Maximum Entropy and the Variational Method in Statistical Mechanics: an Application to Simple Fluids

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Abstract

We develop the method of Maximum Entropy (ME) as a technique to generate approximations to probability distributions. The central results consist in (a) justifying the use of relative entropy as the uniquely natural criterion to select a "best" approximation from within a family of trial distributions, and (b) to quantify the extent to which non-optimal trial distributions are ruled out. The Bogoliubov variational method is shown to be included as a special case. As an illustration we apply our method to simple fluids. In a first use of the ME method the "exact" canonical distribution is approximated by that of a fluid of hard spheres and ME is used to select the optimal value of the hard-sphere diameter. A second, more refined application of the ME method approximates the "exact" distribution by a suitably weighed average over different hard-sphere diameters and leads to a considerable improvement in accounting for the soft-core nature of the interatomic potential. As a specific example, the radial distribution function and the equation of state for a Lennard-Jones fluid (Argon) are compared with results from molecular dynamics simulations.

KEY WORDS: Variational method; maximum entropy; simple fluids

1 Introduction

A common problem is that our beliefs and our knowledge are often represented by a probability distribution $P(x)$ that is too complicated to be useful for practical calculations and we need to find a more tractable approximation. A possible
solution is to identify a family of trial distributions \( \{ p(x) \} \) and select the member of the family that is closest to the exact distribution \( P(x) \). The problem, of course, is that it is not clear what one means by ‘closest’. We could minimize

\[
\int dx \ [p(x) - P(x)]^2 ,
\]

but why this particular functional and not another? And also, why limit oneself to an approximation by a single member of the trial family? Why not consider some linear combination of the trial distributions, some kind of average over the trial family? But then, how should we choose the optimal weight assigned to each \( p(x) \)? And again, what does ‘optimal’ mean? We propose to tackle these questions using the method of maximum entropy.

The method of Maximum Entropy as advocated by Jaynes (MaxEnt) is a method to assign probabilities on the basis of partial information [1]. The core of the MaxEnt method resides in interpreting entropy, through the Shannon axioms, as a measure of the “amount of uncertainty” or of the “amount of information that is missing” in a probability distribution. This was an important step forward because it extended the applicability of the notion of entropy far beyond its original roots in thermodynamics but it was not entirely free from objections. For example, one problem is that the Shannon axioms refer to probabilities of discrete variables; the entropy of continuous distributions was not defined. A second, perhaps more serious problem is that other measures of uncertainty were subsequently found. This immediately raised the question of which among the alternatives should one choose and motivated attempts to justify the method of maximum entropy directly as a method of inductive inference without referring to any specific measure of uncertainty [2]–[7]. What eventually emerged is an extended form of the method of Maximum Entropy, which we abbreviate as ME to distinguish it from the original MaxEnt. The core of ME is a concept of (relative) entropy that reduces to the usual entropy in the special case of a uniform prior or uniform background measure and that does not require an interpretation in terms of heat, disorder, uncertainty, or even in terms of an amount of information: in the context of ME entropy needs no interpretation.

The ME method is designed for processing information, for updating from a prior probability distribution (which in statistical mechanics is generally postulated to be uniform) to a posterior distribution when new information in the form of constraints becomes available [8]. The chosen posterior distribution should coincide with the prior as closely as possible: ME implements the minimal changes that are required to satisfy the new constraints. The significance of this development is that it allows one to tackle problems lying beyond the restricted scope of MaxEnt [9].

The main purpose of this paper is to extend the use of the ME method beyond processing information to a method to generate approximations [10]; a second purpose is to illustrate the method by applying it to simple fluids.

The general formalism, which is the main result of this paper, is developed in section 2. In section 2.1 we justify the use of relative entropy as the uniquely
natural criterion to select the best approximation. In section 2.2 as a simple
illustration, the ME method is applied to trial distributions of the canonical
Boltzmann-Gibbs form. The result, when expressed in terms of free energies, is
recognized as the Bogoliubov variational principle 13, which is now seen as a
special case of ME 14. The first part of our paper concludes in section 2.3 with
a quantitative analysis of the extent to which the distribution that maximizes the
relative entropy is preferred over other members of the trial family. We show
that our entropic argument does not completely rule out those distributions
that fail to maximize the entropy. Therefore a suitably weighted average over
the whole family of trial distributions with the optimal weight calculated using
the ME method provides a better approximation than can be expected from
any individual member of the trial family.

The discussion up to this point is general – the ME method of generating
best approximations is of general applicability – but it is useful to see how it
is applied to a specific problem. In the second part of the paper we apply the
ME method to simple classical fluids. The study of classical fluids is an old
and mature field. There exist extensive treatments in many excellent books and
reviews 15-17. Our goal is to use this well-explored but still non-trivial field
as a testing ground for the ME method. At this early stage in the development
of the ME method we are not concerned with contributing to the study of the
fluids themselves. Indeed, the reason we choose such a well-explored problem,
is not because we are eager to find new results about fluids but because we
can compare our results with those obtained using alternative approximation
methods already in existence. We find that our results are quite competitive
with those obtained using the best perturbative methods developed to date.

The practical success or failure of the method hinges on choosing a family of
trial distributions that incorporates the information that is relevant to the prob-
lem of interest. In our example – simple fluids – it turns out that their structure
is dominated, particularly at liquid densities, by the short-range repulsions be-
tween molecules. The effects of the long-range attractions are averaged over
many molecules and are less important, except at low densities. Accordingly
we choose a fluid of hard spheres 15-17 as our (almost) tractable trial model
(section 3). The ME method is then used (section 4) to select the optimal
value of the hard-sphere diameter. This is equivalent to applying the Bogoli-
ubov variational principle and reproduces the results obtained by by Mansoori
et al. 18, and independently by Stell et al. 19.

A very different approximation scheme can be traced back to Lewis who used
a maximum entropy argument to derive the Boltzmann equation 20, and was
further developed by Karkheck, Stell and coworkers 21. Instead of selecting
the optimal distribution from within a family of trial approximations, which is
what we do here, in their “kinetic variational theory” an entropy is maximized
to determine the optimal closure for the BBGKY hierarchy of equations. Their
method is suitable for tackling transport problems in dense simple fluids with
potentials that are more realistic than just hard spheres.

Alternative approaches to the study of fluids include perturbation theory. In
such schemes the intermolecular potential $u$ is written as $u_0 + \delta u$, where $u_0$ is a
strong short-range repulsion, which is eventually approximated by a hard-sphere potential $u_{hs}$, and $\delta u$ is a long-range attraction treated as a perturbation. At high densities first order theory is quite accurate but at lower densities higher-order corrections must be included. There exist several proposals for how to separate $u$ into $u_0$ and $\delta u$, for choosing the particular stage in the calculation where $u_0$ is replaced by $u_{hs}$, and also for choosing the best hard-sphere diameter. The most successful are those by Barker and Henderson [15] and by Weeks, Chandler and Andersen (WCA) [22]. The latter succeeds in using the hard-sphere potential $u_{hs}$ while effectively representing some of the effects of the soft-core potential $u_0$. For a recent discussion of some of the strengths and limitations of the perturbative approach see [23].

