SEMIGRAND CANONICAL MONTE CARLO SIMULATION; INTEGRATION ALONG COEXISTENCE LINES

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I. INTRODUCTION

This chapter reviews two topics: the simulation of mixtures in a semigrand ensemble, and the evaluation of phase coexistence lines by the Gibbs-Duhem integration method. The notion of a semigrand ensemble has its roots in the work of Griffiths and Wheeler [1], who developed and applied it for the study of critical phenomena in mixtures (one might even argue that the concept goes back to the Ising model). The idea was rekindled in the work of Brianzo and Glandt [2], which formed the foundation for the first (off-lattice) Monte Carlo simulations in the ensemble, conducted by Kofke and Glandt [3-5]. At about the same time Sariban and Binder [6] applied semigrand Monte Carlo simulation to study a lattice model of polymer mixtures. Since then the ensemble has surfaced in a variety of places, some of which will be described in the review to follow. The Gibbs-Duhem integration method was inspired by the Gibbs ensemble methodology of Panagiotopoulos [7]. The approach was conceived by the author in 1992 during a one-month visit with the research group of Daan Frenkel in the Netherlands. The method has found a niche in applications to phase equilibria involving solids and ordered phases, although it is equally applicable to other phase-coexistence phenomena.

These two topics that form the subject of this review are disconnected in general, but there are important instances in which they may be used together to good effect. Most notably, Gibbs-Duhem integrations that trace coexistence lines for mixtures rely on the semigrand formalism, so it is appropriate that we review the latter first. We begin each review by discussing the basic idea underlying the simulation methodology, followed by a presentation of the formalism needed for its application. We review details of the methods before going on to summarize the applications each has seen to date. We finish the chapter with a detailed example of an application of the Gibbs-Duhem integration methodology.

II. SIMULATION IN SEMIGRAND ENSEMBLES

A. Concept

An ensemble is characterized by its independent variables, specifically, those thermodynamic quantities that the investigator uses to define the state of the system [8]. A familiar example is the choice between isochoric (fixed-volume) and isobaric (fixed-pressure) ensembles. The choice is usually made as a matter of convenience—data may be more easily analyzed in one or the other formalism, or an experiment may be more easily constructed with one or the other quantity held fixed. Implicit in the choice of an independent variable is the selection of its conjugate dependent variable [9]. Thus in taking the pressure as a chosen quantity, one simultaneously assigns the volume (or density) to a dependent role; it is given as an ensemble average, and it must be measured (or calculated) for its value to be known.

The notion of a semigrand ensemble arises when this decision is made in the context of mixture composition variables. Experience tells us that mole numbers or mole fractions are the most natural way to specify a mixture composition, and indeed anyone unfamiliar with the formalism of thermodynamics may not conceive that there exists an alternative. Of course, the component chemical potentials provide just this alternative, and their selection as independent thermodynamic variables in lieu of mole numbers is no less valid than the substitution of the pressure for the volume. In fact there are very familiar physical manifestations of semigrand ensembles in Nature. For example, in osmotic systems the amount of one component is not fixed, but takes a value to satisfy equality of chemical potential with a solvent bath. Another example is seen in systems undergoing chemical reaction, where the amounts of the various components are subject to chemical equilibrium.

A marvelous feature of molecular simulation (and thermodynamics in general) is that one need not work with the formalism (ensemble) that is most easily realized physically. Thus one may invoke a semigrand ensemble outside of applications involving osmotic or chemical equilibria. Often this option proves very convenient and desirable. The main point to keep in mind is that one fixes the chemical potential of some components of the mixture and one measures (or calculates) the composition. To proceed, one must surmount the minor conceptual hurdle of working with a system of variable composition absent any plausible reaction mechanism (or even stoichiometry). One can then play many variations on this theme.

B. Formalism

1. Ensembles

A natural starting point is the fundamental equation in a canonical ensemble of c components, for which the independent variables are the temperature T, the volume V, and the number of molecules of each species, N_j, j = 1, ..., c; the potential is the Helmholtz free energy A

$$A = U - TS = -PV + \sum_{j=1}^{c} N_j \mu_j$$  \hspace{1cm} (2.1a)

$$d(\beta A) = U \ d\beta - \beta P \ dV + \sum_{j=1}^{c} \beta \mu_j \ dN_j$$  \hspace{1cm} (2.1b)
where \( U \) is the internal energy, \( S \) is the entropy, \( P \) is the pressure, and \( \mu_i \) is the chemical potential of species \( i \); the reciprocal temperature is \( \beta = 1/k_B T \), where \( k_B \) is Boltzmann's constant. The latter equality in Eq. (2.1a) is a statement of Euler's relation. Legendre transformation [9] of all the chemical terms yields the grand-canonical ensemble, for which the independent variables are \( T, V, \) and \( \mu_i, i = 1, \ldots, c. \)

\[
L \equiv A - \sum_{j=1}^{c} N_j \mu_j = -PV
\]  

(2.2a)

\[
d(\beta L) = U \, d\beta - \beta P \, dV - \sum_{j=1}^{c} N_j \, d(\beta \mu_j)
\]  

(2.2b)

Semigrand ensembles—as the term implies—lie between the canonical and the full grand-canonical ensembles. They are formulated by Legendre transformation of some, rather than all, of the chemical terms. Thus we derive an osmotic semigrand ensemble by the most straightforward variant; we transform some terms \( (j = 1 \cdots m) \), and leave others \( (j = m + 1, \ldots, c) \):

\[
Y_{\mu} \equiv G - \sum_{j=1}^{m} N_j \mu_j = \sum_{j=m+1}^{c} N_j \mu_j
\]  

(2.3a)

\[
d(\beta Y_{\mu}) = H \, d\beta + \beta V \, dP + \sum_{j=m+1}^{c} \beta \mu_j \, dN_j - \sum_{j=1}^{m} N_j \, d(\beta \mu_j)
\]  

(2.3b)

We prefer to continue the development using isobaric ensembles, which can be done with semigrand ensembles but not with the fully grand ensemble. We have exercised this option in the Eq. (2.3). Here \( G = A - PV \) is the Gibbs free energy and \( H = U + PV \) is the enthalpy.

Often it is advantageous to group some of the chemical terms together before applying the transformation. For example, addition and subtraction of \( \sum_{j=1}^{c} \beta \mu_j \, dN_j \) leaves Eq. (2.1) looking different although it is, of course, inherently unchanged (except we now present its isobaric form):

\[
d(\beta G) = H \, d\beta + \beta V \, dP + \beta \mu_1 \, dN + \sum_{j=2}^{c} \beta \Delta \mu_j \, dN_j
\]  

(2.4)

where \( \Delta \mu_j = \mu_j - \mu_1 \) and we have exploited \( dN = \sum_{j} dN_j \). In writing this form we have singled out a component (labeled "1") from the others. The selection of this "reference" component is arbitrary, although in specific applications a choice may present itself naturally. Legendre transformation can be applied to this reformulation to yield a new ensemble, for which the set of chemical potential differences \( \Delta \mu_i \) is among the independent variables:

\[
Y_{Y_{\mu}} \equiv G - \sum_{j=2}^{m} N_j \Delta \mu_j = N\mu_1
\]  

(2.5a)

\[
d(\beta Y_{Y_{\mu}}) = H \, d\beta + \beta V \, dP + \beta \mu_1 \, dN - \sum_{j=2}^{m} N_j \, d(\beta \Delta \mu_j)
\]  

(2.5b)

A unique feature of this ensemble is that the total number of molecules \( N \) is an independent quantity, even though no species mole numbers are specified. This outcome is appealing because it means that a simulation can be conducted in this "isomolar semigrand" ensemble without requiring trials in which molecules are inserted in or deleted from the simulation volume. Such steps are often problematic because they can be difficult to accomplish without causing a very large fluctuation in the internal energy; in a Monte Carlo simulation this means that such trials are rarely accepted. Also, in simulating solids it is desirable to work at constant \( N \) to avoid problems with lattice defects, and even more severe problems associated with the use of periodic boundaries.

