropy that can yield different (known) closures. In fact, a somewhat similar approach is used in density functional theory (DFT). In the DFT problem setup, a functional of the pair correlation function (e.g., the Helmholtz free energy) is maximized. The function that brings the given functional to its maximal value is the resulting pair correlation function. Using this method, one can recover some of the Ornstein-Zernike integral closures that relate the direct and indirect correlation functions, such as the PY closure, for instance. Our approach differs from that of the DFT in that we optimize over relations between the probability correlation (density) functions of successive orders, rather than over relations between the direct and indirect correlation functions.

In this paper we have used the maximum entropy principle to derive a closure relation for the BBGKY hierarchy. This approach to the closure problem appears to be new. We proved that for systems in the entire space, the maximum entropy closure relation coincides with the probabilistic Kirkwood SA for all orders of the hierarchy. In finite systems the maximum entropy closure differs from Kirkwood's SA. In particular, when applied to the highest level of the hierarchy, the maximum entropy closure is exact, whereas the probabilistic Kirkwood approximation is not. Besides the advantage of generality, the maximum entropy closures are expected to perform better than the Kirkwood SA, even in low order approximations. We expect the differences between the pair correlation functions predicted by the two methods to be significant especially near the domain boundaries. The maximum entropy closure may be applicable to nonequilibrium systems, and in particular to systems with spatially inhomogeneous boundary conditions. That implementation of the maximum entropy closure will be the subject of a separate paper.

ACKNOWLEDGMENTS

The author is most grateful to Zeev Schuss and Bob Eisenberg for introducing the closure problem to him and for their guidance. The author would also like to thank Douglas Henderson, Roland Roth, and Stuart A. Rice for several suggestions which were incorporated into the manuscript. This research was partially supported by research grants from the Israel Science Foundation, US-Israel Binational Science Foundation, DARPA and the NIH Math Grant No. UPSHS 5 RO1 GM 067241.

[1] R. S. Berry, S. Rice, and J. Ross, *Physical Chemistry*, 2nd ed. (Oxford University Press, New York, 2000).
[2] J. M. G. Barthel, H. Krienke, in *Physical Chemistry of Electrolyte Solutions: Modern Aspects*, edited by A. H. Baumgartel (Steinkopf, Dresden, 1998).
[3] H. T. Davis, *Statistical Mechanics of Phases, Interfaces, and Thin Films*, Advances in Interfacial Engineering Series (Wiley, New York, 1995).
[4] *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992).
[5] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1990).
[6] R. L. Rowley, *Statistical Mechanics for Thermophysical Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1994).
[7] J. G. Kirkwood, J. Chem. Phys. **3**, 300 (1935).
[8] J. G. Kirkwood and E. M. Boggs, J. Chem. Phys. **10**, 394 (1942).
[9] I. Z. Fisher and B. I. Kopeliovich, Dokl. Akad. Nauk SSSR **133**, 81 (1960) [Sov. Phys. Dokl. **5**, 761 (1960)].
[10] Y.-T. Lee, F. H. Ree, and T. Ree, J. Chem. Phys. **48**, 3506 (1968).
[11] F. H. Ree, Y.-T. Lee, and T. Ree, J. Chem. Phys. **55**, 234 (1971).
[12] R. S. Eisenberg, Biophys. Chem. **100**, 507 (2003).
[13] S. A. Rice and J. Lekner, J. Chem. Phys. **42**, 3559 (1965).
[14] S. A. Rice and D. A. Young, Discuss. Faraday Soc. **43**, 16 (1967).
[15] E. Meeron, J. Chem. Phys. **27**, 1238 (1957).
[16] E. E. Salpeter, Ann. Phys. (N.Y.) **5**, 183 (1958).
[17] J. S. Rowlinson, Mol. Phys. **6**, 517 (1963).
[18] Z. M. Hu, H. H. Gan, and B. C. Eu, Physica A **184**, 71 (1992).
[19] J. M. Richardson, J. Chem. Phys. **23**, 2304 (1955).
[20] T. M. Cover and J. A. Thomas, *Elements of Information Theory* (Wiley, New York, 1991).
[21] E. L. Lehmann, *Testing Statistical Hypotheses*, 2nd ed. (Springer, Berlin, 1997).
[22] E. L. Lehmann and G. Casella, *Theory of Point Estimation*, 2nd ed. (Springer, Berlin, 1998).
[23] R. D. Rosenkrantz, *Papers on Probability, Statistics, and Statistical Physics*, edited by E. T. Jaynes (Kluwer, Boston, 1989).
[24] *Maximum Entropy in Action*, edited by B. Buck and V. A. Macaulay (Oxford, New York, 1995).
[25] S. R. DeGroot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
[26] R. S. Eisenberg, J. Membr. Biol. **115**, 112 (1990).
[27] R. S. Eisenberg, J. Comput. Electron. **2**, 245 (2003).