An advantage of the variational and the ME methods over the perturbative approaches is that there is no need for ad hoc criteria dictating how to separate $u$ into $u_0$ and $\delta u$, and how to choose a hard-sphere diameter. A disadvantage of the standard variational approach is that it fails to take the softness of the repulsive core into account, which leads, at high temperatures, to results that are inferior to the perturbative approaches. As we shall see below this limitation does not apply to the ME method.

The standard variational approach allows one to select the optimal value of a parameter, in this case the hard-sphere diameter; all non-optimal values are ruled out. But, as discussed in [7] and [24], the ME method allows one to quantify the extent to which non-optimal values should contribute. In this more complete use of the ME method (presented in section 5) the “exact” probability distribution of the fluid is approximated by a statistical mixture of distributions corresponding to hard spheres of different diameters. This is a rather simple and elegant way to take into account the fact that the actual atoms are not hard spheres. The full ME analysis leads to significant improvements over the variational method.

In section 6 we test our method by comparing its predictions for a Lennard-Jones model for Argon with the numerical molecular dynamics simulation data ([25], [26]). We find that the ME predictions for thermodynamic variables and for the radial distribution function are considerable improvements over the standard Bogoliubov variational result, and are comparable to the perturbative results. Finally, our conclusions and some remarks on further improvements are presented in section 7.

2 Using ME to generate approximations

The goal is to select from a family of trial distributions $p(x)$ (the possible posteriors) that which is closest to a given “exact” distribution $P(x)$ (the prior). The family of trials can be defined in a variety of ways. For example, one can specify a functional form $p_{\theta}(x)$, each member of the trial family being labelled by one or more parameters $\theta$. More generally, one could define the trial family in a non-parametric way by specifying various constraints.

The discussion below which develops the use of ME to generate approxi-
mations follows [7] where the ME method is developed for a different purpose, namely, as a method for processing information to update distributions.

2.1 The logic behind the ME method

The selection of one distribution from within a family is achieved by ranking the distributions according to increasing preference. Before we address the issue of what it is that makes one distribution preferable over another we note that there is one feature we must impose on any ranking scheme. The feature is transitivity: if distribution \( p_1 \) is preferred over distribution \( p_2 \), and \( p_2 \) is preferred over \( p_3 \), then \( p_1 \) is preferred over \( p_3 \). Such transitive rankings are implemented by assigning to each \( p(x) \) a real number \( S[p] \) which we call the “entropy” of \( p \). The numbers \( S[p] \) are such that if \( p_1 \) is preferred over \( p_2 \), then \( S[p_1] > S[p_2] \). Thus, by design, the “best” approximation \( p \) is that which maximizes the entropy \( S[p] \).

Next we determine the functional form of \( S[p] \). This is the general rule that provides the criterion for preference; in our case it defines what we mean by the “closest” or “best” approximation. The basic strategy [3] is one of induction: (1) if a general rule exists, then it must apply to special cases; (2) if in a certain special case we know which is the best approximation, then this knowledge can be used to constrain the form of \( S[p] \); and finally, (3) if enough special cases are known, then \( S[p] \) will be completely determined.

The known special cases are called the “axioms” of ME and they reflect the conviction that one should not change one’s mind frivolously, that whatever information was originally codified into the exact \( P(x) \) is important and should be preserved. The selected trial distribution should coincide with the exact one as closely as possible and one should only tolerate those minimal changes that are demanded by the information that defines the family of trials. Three axioms and their consequences are listed below. Detailed proofs and more extensive comments are given in [7].

Axiom 1: Locality. Local information has local effects. If the constraints that define the trial family do not refer to a certain domain \( D \) of the variable \( x \), then the conditional probabilities \( p(x|D) \) need not be revised, \( p(x|D) = P(x|D) \). The consequence of the axiom is that non-overlapping domains of \( x \) contribute additively to the entropy: \( S[p] = \int dx \, F(p(x), x) \) where \( F \) is some unknown function.

The motivation behind this axiom is the following. Suppose that the information, that is, the constraint, that defines the trial family, does not refer to a particular subdomain \( D \) of the variable \( x \). This means that the probability of \( x \) conditional on its being in \( D \) is completely unconstrained, and \( p(x|D) \) can take whatever value we desire. In other words, the family of trial distributions includes members that are capable of reproducing the conditional probability \( P(x|D) \) exactly. Axiom 1 says that if we can reproduce \( P(x|D) \) exactly then we should; that is, among the possible trials choose one such that \( p(x|D) = P(x|D) \). Clearly this is not just a good approximation, it is the best we can possibly do.

Axiom 2: Coordinate invariance. The ranking should not depend on the system of coordinates. The coordinates that label the points \( x \) are ar-
bitrary; they carry no information. The consequence of this axiom is that 
\[ S[p] = \int dx \, p(x) f(p(x)/m(x)) \] 
involves coordinate invariants such as \( dx \, p(x) \) and \( p(x)/m(x) \), where the function \( m(x) \) is a density, and both functions \( m \) and \( f \) are, at this point, unknown.

Next we make a second use of Axiom 1 (locality). When there are no constraints at all the family of trials includes the exact \( P(x) \) and the selected trial should coincide with \( P(x) \); that is, the best approximation to \( P(x) \) is \( P(x) \) itself. The consequence is that up to normalization the previously unknown density \( m(x) \) is the exact distribution \( P(x) \).

**Axiom 3: Consistency for independent subsystems.** When a system is composed of subsystems that are believed to be independent it should not matter whether the approximation procedure treats them separately or jointly. Specifically, if \( x = (x_1, x_2) \), and the exact distributions for the subsystems, \( P_1(x_1) \) and \( P_2(x_2) \), are respectively approximated by \( p_1(x_1) \) and \( p_2(x_2) \), then the exact distribution for the whole system \( P_1(x_1)P_2(x_2) \) should be approximated by \( p_1(x_1)p_2(x_2) \). This axiom restricts the function \( f \) to be a logarithm.

The overall consequence of these axioms is that the trial approximations \( p(x) \) should be ranked relative to the exact \( P(x) \) according to their (relative) entropy,

\[ S[p|P] = -\int dx \, p(x) \log \frac{p(x)}{P(x)}. \] (2)

The derivation has singled out the relative entropy \( S[p|P] \) as the unique functional to be used for the purpose of selecting an optimal approximation. Other functionals, may be useful for other purposes, but they are not a generalization from the simple cases described in the axioms above.