The isomolar semigrand ensemble is a specific instance of the more general case of semigrand ensembles that are formed while meeting certain constraints, such as fixing the total number of segments in a polymer mixture [10], or fixing the surface area in a model colloid. In most cases of practical interest the constraints depend linearly on the mole numbers. If there are \( r \) such constraints, they can be written

\[
\sum_{j=1}^{c} g_j^{(k)} N_j = G_k, \quad k = 1, \ldots, r
\]  

(2.6)

where \( g_j^{(k)} \) is the multiplier for \( j \)th component in the \( k \)th constraint, and \( G_k \) quantifies the constraint. For example, if the \( k \)th constraint fixes the total number of segments in a polymer mixture, then \( g_j^{(k)} \) represents the number of segments in a species-\( j \) chain, and \( G_k \) is the total number of segments in the system. Of course, we require \( r \leq c \). We choose \( r \) of the \( c \) components arbitrarily as reference species, and we can solve the set of linear equations for their molecule numbers in terms of the \( G_k \). The general form of the
solution defines the coefficients $h_{i}^{(j)}$

$$N_{j} = \sum_{k=1}^{r} h_{k}^{(j)} G_{k} + \sum_{l=1}^{c} h_{l}^{(j)} N_{l}, \quad j = 1, \ldots, r$$  \hspace{1cm} (2.7)$$

where for convenience of notation we have taken the first $r$ components as the reference species. When this result is substituted into the fundamental equation, we Legendre-transform with respect to the non-reference-species molecule numbers to obtain the “constrained semigrand” ensemble

$$Y_{c} = G - \sum_{j=r+1}^{c} N_{j} \mu_{j}^{c} = \sum_{k=1}^{r} \beta \mu_{k}^{(0)} G_{k}$$  \hspace{1cm} (2.8a)$$

$$d(\beta Y_{c}) = H \, d\beta + \beta V \, dP + \sum_{k=1}^{r} \beta \mu_{k}^{(0)} \, dG_{k} - \sum_{j=r+1}^{c} N_{j} \, d(\beta \mu_{j}^{c})$$  \hspace{1cm} (2.8b)$$

where

$$\mu_{j}^{c} = \mu_{j} + \sum_{k=1}^{r} h_{k}^{(j)} \mu_{k}, \quad \mu^{(0)} = \sum_{j=1}^{r} h_{j}^{(0)} \mu_{j}$$  \hspace{1cm} (2.8c)$$

Our outline for formulating semigrand ensembles with constraints follows naturally from Krishna Pant and Theodorou’s [10] development for polymer mixtures.

Another way to regroup the chemical terms may be suggested by the occurrence of reaction equilibria in the system of interest [11,12]. The resulting formulation is a special case of the constrained semigrand ensemble just described, but it has simplifying features and established notation that make its separate description worthwhile. If the chemical reaction is written in the general form

$$\sum_{i} \nu_{i} M_{i} = 0$$  \hspace{1cm} (2.9)$$

where $\nu_{i}$ is the stoichiometric coefficient (positive for product, negative for reactant) of component $M_{i}$, then the number of moles of a particular species will be

$$N_{i} = N_{i}^{o} + \nu_{i} \xi$$  \hspace{1cm} (2.10)$$

where $N_{i}^{o}$ is the initial (original) number of moles of species $i$, and $\xi$ is the extent of reaction. The $dN_{i}$ in the fundamental equation are then written in terms of the $N_{i}^{o}$ and $\xi$, thus (assuming no inert components)

$$d(\beta G) = H \, d\beta + \beta V \, dP + \sum \beta \mu_{i} \, dN_{i}^{o} + (\sum \nu_{i} \beta \mu_{i}) \, d\xi$$  \hspace{1cm} (2.11)$$

Legendre transformation with respect to the last term yields a “reactive semigrand” ensemble

$$Y_{c} = G - (\sum \nu_{i} \beta \mu_{i}) \xi$$

$$d(\beta Y_{c}) = H \, d\beta + \beta V \, dP + \sum \mu_{i} \, dN_{i}^{o} - \xi \, (\sum \nu_{i} \beta \mu_{i})$$  \hspace{1cm} (2.12)$$

Setting the new independent variable $\sum \nu_{i} \beta \mu_{i}$ to zero puts the ensemble in correspondence with the actual chemical equilibrium that inspires its construction. Any other choice would correspond to a completely fictitious field that artificially drives the reaction one way or the other. We will not consider this variant in any detail as ensembles for reacting systems are presented more fully in the chapter by Johnson.

2. Fugacity and Fugacity Fraction

At times it is convenient to work with the fugacity in lieu of the chemical potential. The fugacity $f_{i}$ of a species in a mixture is defined [13]

$$\beta \mu_{i} = \beta \mu_{i}^{c}(\beta) + \ln f_{i}$$  \hspace{1cm} (2.13)$$

where $\mu_{i}^{c}$ is the chemical potential of species $i$ in the ideal-gas state at unit pressure and unit mole fraction, and (as indicated) is a function of temperature alone. Consequently differential changes in the chemical potential can be written to group this temperature-explicit contribution with the enthalpic term, using

$$d(\beta \mu_{i}) = h_{i}^{f} \, d\beta + d \ln f_{i}$$  \hspace{1cm} (2.14)$$

where $h_{i}^{f}$ is the ideal-gas enthalpy per molecule for component $i$. Thus, for example, Eqs. (2.3) can be written

$$\sum_{j=1}^{c} x_{j} \, d \ln f_{j} = h_{r} \, d\beta + \beta \nu \, dP - \sum_{j=2}^{c} x_{j} \, d \ln f_{j}$$  \hspace{1cm} (2.15)$$

where $h_{r} = h - \sum_{j} x_{j} h_{j}^{f}$ is the residual enthalpy per molecule, $\nu$ is the volume per molecule, and $x_{j}$ is the mole fraction of species $j$. We have
applied a few additional manipulations to cast this result in the form of a Gibbs-Duhem equation, which will be of use to the discussion in Section III.

The final variation of this formalism we consider employs the fugacity fraction as an independent variable \([14]\). The fugacity fraction of component \(i\) \(\xi_i\) is defined as

\[
\xi_i = \frac{f_i}{\sum_{j=1}^{\infty} f_j}
\]  

(2.16)

The fugacity fraction is a convenient quantity because it is bounded between zero and unity, and it has a qualitative correspondence with the mole fraction. The set of fugacity fractions are not independent, as they must sum to unity. Instead the complete set of independent chemical variables is specified by \(m - 1\) fugacity fractions together with the sum \(\sum_{j=1}^{\infty} f_j\).