### 2.2 A special case: the variational method

As an illustration consider a system with microstates labelled by \( q \) (for example, the location in phase space or perhaps the values of spin variables). Let the probability that the microstate lies within a particular range \( dq \) be given by the canonical distribution

\[ P(q)dq = \frac{e^{-\beta H(q)}}{Z} dq, \] (3)

where

\[ Z = e^{-\beta F} = \int dq \, e^{-\beta H(q)}. \] (4)

We want to approximate the “exact” \( P \) by a more tractable distribution \( p \). The first step is to identify a family of trial distributions that are simple enough that actual calculations are feasible and that incorporates the appropriate relevant information. This step is difficult because there is no known systematic procedure to carry it out; it is a matter of trial and error guided by intuition. We will consider a family of trial distributions \( p_\theta(q) \) that are canonical with a Hamiltonian \( H_\theta(q) \) that depends on parameters \( \theta = \{\theta^1, \theta^2, \ldots, \theta^n\} \),

\[ p_\theta(q)dq = \frac{e^{-\beta H_\theta(q)}}{Z_\theta} dq, \] (5)
where
\[ Z_\theta = e^{-\beta F_\theta} = \int dq e^{-\beta H_\theta(q)}. \] (6)

The next step is to select the \( p_\theta \) that maximizes \( S[p_\theta|P] \). Substituting into eq.(2) gives,
\[ S[p_\theta|P] = \beta (\langle H_\theta - H \rangle_\theta - F_\theta + F), \] (7)
where \( \langle \ldots \rangle_\theta \) refers to averages over the trial \( p_\theta \). The inequality \( S[p_\theta|P] \leq 0 \), can then be written as
\[ F \leq F_\theta + \langle H - H_\theta \rangle_\theta. \] (8)

Thus, maximizing \( S[p_\theta|P] \) is equivalent to minimizing the quantity \( F_\theta + \langle H - H_\theta \rangle_\theta \). This alternate form of the variational principle and its use to generate approximations is well known. It is usually associated with the name of Bogoliubov [13] and it is the main technique to generate mean field approximations for discrete systems of spins on a lattice. What is perhaps not as widely known is that the Bogoliubov variational principle is just the special case of applying the ME method to trial distributions of the canonical Boltzmann-Gibbs form.

2.3 To what extent are non-optimal distributions ruled out?

The example above does not exhaust the power of the ME method: we have found a way to determine the optimal choice of \( \theta \) but ME allows us to go further and quantify the extent to which the optimal \( \theta \) is preferred over other non-optimal values ([7], [24]).

To what extent do we believe that any particular \( \theta \) should have been chosen? This is a question about the probability of \( \theta \), \( p(\theta) \). The original problem of assigning a probability to \( q \) is now broadened into assigning probabilities to \( q \) and \( \theta \). Here, we use ME not just to find the optimal approximation \( p(q) \) but also to find the optimal joint distribution \( p(q, \theta) \).

Notice that this is the kind of problem where it is necessary to adopt a Bayesian interpretation of probabilities. Within a frequentist interpretation it makes no sense to talk about \( p(\theta) \) or \( p(q, \theta) \) because \( \theta \) is not a random variable; the value of \( \theta \) is unknown but it is not random.

To proceed we must address two questions. First, what is the prior distribution, that is, what do we know about \( q \) and \( \theta \) before we are given the constraints? And second, what are the constraints that define the family of joint trials \( p(q, \theta) \)?

When we know nothing about the \( \theta \)s we know neither their physical meaning nor whether there is any relation to the \( q \). A joint prior \( m(q, \theta) \) that reflects this lack of correlations is a product, \( m(q, \theta) = P(q)\mu(\theta) \), where \( P(q) \) is the “exact” distribution, say eq.(3), and \( \mu(\theta) \) should reflect our ignorance about \( \theta \): it should be as uniform as possible and make every volume element in \( \theta \) space as likely as any other. But if we know absolutely nothing about \( \theta \) we also do not know how to measure volumes in \( \theta \) space.
To make further progress we need the additional information that provides meaning to the $\theta$s, namely, that they are parameters labeling the family of distributions $p_\theta(q)$. Remarkably this is sufficient to allow us to introduce a measure of distance in $\theta$ space that is both natural and unique: we define the distance between $\theta$ and $\theta + d\theta$ to be the same as the distance between the corresponding $p_\theta$ and $p_{\theta + d\theta}$ which is given by the Fisher-Rao metric $d\ell^2 = \gamma_{ij}d\theta^i d\theta^j$, where

$$\gamma_{ij} = \int dq \ p_\theta(q) \frac{\partial \log p_\theta(q)}{\partial \theta^i} \frac{\partial \log p_\theta(q)}{\partial \theta^j}.$$  \hspace{1cm} (9)

This is the only Riemannian metric that takes proper account of the fact that the $\theta$s are not just structureless points but represent probability distributions [27]. Accordingly, the volume of a small region $d\theta$ is $\gamma^{1/2}(\theta)d\theta$, where $\gamma(\theta)$ is the determinant of $\gamma_{ij}$. Up to an irrelevant normalization, the distribution $\mu(\theta)$ that is uniform in $\theta$ is given by

$$\mu(\theta) = \frac{\gamma^{1/2}(\theta)}{\zeta}.$$  \hspace{1cm} (10)

Eq.(11) tells us that the preferred value of $\theta$ maximizes the entropy $S[p_\theta|\gamma^{1/2}P]$, because this maximizes the probability density $\exp S[p_\theta|\gamma^{1/2}P]$. It also tells us the degree to which values of $\theta$ away from the maximum are ruled out. For macroscopic systems the preference for the ME distribution can be overwhelming. Note also that the density $\exp S[p_\theta|\gamma^{1/2}P]$ is a scalar function and the presence of the Jacobian factor $\gamma^{1/2}(\theta)$ makes Eq.(11) manifestly invariant under changes of the coordinates $\theta$.

Finally, now that we have determined the joint distribution $p(q, \theta) = p(\theta)p_\theta(q)$ we can marginalize $\theta$ and use the average

$$\bar{p}(q) = \int d\theta \ p(\theta)p_\theta(q)$$  \hspace{1cm} (12)

as the best approximation we can construct out of the given trial family. This approximation is expected to be better than any individual $p_\theta(q)$ for the same
reason that the mean is expected to be a better estimator than the mode – it
minimizes the variance.

This idea of introducing mixtures of probability distributions as in eq.(12)
might seem strange at first sight but it is actually quite natural. For example,
if we know that a system is in thermal equilibrium at temperature $T$ then we
describe its macrostate using the canonical distribution. But if we are uncertain
about the actual value of the temperature then a better description is given by
a suitable weighted average over $T$. Eq.(11) gives the appropriate weights.