In terms of fugacity fractions the isomolar semigrand ensemble of Eq. (2.5) is expressed

\[
d \ln \left[ \sum_{i=1}^{\infty} f_i \right] = \Lambda_i d\beta + \beta\nu dP - \sum_{n=1}^{\infty} \frac{\sum_{n=1}^{\xi_n}}{\sum_{n=1}^{\xi_n}} d\xi_n
\]  

(2.17)

The equation is written this way because it has an appealing symmetry, but it should be remembered that the \(d\xi_n\) terms are not independent. So, for example, with \(c = 2\), \(d\xi_1 = -d\xi_2\), and the equation is

\[
d \ln (f_1 + f_2) = \Lambda_i d\beta + \beta\nu dP - \frac{\xi_2 - \xi_1}{\xi_2(1 - \xi_2)} d\xi_2
\]  

(2.18)

3. Partition Functions

It is necessary to know the form of the partition functions to construct transition probabilities that properly sample the ensemble. For instructional purposes we record here the (semiclassical) partition functions that correspond to the osmotic and isomolar semigrand ensembles described above. In both ensembles one must average over moles of the Legendre-transformed species. Thus the osmotic semigrand ensemble partition function is

\[
Y_r = \left[ \prod_{j=m+1}^{\infty} \left( \frac{q_j}{\Lambda_j^2} \right) \right] \sum_{n_1=0}^{\infty} (\beta f_1)^{N_1} \sum_{n_2=0}^{\infty} (\beta f_2)^{N_2} \cdots \sum_{n_m=0}^{\infty} (\beta f_m)^{N_m} \\
\times \left[ \prod_{j=1}^{\infty} N_j \right]^{-1} \int dV \int dt^{(N)} \exp \left[ -\beta(U + PV) \right]
\]  

(2.19)

where \(q_j\) is the molecular partition function for species \(j\) and \(\Lambda_j\) is its corresponding de Broglie wavelength; conveniently, for the osmotic species these contributions are canceled when the fugacity is inserted in place of the chemical potential. The isomolar semigrand partition function is written in a form similar to that above, but each sum over mole numbers must recognize the upper limit of \(N\) total molecules. This is cumbersome, and it is preferable to apply an analytic trick that converts the \(c\) coupled-limit sums over \(N_j\) into \(N\) uncoupled sums—one for each molecule—over species identities \(I_j\) [2]. The result is particularly clean when written in terms of fugacity fractions, which absorb all the molecular and momentum partition functions

\[
Y_r = \frac{1}{N!} \sum_{I_1=1}^{\infty} \sum_{I_2=1}^{\infty} \cdots \sum_{I_{c-2}=1}^{\infty} \left[ \prod_{I_j=1}^{\xi_j} \right] \int dV \int dt^{(N)} \\
\times \exp \left[ -\beta(U + PV) \right]
\]  

(2.20)

This transformation highlights the view in which the species identity forms another dimension—in addition to the spatial \(x\), \(y\), and \(z\) coordinates—that is sampled by each molecule. The fugacity fraction then plays the role of an external field that influences the sampling in this "direction."

C. Simulation Algorithm

Simulations in a semigrand ensemble require exploration of compositions—the average composition is a result of a semigrand simulation. In an osmotic ensemble composition sampling is conducted exactly as it is performed in a grand-canonical ensemble [15], except that insertions and deletions are not attempted for all species. Composition sampling in an isomolar semigrand ensemble is accomplished by permitting each molecule to adopt varying species identity, exactly as they adopt varying spatial coordinates to sample configuration space. There are some subtleties in the implementation. For example, the acceptance criteria differ depending on whether a molecule is chosen first, regardless of its species identity, or whether a species is first chosen, and then a molecule of that species is selected for an identity-change trial [5]. It is particularly important when working with a new ensemble [such as an instance of the constrained semigrand ensemble of Eq. (2.8)] to write down the partition function (i.e., the limiting distribution), carefully examine the trial-transition probabilities, and construct the acceptance probabilities that ensure microscopic reversibility [15]. Examples of the process have been presented several times elsewhere [5,10,16,17], and will not be repeated here. When in doubt, it is useful
to verify a proposed algorithm by performing a simulation of the ideal-gas mixture obtained when all intermolecular interactions are set to zero. The average composition taken from such a simulation can then be compared to an exact result. As a final caveat we can add that one should be careful to include any changes in the long-range correction to the potential energy when deciding acceptance of a trial identity change [18].

D. Summary of Applications

Glandt and co-workers [2–4] originally devised the (isomolar) semigrand ensemble as a means to study polydisperse mixtures. Polydisperse mixtures in principle have an infinite number of components, so their treatment by canonical-ensemble molecular simulation can only be approximate. Isomolar semigrand Monte Carlo is particularly well suited for these systems because species-identity changes can be accomplished in a continuous fashion—this, coupled with the absence of particle insertion/deletion trials, permits the simulations to converge very well. For polydisperse mixtures, the free energy and the partition function become functionals of the chemical potential difference function \( \Delta \mu(I) \). A general form for the dependence in the species identity \( I \) can be used:

\[
\beta \Delta \mu(I) = \beta \mu(I) - \beta \mu(I_0) = c_0 \ln \left( \frac{I}{I_0} \right) + c_1(I - I_0) + c_2(I - I_0)^2 + \cdots
\]

Kofke and Glandt [3,4] originally simulated systems for which \( 1/c_2 \to 0 \), \( c_1 = 0 \) (\( j \neq 2 \)) to study the “nearly monodisperse” case. Subsequently it was observed [19–21] that the “infinitely polydisperse” system for which \( c_j = 0 \) (\( j \neq 0 \)) exhibited very interesting and unusual scaling properties. During this period Stapleton et al. [18] presented semigrand simulations of polydisperse mixtures following a Schultz distribution for \( \Delta \mu(I) \) (nonzero \( c_0 \) and \( c_1 \)). Their study is weakened by the lack of a well-defined formalism, but it is correctly implemented and was more careful than Kofke and Glandt [3,4] in accounting for the long-range correction to the energy during the Markov sampling process.

Subsequent applications of semigrand methods have been numerous, as species-identity changes have become a standard practice when simulating mixtures. We would fail in an attempt to mention all such uses, so instead we will sample some of the more interesting applications and extensions. Hautman and Klein [22] examined, by molecular dynamics a “breathing” Lennard-Jones fluid of fluctuating particle diameter; the breathing modes are introduced to better model molecules that are treated as LJ atoms. Liu and Berne [23] proposed a similar treatment as a means to accelerate the equilibration of some systems. Kofke [16] used the formalism to yield the freezing diagram of three binary mixtures of hard spheres (this was before the development of the Gibbs–Duhem integration technique). Adsorption and wetting of a Lennard–Jones mixture was examined by Fan et al. [24]. The semigrand ensemble has been used often in conjunction with Gibbs ensemble simulations of phase equilibria [7,25]. Stapleton et al. [26] performed the first simulations of phase coexistence for polydisperse fluids using a semigrand formulation of the Gibbs ensemble. Interesting also are symmetric systems, in which the like intermolecular interactions are the same for both components but differ from their cross-interactions. In a semigrand formulation it is necessary to simulate only one of the two phases, as shown by application to a square-well model [27], a Lennard–Jones mixture [24], nonadditive hard spheres [28], and the Widom–Rowlinson model [29]. It is important that such simulations be performed isobarically; otherwise an unnatural suppression of fluctuations results, exacerbating finite-size effects on approach to the critical point [30]. Simulation in a semigrand ensemble can greatly enhance sampling in polymer mixtures. Representative examples include simulations on the lattice [6,31, 32], of confined thin films [33], and off-lattice [10,34]. The work of Krishna Pant and Theodoro [10] was noted above, as they used a semigrand ensemble in which the total number of monomer segments and the total number of chains are fixed, but the chains lengths occupy a distribution obtained by moving segments from one chain to another. Finally we note again that the simulation of chemically reacting systems is naturally accomplished in a semigrand ensemble. The first efforts in this direction are due to Coker and Watts [35,36] and Kofke and Glandt [5]; both studies apply only to mole-conserving reactions. This constraint was first released by Shaw [37], whose work was clarified and applied by Smith and Triska [12] and independently by Johnson et al. [11]. We refer the reader to the chapter by Johnson elsewhere in this volume for additional information on semigrand simulations of reacting mixtures.