The procedure above is mathematically straightforward but the shift from
the original problem of assigning a probability to $q$ into the new problem of
assigning probabilities to $q$ and $\theta$ can be a potential source of confusion. It might
appear that the maximization of the two entropies $S$ in eq.(2) and $\sigma$ in eq.(10)
has lead to two different best approximations: one is $p_\theta(q)$ with $\theta$ maximizing
eq.(7), and the other is $\bar{p}(q)$ in eq.(12). How can we have two different answers to
the same question? The answer is that we actually have two different questions.
Maximizing $S$ answers the question: “What is the best single $p_\theta(q)$? Or, what
is the best approximation obtainable in terms of a single trial?” Maximizing $\sigma$
answers a different question: “What is the best joint distribution $p(q, \theta)$? Or,
equivalently, what is the best approximation when we are not restricted to a
single trial?”

This concludes the first part of our paper. To summarize: our main results
consist in the justification of the relative entropy eq.(2) as the uniquely natural
functional to select the best approximations and the derivation of a quantitative
measure of the degree to which the various trials are preferred, eq.(11). The
final result for the best approximation is eq.(12).

Next we illustrate how this abstract formalism is used in a specific example.

3 Simple fluids

Here we collect some necessary background material on simple fluids.

We consider a simple fluid composed of $N$ single atom molecules described
by the Hamiltonian

$$H(q_N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U \quad \text{with} \quad U = \sum_{i> j} u(r_{ij}),$$

where $q_N = \{ p_i, r_i; \ i = 1, ..., N \}$ and the many-body interactions are approxi-
imated by a pair interaction, $u(r_{ij})$ where $r_{ij} = |r_i - r_j|$. The probability that
the positions and momenta of the molecules lie within the phase space volume
d$q_N$ is given by canonical distribution, and

$$P(q_N) \ dq_N = \frac{1}{Z} e^{-\beta H(q_N)} \ dq_N,$$

where

$$dq_N = \frac{1}{N! h^{3N}} \prod_{i=1}^{N} d^3 p_i d^3 r_i$$
and
\[ Z = \int dq_N \ e^{-\beta H(q_N)}. \] (16)

For fluids dominated by pair interactions most thermodynamic quantities of interest can be written in terms of the one- and two-particle density distributions
\[ n(r) = \langle \hat{n}(r) \rangle \quad \text{and} \quad n^{(2)}(r_1, r_2) = \langle \hat{n}^{(2)}(r_1, r_2) \rangle \] (17)
where
\[ \hat{n}(r) = \sum_i \delta(r - r_i) \] (18)
and
\[ \hat{n}^{(2)}(r_1, r_2) = \sum_{i,j(i\neq j)} \delta(r_1 - r_i) \delta(r_2 - r_j). \] (19)

It is convenient to introduce the two-particle correlation function
\[ g(r_1, r_2) = \frac{n^{(2)}(r_1, r_2)}{n(r_1)n(r_2)}, \] (20)
which measures the extent to which the structure of liquids deviates from complete randomness. If the fluid is homogeneous and isotropic \( n(r) = \rho = N/V \) and \( g(r_1, r_2) = g(|r_1 - r_2|) = g(r) \) where \( \rho \) is the bulk density and \( g(r) \) is the radial distribution function (RDF). Then, the pressure is given by
\[ \frac{PV}{Nk_B T} = 1 - \frac{\beta\rho}{6} \int d^3r \frac{du(r)}{dr} g(r), \] (21)
where \( \beta \equiv 1/k_B T. \) \[ \] [15]-[17]

The difficulty, of course, is that it is very difficult to calculate \( g(r) \) from the “exact” distribution Eq. (14) and we need to find an approximation that is calculable and still includes the two features of the interaction potential \( u \) that are relevant for explaining most fluid properties: the strong repulsion at short distances and the weak attraction at long distances.

To account for the short-distance repulsion we consider a family of trials composed by distributions that describe a gas of hard spheres of diameter \( r_d. \) For each \( r_d \) the Hamiltonian is
\[ H_{hs}(q_N | r_d) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U_{hs} \] (22)
with
\[ U_{hs} = \sum_{i>j}^{N} u_{hs}(r_{ij} | r_d), \] (23)
where
\[ u_{hs}(r | r_d) = \begin{cases} 0 & \text{for } r \geq r_d \\ \infty & \text{for } r < r_d \end{cases} \] (24)
and the corresponding probability distribution is

\[ P_{hs}(qN|rd) = \frac{1}{Z_{hs}} e^{-\beta H_{hs}(qN|rd)}. \]  

(25)

The partition function and the free energy \( F_{hs}(T, V, N|rd) \) are

\[ Z_{hs} = \int dqN \ e^{-\beta H_{hs}(qN|rd)} \overset{\text{def}}{=} e^{-\beta F_{hs}(T, V, N|rd)}. \]  

(26)

Two objections that can be raised to the choosing \( P_{hs}(qN|rd) \) as trials are, first, that they do not take the long-range interactions into account; and second, that the actual short range potential is not that of hard spheres. These are points to which we will return later. A third objection, and this is considerably more serious, is that the exact hard-sphere RDF is not known. However, it can be calculated within the approximation of Percus and Yevick (PY) for which there exists an exact analytical solution \([28], [29]\) which is reasonably simple and in good agreement with numerical simulations over an extended range of temperatures and densities, except perhaps at high densities. There are several successful proposals \([30]\) to improve upon the PY RDF but they also represent an additional level of complication. We feel that the simpler PY RDF is sufficiently accurate for our current objective – to illustrate the application and study the broad features of the ME approach. We will therefore assume that for our purposes the \( P_{hs} \) are sufficiently tractable distributions.

The PY RDF can be written in terms of the Laplace transform of \( r g_{hs}(r|rd) \) \([29]\),

\[ G(s) = \int_0^\infty dx \ x g_{hs}(xrd|rd)e^{-sx}, \]

\[ = \frac{sL(s)}{12\eta[L(s) + M(s)e^s]}, \]

(27)

where \( x \) is a dimensionless variable \( x = r/rd \),

\[ L(s) = 12\eta \left[ \left( 1 + \frac{1}{2\eta} \right) s + (1 + 2\eta) \right], \]

(28)

\[ M(s) = (1 - \eta)^2 s^3 + 6\eta (1 - \eta) s^2 \]

\[ + 18\eta^2 s - 12\eta (1 + 2\eta), \]

(29)

and \( \eta \) is the packing fraction,

\[ \eta \overset{\text{def}}{=} \frac{1}{6} \pi \rho r_d^3 \quad \text{with} \quad \rho = \frac{N}{V}. \]

(30)

The RDF \( g_{hs}(r|rd) \) is obtained from the inverse transform using residues \([31]\).
The equation of state can then be computed in two alternative ways, either from the “pressure” equation or from the “compressibility” equation but, since the result above for \( g_{hs}(r | r_d) \) is not exact, the two results do not agree. It has been found that better agreement with simulations and with virial coefficients is obtained taking an average of the two results with weights 1/3 and 2/3 respectively. The result is the Carnahan-Starling equation of state, \([15]-[17]\)

\[
\left( \frac{PV}{Nk_B T} \right)_{hs} = 1 + \eta + \frac{\eta^2 - \eta^3}{(1 - \eta)^3}.
\] (31)

The free energy, derived by integrating the equation of state, is

\[
F_{hs}(T, V, N | r_d) = Nk_B T \left[ -1 + \ln \rho \Lambda^3 + 4\eta - 3\eta^2 \right],
\] (32)

where \( \Lambda = \left(2\pi \bar{h}^2 / mk_BT\right)^{1/2} \), and the entropy is

\[
S_{hs} = - \left( \frac{\partial F_{hs}}{\partial T} \right)_{N,V} = \frac{F_{hs}}{T} + \frac{3}{2} Nk_B.
\] (33)

It must be remembered that these expressions are not exact. They are reasonable approximations for all densities up to almost crystalline densities (about \( \eta \approx 0.5 \)). However, they fail to predict the face-centered-cubic phase when \( \eta \) is in the range from 0.5 up the close-packing value of 0.74.

4 The optimal hard-sphere diameter

As discussed in section 2, the trial \( P_{hs}(q_N | r_d) \) that is “closest” to the “exact” \( P(q_N) \) is found by maximizing the relative entropy,

\[
S[P_{hs}|P] = - \int dq_N P_{hs}(q_N | r_d) \log \frac{P_{hs}(q_N | r_d)}{P(q_N)} \leq 0.
\] (34)

Substituting Eqs. (14) and (25) we obtain

\[
S[P_{hs}|P] = \beta [F - F_{hs} - (U - U_{hs})_{hs}] \leq 0,
\] (35)

where \( \langle \cdots \rangle_{hs} \) is computed over the hard-sphere distribution \( P_{hs}(q_N | r_d) \). Eq. (35) can be rewritten as

\[
F \leq F_U \overset{\text{def}}{=} F_{hs} + (U - U_{hs})_{hs},
\] (36)

which shows that maximizing \( S[P_{hs}|P] \) is equivalent to minimizing \( F_U \) over all diameters \( r_d \). Thus, the variational approximation to the free energy is

\[
F(T, V, N) \approx F_U(T, V, N | r_m) \overset{\text{def}}{=} \min_{r_d} F_U(T, V, N | r_d),
\] (37)
where \( r_m \) is the optimal diameter.

To calculate \( F_U \) use

\[
\langle U - U_{hs} \rangle_{hs} = \frac{1}{2} \int d^3r d^3r' \ n_{hs}^{(2)}(r, r') [u(r - r') - u_{hs}(r - r'|r_d)] ,
\]

(38)

where \( n_{hs}^{(2)}(r, r') = \langle \hat{n}^{(2)}(r, r') \rangle_{hs} \). But \( u_{hs}(r - r'|r_d) = 0 \) for \(|r - r'| \geq r_d\) while \( n_{hs}^{(2)}(r, r') = 0 \) for \(|r - r'| \leq r_d\), therefore

\[
F_U = F_{hs} + \langle U \rangle_{hs}
\]

(39)

with

\[
\langle U \rangle_{hs} = \frac{1}{2} N \rho \int d^3r \ u(r) g_{hs}(r \mid r_d),
\]

(40)

where we have assumed that the fluid is isotropic and homogeneous, \( n_{hs}^{(2)}(r, r') = n_{hs}^{(2)}(|r - r'|) \), and introduced the hard-sphere radial distribution function

\[
g_{hs}(r \mid r_d) \overset{\text{def}}{=} \frac{n_{hs}^{(2)}(r)}{\rho^2}.
\]

(41)

Notice that the approximation does not consist of merely replacing the exact free energy \( F \) by a hard-sphere free energy \( F_{hs} \) which does not include the effects of long range attraction; \( F \) is approximated by \( F_U(r_m) \) which includes attraction effects through the \( \langle U \rangle_{hs} \) term in eq. (39). This addresses the first of the two objections mentioned earlier: the real fluid with interactions given by \( u \) is not being replaced by a hard-sphere fluid with interactions given by \( u_{hs} \): it is just the probability distribution that is being replaced in this way.

The internal energy is approximated by \( \langle H \rangle_{hs} = \frac{3}{2} N k_B T + \langle U \rangle_{hs} \) and not by \( \langle H_{hs} \rangle_{hs} = \frac{3}{2} N k_B T \).

To calculate \( \langle U \rangle_{hs} \) it is convenient to write it in terms of \( V(s) \), the inverse Laplace transform of \( ru(r) \),

\[
xu(xr_d) = \int_0^\infty ds \ V(s)e^{-sx}.
\]

(42)

For example, for a Lennard-Jones potential,

\[
u(r) = 4 \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right],
\]

(43)

we have

\[
V(s) = 4 \varepsilon \left[ \left( \frac{\sigma}{r_d} \right)^{12} \frac{s^{10}}{10!} - \left( \frac{\sigma}{r_d} \right)^6 \frac{s^4}{4!} \right].
\]

(44)
Then, using eq. (39) and eq. (27) gives

\[
\langle U \rangle_{hs} = 12N\eta \int_0^\infty ds \, V(s)G(s).
\] (45)

Finally, it remains to minimize \( F_U \) in eq. (39) to determine the optimal diameter \( r_m \). This is done numerically; an explicit example for Argon is calculated in section 5.

As mentioned earlier the problem with the approach outlined above is that it fails to take the softness of the repulsive core into account. This flaw is manifested in a less satisfactory prediction of thermodynamic variables at high temperatures, and also, as will be shown by the numerical calculations in section 6, in a poor prediction of the radial distribution function.

5 Beyond the Variational Principle

The ME method as pursued in the last section has led us to determine an optimal value of the hard-sphere diameter. Next we consider whether the correct choice should have been some other value \( r_d = r_m + \delta r \) rather than the optimal \( r_d = r_m \). As discussed in section 2.3, this is a question about the probability of \( r_d \), \( P_d(r_d) \). Thus, we are uncertain not just about \( q_N \) but also about \( r_d \) and what we actually seek is the joint probability of \( q_N \) and \( r_d \), \( P_J(q_N, r_d) \). Once this joint distribution is obtained our best assessment of the distribution of \( q_N \) is given by the marginal over \( r_d \),

\[
P_{hs}(q_N) \quad \text{def} \quad \int dr_d \, P_J(q_N, r_d)
= \int dr_d \, P_d(r_d)P_{hs}(q_N | r_d).
\] (46)

By recognizing that diameters other than \( r_m \) are not ruled out and that a more honest representation is an average over all hard-sphere diameters we are effectively replacing the hard spheres by a soft-core potential.