III GIBBS-DUHEM INTEGRATION: TRACING COEXISTENCE LINES

A. Concept

Prior to the introduction of the Gibbs ensemble, the evaluation of thermodynamic phase coexistence was a tedious affair, often requiring many simulations in an attempt to locate the state point at which the temperature, pressure, and all species fugacities were equal between two phases. The identification of this state point is often troublesome even when
working with an empirical equation of state. It is all the more difficult with simulation because evaluating the thermodynamic properties at a trial solution is very expensive computationally; moreover, the evaluation of the fugacity is problematic. Two complementary approaches to fugacity evaluation are often considered [15,38,39]. Widom test-particle insertion is most convenient, as it can be conducted in a single simulation without requiring any clever biasing of configurations. Unfortunately the method is of limited reliability, and it is known to fail (more to the point, it becomes very inefficient) at high densities [40]. Complementing this approach is thermodynamic integration, which yields the fugacity through a series of simulations that connects the state of interest to some reference state of known properties. This method is very reliable, but inherently inefficient as it requires a number of simulations at “uninteresting” state points. Some efficiency can be recovered by conducting the integration in conjunction with the search for the coexistence state, but the whole procedure is still unappealing.

The key idea of the Gibbs ensemble [7,25] (GE) is that the process of searching for the coexistence point can be elegantly bundled up with the process of measuring the pressure and fugacity if the two coexisting phases are simulated simultaneously. The chemical potential measurement is done in a manner analogous to Widom insertion. The Gibbs–Duhem integration (GDI) method complements the Gibbs ensemble, in the same sense that test-particle insertion and thermodynamic integration are complementary methods for fugacity evaluation. The idea of GDI is to perform the integration along the coexistence line, which itself is being determined as the integration proceeds. As with the Gibbs ensemble, this procedure entails simultaneous simulation of the two (or more) coexisting phases. A very useful feature of the GDI method is that the coexistence line need not be of the traditional variety, and that phase equilibria may be evaluated along a multitude of path types, for example, one in which the intermolecular potential mutates from one form to another.

B. Formalism

1. Clapeyron Equations

The starting point for the formalism is the Gibbs–Duhem equation, which we write first for a pure fluid [13]:

$$d\mu = h \, d\beta + \beta \, dP$$

(3.1)

The Clapeyron equation is derived [13] by writing this formula twice, once for each of two coexisting phases α and β. Given a point on the coexistence line, one is interested in how $\beta (1/k_B T)$ and $P$ must change in concert so that the chemical potentials of the two phases change by equal amounts: $d\mu^\alpha = d\mu^\beta$. This requirement is used to eliminate $d\beta$ between the equations, and the result takes the form of a first-order differential equation

$$\left(\frac{dP}{d\beta}\right)_c \frac{\Delta h}{\beta \Delta v}$$

(3.2)

where the $c$ subscript reminds us that the derivative is taken along the saturation line. The $\Delta s$ here indicate a difference between the $\alpha$ and $\beta$ phases. The right-hand side is a complicated function of pressure and temperature, but it can be evaluated by molecular simulation without much difficulty. The essence of the method is the integration of this equation over temperature using standard methods for the numerical treatment of differential equations.

The approach has been extended in two fundamental ways: (1) one may consider variations in “field” variables [1] other than temperature and pressure; and (2) one may consider additional phases, so that (for example) three-phase coexistence lines are produced. Both extensions start with a more general form of the Gibbs–Duhem equation, which we write as follows:

$$\rho_0 \, d\phi_0 = \rho_1 \, d\phi_1 + \rho_2 \, d\phi_2 + \rho_3 \, d\phi_3 + \cdots$$

(3.3)

In this relation, $\phi_i$ is a “field” variable and $\rho_i$ is its conjugate “density” [1]. Field variables are those that must be equal among coexisting phases; examples include the temperature, pressure, fugacity fraction, or (in our interpretation) a parameter defining the intermolecular potential (such as a Lennard-Jones diameter). Examples of the corresponding conjugate density would be the molar enthalpy, molar volume, or mixture mole fraction. The “0” subscript designates the “hidden” field variable (a thermodynamic potential, or free energy) that the integration procedure is designed to keep equal between coexisting phases. With this notation the generalized Clapeyron equation for two-phase coexistence is

$$\left(\frac{d\phi_2}{d\phi_1}\right)_c \frac{\Delta (\rho_1/\rho_0)}{\Delta (\rho_2/\rho_0)}$$

(3.4)

So, for example, the isothermal variation of pressure with species 2 fugacity when integrating along coexistence in an osmotic ensemble can be read
directly from Eq. (2.15) (for c = 2)

\[
\left( \frac{dP}{d\phi} \right)_{\phi_0, T} = \frac{\Delta(x_2/x_1)}{\Delta(\beta_0/x_1)}
\]  

(3.5)

Extension to multiple-phase equilibria is straightforward, although the algebraic expressions become correspondingly more complex [13]. In the general case involving n coexisting phases, with \( \phi_1 \) selected as the independent variable, the desired \((n - 1)\) derivatives are obtained from the solution of the following system of \((n - 1)\) linear equations:

\[
\Delta(\phi) \frac{dd_0}{d\phi_1} + \Delta(\phi) \frac{dd_1}{d\phi_1} + \cdots + \Delta(\phi) \frac{dd_{n-1}}{d\phi_1} = \Delta(\phi), \quad j = 1 \ldots n - 1
\]  

(3.6)

where \( \Delta(\phi) \) indicates the difference in \( \rho_0/\rho_0 \) between phase \( j \) and phase \( n \) (selected arbitrarily). For three-phase coexistence we have

\[
\frac{dd_0}{d\phi_1} = \frac{1}{D} \left[ \Delta_0^{(2)} \Delta_1^{(1)} - \Delta_0^{(1)} \Delta_1^{(2)} \right]
\]

\[
\frac{dd_1}{d\phi_1} = \frac{1}{D} \left[ \Delta_1^{(2)} \Delta_1^{(1)} + \Delta_2^{(1)} \Delta_1^{(2)} \right]
\]

\[
D \equiv \Delta_0^{(1)} \Delta_2^{(1)} - \Delta_1^{(1)} \Delta_1^{(1)}
\]  

(3.7)

Coexistence among more than three phases is easily handled by solving the system of linear equations (3.6) using standard numerical methods.