However, we should emphasize that the distribution over the hard-sphere diameters \( P_d(r_d) \) is not being introduced in an ad hoc way in order to account for the softness of the LJ potential. The introduction of \( p(\theta) \) in general (section 2.3), and of \( P_d(r_d) \) in particular, are mandated by the ME method. The distribution \( p(\theta) \) would also arise if one were trying to find an ME approximation to other problems which do not involve hard spheres at all.

The distribution of diameters is given by eq. (11)

\[
P_d(r_d)dr_d = e^{S[P_{hs}|P]} \zeta \frac{1}{\sqrt{2\pi \gamma}} e^{-\beta F_U} \zeta_U \gamma^{1/2} (r_d) dr_d = e^{-\beta F_U} \zeta_U \gamma^{1/2} (r_d) dr_d,
\] (47)

where \( S[P_{hs}|P] = \beta (F - F_U) \), the partition functions \( \zeta \) and \( \zeta_U \) are given by

\[
\zeta = e^{\beta F} \zeta_U \quad \text{with} \quad \zeta_U = \int dr_d \, \gamma^{1/2} (r_d) e^{-\beta F_U},
\] (48)
and the natural distance \( d^2 = \gamma(r_d)dr_d^2 \) in the space of \( r_d \)s is given by the Fisher-Rao metric,

\[
\gamma(r_d) = \int dq_N P_{hs}(q_N | r_d) \left( \frac{\partial \log P_{hs}(q_N | r_d)}{\partial r_d} \right)^2 .
\]  

(49)

The remaining problem in the above equations is the calculation of the Fisher-Rao measure \( \gamma^{1/2} \) and this is conveniently done by considering the entropy of \( P_{hs}(q_N | r_d') \) relative to \( P_{hs}(q_N | r_d) \). A straightforward differentiation shows that

\[
- \frac{\partial^2 S [P_{hs}(\cdot | r_d')] P_{hs}(\cdot | r_d)]}{\partial r_d^2} \bigg|_{r_d'=r_d} = \gamma(r_d).
\]  

(50)

Substituting the distributions \( P_{hs}(q_N | r_d') \) and \( P_{hs}(q_N | r_d) \) gives

\[
S [P_{hs}(\cdot | r_d')] P_{hs}(\cdot | r_d)] = \beta \left( F_{hs} | r_d' \right) - \left( U_{hs} | r_d' \right) ,
\]  

(51)

where \( \langle \cdots \rangle_{r_d'} \) is the average over \( P_{hs}(q_N | r_d') \). As we argued above eq. (53) the expectation of the potential energy \( \langle U_{hs}(r_d') \rangle_{r_d'} \) vanishes because the product \( u(r | r_d')g_{hs}(r | r_d') \) vanishes for both \( r < r_d' \) and \( r > r_d' \). Similarly, \( \langle U_{hs}(r_d) \rangle_{r_d'} = 0 \) when \( r_d' > r_d \). However, when \( r_d' < r_d \) the expectation \( \langle U_{hs}(r_d) \rangle_{r_d'} \) diverges, \( S \) is not defined and eq. (50) is not applicable. We can argue our way out of this quandary by pointing out that the divergence is a consequence of the unphysical idealization involved in taking a hard-sphere potential seriously. For more realistic continuous potentials the distance between \( r_d' = r_d + dr_d \) and \( r_d \) is the same as the distance between \( r_d' = r_d - dr_d \) and \( r_d \). We can then always choose \( r_d' \geq r_d \) and define \( \gamma(r_d) \) in eq. (51) as the limit \( r_d' = r_d + 0^+ \). Then, using eq. (52), we have

\[
\gamma(r_d) = \beta \frac{\partial^2 F_{hs}(r_d')}{\partial r_d^2} \bigg|_{r_d'=r_d+0^+} = N \pi r_d^2 \frac{4 + 9 \eta - 4 \eta^2}{(1 - \eta)^4} .
\]  

(52)

To summarize, the distribution of diameters \( P_d(r_d) \) is given by eq. (47) with \( F_U \) given by Eqs. (53) (55) and \( \gamma \) given by (52). Our best approximation to the "exact" \( P(q_N) \) is the \( P_{hs}(q_N) \) given in eq. (40). The corresponding best approximation to the radial distribution function is

\[
\bar{g}_{hs}(r) = \int dr_d P_d(r_d) g_{hs}(r | r_d) .
\]  

(53)

Since \( \bar{g}_{hs}(r) \) takes into account soft-core effects while \( g_{hs}(r | r_m) \) does not, we expect that it will lead to improved estimates for all other thermodynamic quantities. However, there is a problem. Since the free energy \( F_U \) is an extensive quantity, \( F_U \propto N \), for large \( N \) the distribution \( P_d(r_d) \sim \exp -\beta F_U \) is very sharply peaked at the optimal diameter \( r_m \). This result must be interpreted...
with care: when choosing a single optimal diameter for a macroscopic fluid sample we find that ME confers overwhelming probability to the optimal value. This is not surprising. The same thing happens when we calculate the global temperature or density of a macroscopic sample: standard textbook results predict that fluctuations about the expected value are utterly negligible. And yet fluctuations can be important. For example, for small fluid samples, or when we consider the local behavior of the fluid, fluctuations are not merely observable but can be large. Local fluctuations can be appreciable while global fluctuations remain negligible. The question then, is whether these local fluctuations are relevant to the particular quantities we want to calculate. We argue that they are.

The radial distribution function $g(r)$ is the crucial quantity from which all other thermodynamic variables are computed. But from its very definition as the probability that given an atom at a certain place another atom will be found at a distance $r$, it is clear that $g(r)$ refers to purely local behavior and should be affected by local fluctuations. To the extent that the optimal $r_m$ depends on temperature and density we expect that local temperature and/or density fluctuations would induce local diameter fluctuations as well.