2. Intermolecular-Potential-Based Field Parameters

We digress briefly to elaborate on the use of intermolecular-potential parameters as field variables in a Gibbs-Duhem integration. Integration along such a direction may be of interest because it provides a direct, quantitative picture of how some feature of the intermolecular potential affects the phase diagram; alternatively, such a path may be taken simply to establish a coexistence point on the phase diagram—to provide a starting point for a separate, more conventional integration study.

a. General Case. The conjugate density \( \rho \) of a given field variable \( \phi \) is defined as the derivative of an appropriate free energy (designated \( F \)) with respect to \( \phi \). If the corresponding partition function is designated \( Q \) such that \( \beta F = -\ln Q \), then (suppressing nonsalient terms of the partition function)

\[
N \rho = \frac{\partial (\beta F)}{\partial \phi}
\]  

(3.8a)

\[
= -\frac{1}{Q} \frac{\partial Q}{\partial \phi}
\]  

(3.8b)

\[
= -\frac{1}{Q} \frac{\partial}{\partial \phi} \int \exp[-\beta U(\phi)]
\]  

(3.8c)

\[
= -\frac{1}{Q} \int \frac{\partial (-\beta U)}{\partial \phi} \exp[-\beta U]
\]  

(3.8d)

\[
= \left\langle \frac{\partial (\beta U)}{\partial \phi} \right\rangle
\]  

(3.8e)

which shows that the conjugate density is simply the ensemble average of the \( \phi \) derivative of the intermolecular potential.

As an example, we can point to the system of soft spheres studied by Agrawal and Kofke [42–43]. This model is defined by an inverse-power pair potential:

\[
u(r; n) = \frac{(\sigma)}{r^n}
\]  

(3.9)

where \( r \) is the intermolecular separation, \( \sigma \) and \( \varepsilon \) are size and energy parameters, and \( n \) is a parameter that characterizes the hardness of the potential; \( n \to \infty \) corresponds to the hard-sphere model, and as \( n \) decreases the potential becomes softer and longer ranged. This model exhibits no vapor–liquid transition, but it does freeze. Agrawal and Kofke studied the freezing pressure as a function of the softness \( s = 1/n \), from hard spheres \( (s = 0) \) to the limits of the model \( (s = 1/2) \) (a unit \( s \) can be attained if a neutralizing background is introduced to keep the model well defined, but the study did not go this far). Thus in this application \( s \) takes the role of a field variable, and elementary calculus finds that the conjugate density is \(< \partial U/\partial s > = -\beta \varepsilon n^2 \langle (\sigma/r)^n \ln(\sigma/r) \rangle \).

b. Hard Potentials. Except at very small \( s \) the ensemble-averaged derivative described in the soft-sphere example is easy to evaluate in a standard simulation, and indeed it is no less straightforward than the calculation of
the average intermolecular energy. This circumstance is typical of many applications. However, at the hard-sphere limit, problems arise because significant contributions to the average are made by a very narrow range of separations. This difficulty indicates a general problem that surfaces when the parameter \( \phi \) relates to the size or shape of a discontinuous potential. In such circumstances special measures are required to evaluate the derivative. Usually such potentials can be written in the form

\[
\exp[-\beta u(r; \phi)] = e_0(r) + e_\phi H(r - \phi)
\]  

(3.10)

where \( H \) is the Heaviside step function and \( r \) is some suitable measure of separation of the molecules. For example, a square-well potential of well depth \( \epsilon \), \( r \) is the center-to-center distance and we have

\[
\exp[-\beta u_{xw}(r; \phi)] = e^{\phi} H(r - \sigma) + (1 - e^{\phi}) H(r - \lambda)
\]  

(3.11)

for which \( \phi \) may be taken as the hard-core diameter \( \sigma \) or the well extent \( \lambda \).

Two approaches exist to compute the desired derivative. A finite-difference approximation to the right-hand side of Eq. (3.8c) shows that the derivative is related to the fraction of configurations that exhibit overlap when the parameter \( \phi \) is varied by a small amount, thus

\[
N_\rho = -\lim_{\Delta \phi \to 0} \frac{1}{\Delta \phi} \langle \exp[-\beta U(\phi + \Delta \phi)] \rangle_{\Delta \phi = 0}
\]  

(3.12)

where \( \langle \exp[-\beta U(\phi + \Delta \phi)] \rangle_{\Delta \phi = 0} \) is the overlap fraction, measured in the ensemble for which \( \Delta \phi = 0 \). The right-hand side of Eq. (3.12) is easily measured for a range of \( \Delta \phi \) in a single simulation, and the dependence can be fit to render a good limiting value. This interpretation was taken by the group of Mike Allen when they applied Gibbs–Duhem integration to evaluate the isotropic–nematic coexistence line for a system of hard ellipsoids, as a function of the ellipsoid aspect ratio [44]. The alternative approach is based on Eq. (3.8d), and is best for application to spherically symmetric pairwise additive potentials. In this case the configuration integral on the right-hand side of Eq. (3.8d) can be written in terms of the cavity–cavity correlation function \( y(r) \), which remains smooth regardless of discontinuities in the potential [8]

\[
\rho = 4\pi \phi^2 \epsilon y(\phi)
\]  

(3.13)

where we have applied the notation of Eq. (3.10). Thus the derivative is easily computed if the correlation function is tabulated. We employ this approach in a detailed example below of the effect of the well width on freezing in the square-well model system.

3. Free Energies and the Emergence of New Phases

With little additional effort it is possible to obtain values of the thermodynamic potential \( \phi_0 \) along the integration path. This information is needed to establish the stability of the coexisting phases relative to another phase that might be adopted by the system. The construction is depicted in Figure 1. In panel (a) the value of \( \phi_0 \) in the third (\( \gamma \)) phase is computed along the \( \phi_\gamma - \phi_\alpha \) path that is traced by the coexistence of the \( \alpha \) and \( \beta \) phases. At the intersection of the \( \phi_0 - \phi_\alpha \) lines all three phases are equally stable, and a triple-point heralds the emergence of the \( \gamma \) phase. Subsequent integration in the \( \phi_\gamma - \phi_\alpha \) plane must be done in a way that traces coexistence of the \( \gamma \) phase with either the \( \alpha \) or \( \beta \) phase. Either may be taken, but one should be careful to continue \( \phi_\alpha \) in the direction that finds the third phase unstable with respect to the two newly coexisting phases.

In Figure 1b a different construction is described. In this situation two coexistence lines are being traced by the Gibbs–Duhem method, each line having one phase (\( \alpha \)) in common. The point where the \( \beta - \alpha \) coexistence coincides with the \( \gamma - \alpha \) coexistence again forms a triple point. Subsequent integration then follows coexistence between the \( \gamma \) and \( \beta \) phases. It might be

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Schematic of construction used to detect emerging phases. (a) Integration is conducted along coexistence line of \( \alpha \) and \( \beta \) phases, and free energy of \( \gamma \) phase is computed along the same path in the \( \phi_\gamma - \phi_\alpha \) plane; thus both lines have same value of \( \phi_\alpha \) at any \( \phi_\gamma \). To the left of the triple point the \( \gamma \) phase is unstable with respect to the others; to the right it is the stable phase, so at the triple point a different coexistence should be followed (not shown). (b) Separate integration series are conducted along \( \beta - \gamma \) and \( \gamma - \alpha \) coexistence lines, respectively. Crossing of these lines in either the \( \phi_0 - \phi_\alpha \) or the \( \phi_\gamma - \phi_\alpha \) planes should occur at the same value of \( \phi_\alpha \).
noted that the free energy $\phi_0$ is not needed to identify three-phase coexistence in this instance, because the coexistence lines will also coincide in the $\phi_x\phi_1$ plane. However, examination of the free energy provides a valuable check on the calculations. Examples are presented in detail below.