The extended analysis in this section does not yet allow us to pursue the question of local diameter fluctuations in a satisfactory manner. As we mentioned earlier the ME method is quite rigid in that the only freedom it allows is the choice of trial distributions. A proper analysis of diameter fluctuations would require enlarging the family of trial distributions to allow for spatial inhomogeneities in the diameters of the hard spheres. It may be worthwhile spelling out one possible such enlargement. We could imagine a trial model where the molecules are hard spheres with a diameter that depends on their location $r_d(\vec{r})$. As a molecule moves around its diameter shrinks and expands according to a prescribed function $r_d(\vec{r})$ which thus acquires the character of an external “field”. To each possible choice of the diameter field $r_d(\vec{r})$ there corresponds one trial distribution. This means that instead of a one-dimensional family of trials labelled by the single parameter $r_d$ we would have to deal with an infinite-dimensional family labeled by the fields $r_d(\vec{r})$. One should remark that these trial distributions do not describe any “physical system but this in itself is not a problem. The ME method does not attempt to approximate one physical system by another physical, albeit idealized system; it just attempts to approximate one mathematical distribution by another; there is no requirement that the latter be interpretable in terms of physically realizable Hamiltonians. The real problem, of course, is that these inhomogeneous trial models are not (at present) sufficiently tractable. However, we could divide the fluid into mesoscopic cells and consider trial models where the diameters $r_d(i)$ are uniform within each cell $i$, which allows a local Percus-Yevick approximation. The ME method would then be applied to determine not only the distribution of diameters within each cell but also the optimal size of the cells. This is a development we plan to pursue in future work.

For the purpose of this paper, however, we can quickly estimate the effects of local fluctuations by pointing out that the size of the region (i.e., the size of
the cell) that is locally relevant to the calculation of \( g(r) \) contains an effective number of atoms \( N_{\text{eff}} \) that can be estimated directly from a feature of the exact RDF that turns out to be known. (What we are doing is making the best use of information that happens to be available, which is quite in the spirit of our information theory-maximum entropy approach.)

The basic idea is intuitively simple: at very short distances the form of the true, exact RDF \( g(r) \) is dominated by the repulsive part of the potential. If the size of the molecule is given by the Lennard-Jones parameter \( \sigma \), eq.(43), the asymptotic form of \( g(r) \) is given by

\[
g(r) \to e^{-\beta u(r)} \quad \text{for} \quad r \ll \sigma .
\]  

(54)

For a sufficiently dilute gas \( g(r) \approx e^{-\beta u(r)} \) holds for all distances \( r \); for dense fluids eq.(54) is valid only for \( r \to 0 \). (This follows from a clever trick due to Percus which allows one to write an exact expression for the two-particle distribution function for a fluid in terms of the single particle density of the same fluid placed in a suitable external potential \( [32] \).) A fluid of hard spheres gives \( g(r|_{rd}) = 0 \) for \( r < rd \) and cannot reproduce the behavior (54). However, once we recognize that we can use a statistical mixture, eq.(46), we can tune the size \( N_{\text{eff}} \) of the cell and thereby change the width of \( P_{\text{d}}(rd) \) so that the radial distribution function \( \bar{g}_{\text{hs}}(r) \) of (53) reproduces the known short-distance behavior. This we proceed to do in the next section.

6  An example: Lennard-Jones “Argon”

One of the difficulties in testing theories about fluids against experimental data is that it is not easy to see whether discrepancies are to be blamed to a faulty approximation or to a wrong intermolecular potential. This is why theories are normally tested against molecular dynamics numerical simulations where there is control over the intermolecular potential. In this section we compare ME results against simulation results \( [25] \) for a fluid of monatomic molecules interacting through a Lennard-Jones potential, eq.(43). The parameters \( \varepsilon \) and \( \sigma \) (the depth of the well, \( u|_{\text{min}} = -\varepsilon \), and the radius of the repulsive core, \( u(\sigma) = 0 \), respectively) are chosen to model Argon: \( \varepsilon = 1.03 \times 10^{-2} \) eV and \( \sigma = 3.405 \) Å.

6.1  The free energy \( F_U \)

Figure \( \text{A} \) shows the free energy \( F_U/Nk_B T \) as a function of hard-sphere diameter \( rd \) for Argon at a fixed density of \( \rho a^3 = 0.65 \) for different temperatures. Figure \( \text{B} \) shows \( F_U/Nk_B T \) as a function of \( rd \) for several densities at fixed \( T = 107.82 \) K. Since the critical point for Argon is at \( T_c = 150.69 \) K and \( \rho_c a^3 = 0.33 \) all these curves, except that at 300 K, lie well within the liquid phase. The increase of \( F_U/Nk_B T \) for high values of \( rd \) is due to short range repulsion between the hard spheres described by \( F_{\text{hs}}/Nk_B T \). The increase for low \( rd \) is due to the Lennard-Jones short-range repulsion as described by \( \langle U \rangle_{\text{hs}}/Nk_B T \).
The best $r_d$ is that which minimizes $F_U$ and depends both on temperature and density. The best diameter decreases as the temperature increases because atoms with higher energy can penetrate deeper into the repulsive core. The dependence with density is less pronounced.

(A) $\rho \sigma^3 = 0.65$ for different temperatures. The best $r_d$ is that which minimizes $F_U$. (B): $F_U$ as a function of $r_d$ for Argon at $T = 107.82$ K for different densities.

Figure 1: (A): The free energy $F_U$ as a function of hard-sphere diameter $r_d$ for Argon at a density of $\rho \sigma^3 = 0.65$ for different temperatures. The best $r_d$ is that which minimizes $F_U$. (B): $F_U$ as a function of $r_d$ for Argon at $T = 107.82$ K for different densities.

6.2 The distribution of diameters $P_d(r_d)$

In section 5 we argued that the effective number of molecules that is relevant to the local structure of the fluid is not the total number of molecules in the system $N$, but a smaller number, $N_{\text{eff}}$. In Fig. 2 (A) we plot the distribution of diameters $P_d(r_d)$ for different temperatures, for a fixed fluid density of $\rho \sigma^3 = 0.65$, and for an arbitrarily chosen $N_{\text{eff}} = 13500$. As expected the distribution shifts to higher diameters as the temperature decreases. Notice also that the distribution becomes narrower at lower temperatures in agreement with the fact that a hard-sphere approximation is better at low $T$.\[15\]

Figure 2 (B) shows that increasing $N_{\text{eff}}$ (with fixed density $\rho$) decreases the width of $P_d(r_d)$ (solid lines) and induces a slight shift of the whole distribution. This is due to the dependence $\sim (N_{\text{eff}} r_d)^{1/2}$ of the Fisher-Rao measure $\gamma^{1/2}(r_d)$ in Eq. (52). Figure 2 (B) also explores the influence of $\gamma^{1/2}(r_d)$ by comparing the actual distributions $P_d(r_d)$ (solid lines) with the distributions $e^{-\beta F_U(r_d)}$ (dotted lines) which are obtained by setting $\gamma^{1/2} = 1$ in Eq. (47). The effect of $\gamma^{1/2}$ is to shift the distribution slightly to higher $r_d$.