The best approach to evaluation of $\phi_0$ along the integration path is (no surprise) thermodynamic integration. The relevant formula is easily derived from Eq. (3.3). A one-dimensional quadrature can be constructed using the derivatives that guide the integration procedure [see Eq. (3.4)]; thus

$$\phi_0 = \phi_0 + \int_{\phi_1^0}^{\phi_1^f} \left[ \frac{\rho_1}{\rho_0} + \left( \frac{\partial \phi_1}{\partial \phi_1} / \rho_0 \right) \rho_2 \right] d\phi_1$$

(3.14)

The extension to three- and higher-phase integrations is obvious.

C. Practical Matters

1. Choosing a Path

The integration path is largely set by the definition of the problem; one knows beforehand the plane in which the coexistence line is desired. However application of simple transformations to the field variables can be beneficial if they reshape the coexistence line into a simpler form. The advantages can be improved accuracy, precision, and stability of the integration. A very familiar example is the conversion from pressure $P$ to $\ln(P)$ in the characterization of vapor–liquid coexistence. The Clapeyron equation in the latter instance is

$$\left( \frac{\partial \ln P}{\partial \beta} \right)_v = \frac{\Delta h}{P \Delta v}$$

(3.15)

The numerator ($\Delta h$) is not affected by the transformation, but it is already insensitive to $P$ and it has a simple dependence on $\beta$. Away from the critical point $v^{c\beta} \gg v^{0\beta}$, so the denominator is dominated by the vapor volume. To a first approximation, the ideal-gas law applies and the denominator is unity. Thus the right-hand side does not vary much (or in a complex way) as the integration proceeds. We emphasize that the integration procedure does not make any of the approximations that we describe; rather, we consider them only to identify forms of the field variables that minimize any numerical inaccuracies inherent in the method. In the ideal situation the right-hand side varies linearly with the independent variable.

A less familiar example is provided by the work of Agrawal and Kofke to establish the complete solid–liquid coexistence line for the Lennard–Jones (6–12) fluid [45]. At sufficiently high temperatures this model behaves as a system of inverse-power ($r^{-12}$) soft spheres. The freezing transition of that system was characterized separately [42, 43], so it is sensible to begin the Gibbs–Duhem integration of the Lennard–Jones system from this point ($\beta = 0$) and integrate toward lower temperatures (increasing $\beta$). Analysis shows that the limiting behavior of the freezing line is

$$\ln(P\beta^{5/4}) \sim \beta^{1/2}, \quad \beta \to 0$$

(3.16)

This result suggests appropriate choices for the integration path, and some quantitative renditions are presented in Figure 2. Obviously, one should work with $P\beta^{5/4}$ in lieu of the pressure $P$ (Fig. 2a), and—less obvious but equally important—it is necessary to work with $\beta^{1/2}$ rather than $\beta$ because the latter finds an infinite slope at the outset of the integration (Fig. 2b). The use of the logarithm is not required, and in fact the complete freezing line takes a simpler form if it is not applied. If one is interested only in the triple-point temperature, and not the pressure, a good value can be obtained by integrating $\beta^{1/2}$ versus $P\beta^{5/4}$ (as dependent and independent variables, respectively). Taking $\beta^{1/2}$ as the independent variable raises the concern of stepping past the triple point and causing the pressure to go negative. In contrast, because the temperature is low $P\beta^{5/4}$ can be taken to zero without too much concern for evaporation of either phase, even though they are then metastable with respect to the vapor. If the triple-point pressure is desired as well, it may be necessary to work with $\ln(\beta\beta^{5/4})$ to resolve the low pressure region. Some adjustment in the integration

![Figure 2. Solid–liquid coexistence line for the Lennard–Jones model, represented for several transformations of the pressure and temperature variables.](image-url)
fugacity fraction vanishes as $x_2 H_2 f_2^*$ as $x_2 \to 0$, and the limiting slope is

$$\left( \frac{\partial P}{\partial \xi_2} \right)_{\alpha, \beta} = \frac{\Delta f_2^*}{\beta \Delta v}$$  \hspace{1cm} (3.19)$$

Thus the ratio of the Henry's constant to the solvent fugacity must be evaluated in each coexisting phase to start the integration. This quantity can be measured in a simulation of pure component 1 by performing test identity changes of individual molecules from species 1 to species 2. Details of this calculation, as well as the limiting formulas appropriate to osmotic-ensemble integrations, have been presented elsewhere [17].

It is difficult to generalize the analysis of the limiting slope. Instead we will refer to the applications summarized below and in Table I. These examples may be instructive when considering other systems.

3. Conducting the Integration

Predictor-corrector methods [47,48] are appropriate for the integration because they require only one evaluation of the slope for each integration step. Molecular simulation is unusual in the context of the numerical treatment of differential equations, because an approximation to the slope is available before the simulation is complete. This information can be used to update the state point as the simulation proceeds. An increment in a typical GDI series entails the following steps, which for concreteness we describe for an integration in the $P-\beta$ plane:

1. Increment the temperature, and apply a predictor to estimate the new value of the pressure. Initiate a NPT simulation at the new temperature and the predicted pressure.

2. Collect averages for the enthalpies and volumes needed to evaluate the slope at the new state condition.

3. Apply a corrector to update the estimate of the pressure, using the slope determined from the current running averages from the full simulation.

4. Repeat from step 2 until convergence.

One should be careful with this procedure, as in principle it renders a Monte Carlo simulation a non-Markov process. The effect is likely to be benign, but the safest way to proceed is to take the corrector updates of the pressure only during the equilibration phase of the simulation (i.e., those cycles normally granted to allow the system to equilibrate to the new state conditions). In our experience the corrector iteration usually converges very quickly, well before the end of the equilibration period. As a check one can
<table>
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| C\(_{60}\)                              | V-S                    | P-T               | Free-energy calculations              | 83  |
| Gay–Berne                              | V-L                    | P-T               | Gibbs ensemble                        | 84  |
| Hard-core Yukawa                       | L-S fcc–bcc            | P-T               | Various                               | 60, 64 |
| Model for colloids dispersed in polymer solution | F-S                   | P-\(\mu_{\text{polymer}}\) | Pure colloid (hard spheres)           | 85  |
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| Square-well octamers (pure)            | V-L                    | \(\mu-T\)         | Gibbs ensemble                        | 49  |
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* Listed are the molecular model, the type of phases in coexistence, the plane in which the integration was conducted, the known coexistence datum used to initiate the series, and the literature citation. Abbreviations for the various phases in the "Coexistence Phenomenon" column are as follows: vapor (V), liquid (L), solid (S), fluid (F), isotropic (I), nematic (N), rotator (R) and smectic (Sm). Abbreviations for the "Integration Plane" column are as defined in the text.
evaluate accurately (and thus requires a lengthy period of simulation before a reasonable estimate of it becomes available). In this case a good predictor value will minimize the amount of iteration needed for the procedure to converge. A good predictor value is needed also if one of the phases cannot be sustained for any period in a metastable state.

No modifications to the predictor-corrector formulas are needed to conduct integrations of coexistence involving more than two phases. In such instances all dependent variables are updated simultaneously by applying the corrector formula to each of the governing differential equations; the simulation then continues with the new values in the manner outlined above.

4. Coupling the Phases

On approach of the critical point a small system cannot be expected to sample only one of two coexisting phases. For obvious reasons the unilateral condensation or evaporation of one of the coexisting phases defeats the GDI technique. To forestall breakdown of the method when a critical point is approached, one can introduce an artificial coupling between the phases. This coupling is designed to mimic the transfer of volume and particles between the phases—in the spirit of a Gibbs ensemble simulation—so that they remain on either side of some chosen density. This device still cannot prevent phase changes, but if they occur, they are bilateral, so that one phase vaporizes if the other condenses. The property differences required by the method then remain available for computation if one is careful to track the occurrence of these phase-identity exchanges.

The coupling is accomplished by rewriting the densities of the two phases in terms of new variables \( X \) and \( Y \), which can be interpreted [51] as the fraction of all particles and the fraction of the total volume, respectively, held by one of the phases. Thus

\[
\nu^\phi = \frac{Y}{X} \nu; \quad \nu^\phi = \frac{1 - Y}{1 - X} \nu
\]  

(3.22)

The “overall” volume \( v \) may be specified arbitrarily, but should lie between the expected molar volumes of the two phases. Instead of sampling the volumes of the phases independently, sampling of \( X \) and \( Y \) is performed. This change of variables is accompanied by a Jacobian

\[
J(v^\phi, \nu^\phi) = -N^\phi N^\theta v \frac{(\nu^\phi - \nu^\phi)^3}{(v - \nu)(\nu^\phi - \nu)}
\]

(3.23)
The usual acceptance criterion for volume changes must be multiplied by the ratio of the Jacobians evaluated in the trial and original states.

We are of the opinion that the tendency of a system to display unilateral or bilateral phase changes is indicative of more serious finite-size effects. Application of the GDI method (or the Gibbs ensemble for that matter) under such circumstances can provide only a qualitative picture of the phase behavior. Histogram-reweighting methods have been developed and refined to the point where they now provide a very precise description of the critical region in the thermodynamic limit. These methods should be applied if a quantitative characterization of the critical region is desired [52–57].

5. Error Estimation and Stability

A GDI series is subject to error from three sources:

- Stochastic errors in the simulation averages
- Systematic errors associated with the predictor-corrector scheme of numerical integration
- Errors introduced by an inaccurate initial condition, that is, an initial state point that does not lie on the true coexistence line

The magnitude of stochastic errors in the simulation averages can be quantified using standard analyses [15] and their influence on the precision of the coexistence line gauged via standard propagation-of-error method [58].

Systematic errors arising from the predictor-corrector integration do not seem to be a problem, judging from the ability of the GDI method to traverse an integration path and yield a result that agrees—within the limits of the stochastic error—with coexistence data obtained independently. Regardless, a simple test can be applied requiring no additional simulations—eliminate half the data and reintegrate the remaining set of slopes to examine the effect on the final coexistence point (alternatively, a higher-order quadrature algorithm could be applied to the full set of data). Any concerns can be alleviated by working with a smaller integration step.

The consequences of error introduced with the initial condition is a matter of stability of the GDI procedure, because in a sense each point along the integration path provides an initial condition for those that follow. If deviations from the true coexistence line give rise to even larger deviations, the integration is unstable. Certainly the opposite situation is greatly preferred, in which deviations become attenuated as the integration proceeds. Fortunately, it is not too difficult to know which situation is in effect, and to what extent.

Returning to the notation of Eq. (3.3), error in the initial state implies that the thermodynamic potential \( \phi_0 \) is not equal between the coexisting phases because \( \phi_2 \) is not at the coexistence value for the initial \( \phi_1 \). The GDI procedure is designed to keep the difference of \( \phi_0 \) between the two phases constant, so stability can be examined by estimating how a constant error in \( \phi_0 \) translates into deviations in \( \phi_2 \). Assuming small errors we can write, at a given point in the integration path and thus for fixed \( \phi_1 \),

\[
\phi_0(\phi_2) = \phi_0(\phi_2^*) + \frac{\rho_2}{\rho_0} \delta\phi_2
\]

(3.24)

where \( \phi_2^* \) is the correct value of \( \phi_2 \) for coexistence at \( \phi_1 \), and \( \delta\phi_2 = \phi_2 - \phi_2^* \) is the error. The difference in \( \phi_0 \) between the two phases is

\[
\phi_0^*(\phi_2) - \phi_0^*(\phi_2) = \Delta \left(\frac{\rho_2}{\rho_0}\right) \delta\phi_2
\]

(3.25)

Assuming that the GDI procedure succeeds in keeping this difference unchanged, the error at a subsequent point in the integration can be related to the error at the initial (origin) point (subscript “0”)

\[
\delta\phi_2 = (\delta\phi_2)_0 \frac{\Delta (\rho_2/\rho_0)}{\Delta (\rho_2/\rho_0)}
\]

(3.26)

The important result is that the error grows or diminishes inversely with the difference in \( \rho_2/\rho_0 \) between the phases. The analysis tells us in which direction to conduct an integration, if given a choice, and permits quantification of the effects of error in the initial state. So, for example, it is advantageous to perform GDI studies of vapor-liquid coexistence by beginning close to the critical point and integrating toward lower temperature.

Examination of the first GDI data ever recorded can illustrate the analysis. Our study [50] of Lennard-Jones vapor-liquid equilibrium first attempted to integrate from low temperature using an established Gibbs ensemble (GE) datum [59]. To the author's dismay, the integration did not proceed through other GE data established at higher temperatures. Further study showed that an integration beginning from a midrange temperature found agreement with all other GE data except the low-temperature value, for which the GE pressure was 13% lower. Moreover, series beginning from the newly established GDI low-temperature datum agreed well with other data. As illustrated in Figure 3, the stability analysis characterizes very well the propagation of error that we now recognize in the low-temperature GE datum. Shown in the figure are the correct coexistence line and the one beginning from the incorrect low-temperature point. Error bars on the correct line indicate how an initial 13% error would propagate in an integration toward high temperature, as determined from the stability analysis.
The estimate exactly describes the course of the ill-fated series. This suggests another use of the stability analysis, namely, to correct a GDI series if its initial state point is subsequently found to be slightly in error. Elements of this idea are exhibited in the coexistence-line free-energy integration approach recently described by Meijer and Azhar [60].

D. Summary of Applications

Applications of the GDI method are summarized in Table I, where we list the molecular model, the type of phase behavior, the plane in which the integration was conducted, and the nature and source of the initial coexistence datum for the integration. Most of the work involves coexistence with solid or ordered phases, as this application is uniquely suited to the GDI method. However, the approach is no less effective at treating fluid–fluid equilibria, although other methods are often applicable in these cases.