6.3 The radial distribution function

We are finally ready to calculate the radial distribution $g(r)$ for Argon. We start by estimating the number of molecules $N_{\text{eff}}$ that are locally relevant; as
Figure 2: (A): The distribution of hard-sphere diameters $r_d$ for Argon for several temperatures at density $\rho \sigma^3 = 0.65$ for $N_{\text{eff}} = 13500$. (B): $P_d(r_d)$ for various $N_{\text{eff}}$ at $T = 107.82$ K and $\rho \sigma^3 = 0.65$. By setting $\gamma^{1/2} = 1$ (dotted lines) we see that the effect of the $\gamma^{1/2}$ factor is to cause a slight shift of the distribution.

explained earlier we choose $N_{\text{eff}}$ so that our best approximation $\tilde{g}_{hs}(r)$, Eq. (53), reproduces the known short-distance behavior $e^{-\beta u(r)}$. We have found that the estimates for $N_{\text{eff}}$ need not be very accurate but that they must be obtained for each value of the temperature and density. In Fig. 3 we show an example of the short-distance behavior of $\tilde{g}_{hs}$ for three values of $N_{\text{eff}}$ at $T = 107.82$ K and $\rho \sigma^3 = 0.65$; using a chi-square fit in the range from $r = 2.9$ to $3.1$ Å the selected best value of $N_{\text{eff}}$ is around 38000.

Figure 3: Estimating $N_{\text{eff}}$ by requiring that $\tilde{g}_{hs}(r)$ have the correct short-distance behavior $e^{-\beta u(r)}$.

In Figs. 4(A)-(D) we compare three different ways to calculate the RDF. The solid line is Verlet’s molecular dynamics simulation [25]; it plays the role of experimental data against which we compare our theory. The dotted line
is $g_{hs}(r|r_m)$ for the hard-sphere fluid with optimal diameter $r_m$. This curve, calculated from eq. (27), is also the result of the variational method and coincides with the ME result for a macroscopically large $N_{\text{eff}} = N$. The dashed line is the averaged $\bar{g}_{hs}(r)$ of the extended ME analysis. Figs. 4(A)-(C) were plotted at three different temperatures $T = 107.82, 124.11$ and $189.76$ K at the density $\rho \sigma^3 = 0.65$. Fig. 4(D) we changed the density and the temperature to $\rho \sigma^3 = 0.5$ and $T = 162.93$ K. The agreement between the ME curve and Verlet’s data is good. The vast improvement over the simpler variational method calculation is clear.

Figure 4: The radial distribution function for (a) the hard-sphere fluid with optimal diameter $r_m$; (b) Verlet’s molecular dynamics simulation; and (c) the improved ME analysis, for Argon at (A): density $\rho \sigma^3 = 0.65$, temperature $T = 107.82$ K, and effective particle number $N_{\text{eff}} = 38000$. (B): $\rho \sigma^3 = 0.65$, $T = 124.11$ K, and $N_{\text{eff}} = 40000$. (C): $\rho \sigma^3 = 0.65$, $T = 189.76$ K, and $N_{\text{eff}} = 50000$. (D): $\rho \sigma^3 = 0.5$, $T = 162.93$ K, and $N_{\text{eff}} = 62000$. One might be tempted to dismiss this achievement as due to the adjustment of the parameter $N_{\text{eff}}$ but this is not quite correct: $N_{\text{eff}}$ has not been adjusted, it
has been calculated on the basis of information that is actually available. Indeed, despite the fact that the hard-sphere trial solutions that we employ are mere approximations, the functional form of the whole curve $\bar{g}_{hs}(r)$ in eq.(53) is reproduced quite well.

6.4 The equation of state

Finally we use the RDF to calculate the equation of state from the pressure equation, Eq. (21). In Fig. 5 we compare the equation of state derived from the $g(r)$ obtained from Verlet’s simulation with calculations using the ME and variational methods and the perturbative theories of Barker and Henderson [15] and of Weeks, Chandler and Anderson [22], at $T = 161.73$ K. The ME results constitute a clear improvement over the plain variational calculation. For low densities all four methods agree with each other but differ from the simulation. A better agreement in this region would probably require a better treatment of two-particle correlations at long distances. At intermediate densities the best agreement is provided by the ME and BH results, while the WCA theory seems to be the best at high densities. Also shown in Fig. 5(A) are experimental data on Argon [33]. The discrepancy between the experimental curve and the Verlet simulation is very likely due to the actual potential not being precisely of the Lennard-Jones type.

In Fig. 5(B) we plot the ME equation of state for three different isotherms ($T = 137.77$, 161.73 and 328.25K). To compare to the simulation of Hansen and Verlet [26] we plot $\beta P$ (rather than $\beta P/\rho$) as a function of density $\rho \sigma^3$ because this kind of plot exhibits the characteristic van der Waals loop that signals the liquid-gas transition as the temperature drops. A more exhaustive exploration lies, however, outside the scope of this paper.

7 Conclusion

The goal of this paper has been to use the ME method to generate approximations and show that this provides a generalization of the Bogoliubov variational principle. This addresses a range of applications that lie beyond the scope of the traditional MaxEnt. To test the method we considered simple classical fluids.

When faced with the difficulty of dealing a system described by an intractable Hamiltonian, the traditional approach has been to consider a similar albeit idealized system described by a simpler more tractable Hamiltonian. The approach we have followed here departs from this tradition: our goal is not to identify an approximately similar Hamiltonian but rather to identify an approximately similar probability distribution. The end result of the ME approach is a probability distribution which is a sum or an integral over distributions corresponding to different hard-sphere diameters. While each term in the sum is of a form that can be associated to a real hard-sphere gas, the sum itself is not of the form $\exp - \beta H$, and cannot be interpreted as describing any physical system.
Figure 5: (A): The Argon equation of state calculated using the ME method, the variational method and the perturbative theories of BH and WCA are compared to the Verlet simulation at $T = 161.73$ K. Also shown are Levelt’s experimental results. (B): $\beta P$ versus the reduced density $\rho_0^3$ calculated using the ME method (solid line) and compared to the Hansen-Verlet simulation for three different isotherms. The graph shows the appearance of the liquid-gas van der Waals loop as the temperature drops.

As far as the application to simple fluids is concerned the results achieved in this paper represent progress but further improvements are possible by using better approximations to the hard-sphere fluid and by choosing a broader family of trial distributions. We argued that an important improvement would be achieved if one could extend the trial probability distributions to include inhomogeneities in the hard sphere diameters. This would lead to a systematic, fully ME method for the determination of the effective number of particles $N_{\text{eff}}$ that are locally relevant.

Many perturbative approaches to fluids had been proposed, and a gradual process of selection over many years of research led to the optimized theories of BH and WCA. The variational approach was definitely less satisfactory than these “best” perturbation theories. With our work, however, the situation has changed: the ME-improved variational approach offers predictions that already are competitive with the best perturbative theories. And, of course, the potential for further improvements of the ME approach remains, at this early date, far from being exhausted.

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