The GDI method has been used to map out the entire phase diagram of the Lennard-Jones model [45,50] (exclusive of any polymorphic fcc-hcp transitions which may exist [61], and a few simple LJ mixtures have been studied [17] using both the isomolar and osmotic formulations of the semigrand ensemble; the triple point as a function of composition has been computed [46] for these systems. The liquid–solid coexistence line of the pure LJ system was examined against several well-established semiempirical melting rules [45]. The effect of size polydispersity on the fluid–solid phase diagram of hard spheres has been examined by Bolhuis and Kofke [62,63]; this study has application to the behavior of colloidal systems. Another model appropriate for colloids—the hard-core Yukawa potential—has been examined in two separate studies [60,64]. Using GDI and GE methods, Tavares and Sandler [65] applied a one-component potential of mean force model to study polymer-induced precipitation of amorphous and crystalline phases of proteins from solution. Two simulation studies have now been conducted to gauge the effect of rigidity on the isotropic–nematic phase behavior of polymeric systems. Dijkstra and Frenkel [66] examined a system of joined spherocylinders using the GDI method, while Escobedo and de Pablo [67] recently reported a study of hard-sphere chains; the latter does not use GDI methods but works instead with pseudo-ensemble concepts [68,69]. In a similar vein, Camp et al. [44] examined the effect of elongation on the isotropic–nematic transition of hard ellipsoids using the GDI method along a path of increasing elongation, while Bolhuis and Frenkel [70] completed a similar study for hard spherocylinders, which has a much more complex phase diagram (including smectic and rotator phases). Bolhuis and Frenkel encountered some difficulty with integration stability that they associated with a poor predictor, and they describe a slightly different integration scheme that alleviates the problem.

Escobedo and de Pablo have proposed some of the most interesting extensions of the method. They have pointed out [49] that the simulation of polymeric systems is often more troubled by the requirements of pressure equilibration than by chemical potential equilibration—that volume changes are more problematic than particle insertions if configurational-bias or expanded-ensemble methods are applied to the latter. Consequently, they turned the GDI method around and conducted constant-volume phase-coexistence simulations in the temperature–chemical potential plane, with the pressure equality satisfied by construction of an appropriate Clapeyron equation [i.e., they take the pressure as \( \phi_0 \) of Eq. (3.3)]. They demonstrated the method [49] for vapor–liquid coexistence of square-well octamers, and have recently shown that the extension permits coexistence for lattice models to be examined in a very simple manner [71].

Another interesting variant has been described by Svensson and Woodward [72]. These workers showed how the width of a planar pore could be varied while keeping the fluid inside at a constant chemical potential, without resorting to grand-canonical methods. Instead, they work in an
isotension ensemble with pressure fixed by considering how the chemical potential would otherwise change with the pore width. Their method is not an example of GDI, but it has enough features in common to warrant mention here. In particular, we see this as a very good example of ways that the GDI method can be generalized. GDI prescribes how two or more state (or potential) parameters must be adjusted simultaneously in order to keep some quantity (viz., the difference in chemical potential between two phases) unchanged. One might consider also integrations that keep other quantities fixed. Examples include fixing the composition of one phase while the pressure and temperature change (thereby permitting dew and bubble lines to be traced), or fixing the enthalpy (say) of a single-phase mixture while adjusting two or more intermolecular potential parameters (useful if fitting parameters to match experiment). We do not expect that these particular extensions would proceed as easily (or perhaps as successfully) as the GDI of phase coexistence, but they are suggestive of an even broader usefulness of the approach.

These workers have since gone on [73,74] to conduct phase-coexistence calculations in pores using these ideas. These recent studies have many notable features, including the use of free-energy perturbation formulas in lieu of thermodynamic integration to maintain the chemical potential equality, and the introduction of a restraining field to eliminate unilateral or bilateral phase changes.

E. Detailed Example: Freezing of the Square-Well Model

To close we present in some detail a study of freezing for the square-well model. This system is described by a hard core of diameter \( \sigma \) (which we take to be unity) that is centered within a well of depth \( \varepsilon \) extending to separations \( \lambda \) [see Eq. (3.11)]. Of some interest is the effect of the well extent \( \lambda \) on the phase diagram. A rather complete characterization was conducted by Young [75], but his results are approximate because they are based on a cell model of the solid phase. However, his study indicates that in general the square-well potential provides a very bad model for solids, as it exhibits disproportionately complex phase diagrams owing to the interplay between the sharp well cutoff and the lattice spacing of the solid. Nevertheless it remains an important model for the fluid phases, and consequently it is helpful to know the conditions under which the fluid is stable with respect to the solid. We do not attempt a complete description here, as our primary interest is to use this calculation to demonstrate various aspects of the GDI method when applied to a complex phase diagram. We will focus attention on the well extent \( \lambda = 1.95 \). In an earlier study [46] we applied the GDI method in the region of \( \lambda = 1.50 \). We have since discovered that the integration path used to reach the solid-fluid coexistence line had crossed a different first-order phase transition (from an expanded to a condensed solid), thereby invalidating the remainder of the series.

Young's cell model applied at \( \lambda = 1.95 \) predicts that fcc (face-centered cubic) is the stable solid at freezing, regardless of the pressure. It also indicates a polymorphic transition to the hcp (hexagonal close-packed) phase at lower temperatures. It does not find any region of stability for the bcc (body-centered cubic) solid; however for some smaller values of \( \lambda \) (beginning below about 1.74) it predicts that bcc is stable at the vapor–liquid–solid triple point, whereas for larger values of \( \lambda \), hcp or bcc may become the stable triple-point solid. This application suggests the first point to be made when attempting to compute phase diagrams by molecular simulation. All the quantitatively accurate methods (especially GDI but also GE) require that some idea of the nature and location of the phase transitions be known beforehand. Simulation is not effective at giving a quick, qualitative picture of complex phase diagrams. If the phase behavior is not otherwise obvious, one should apply an approximate treatment (such as the cell model) to construct a “roadmap” that guides the simulation-based study. Alternatively single-phase NPT simulations can be performed at various state points to get a rough picture of the phase diagram, but even in this case some rough idea of what to expect is very helpful. We will restrict our attention to coexistence between and among the two fluid phases and the fcc solid, with a cursory examination of the stability of other solids as \( \lambda \) is varied.

Application of the GDI method to the coexistence lines requires establishment of a coexistence datum on each. A point on the vapor–liquid line can be determined by a GE simulation. At high pressure the model behaves as a system of hard spheres, and the liquid–solid coexistence line approaches the fluid–solid transition for hard spheres, which is known [76,77]. Integration of liquid–solid coexistence from the hard-sphere transition proceeds much as described in Section III.C.1 for the Lennard-Jones example. The limiting behavior (\( \beta \to 0 \)) finds that \( \beta P \) is well behaved and smoothly approaches the hard-sphere value [76,77] of 11.686 at \( \beta = 0 \) (unlike the LJ case, we need not work with \( \beta^{1/3} \)). Thus the appropriate governing equation for the GDI procedure is

\[
\frac{\partial \beta}{\partial P} = -\frac{\Delta u}{\Delta \varepsilon}
\]

(3.27)

where \( u \) is the energy per molecule. The integration was conducted using eight uniform steps in \( \beta P \) from the hard-sphere coexistence value to \( \beta P = 0 \) (10,000 production cycles per simulation, with about 150 particles in each phase). The coexistence line so computed is presented in Figure 4. Removal
of every other integration point and application of the corrector integrator to the remaining ones (without actually redoing the simulations) alters the final value of $\beta$ by 2%. This provides a conservative upper bound to the error introduced by the finite step of the integration. It indicates that the actual error due to the integrator is of the order of 0.5% or less.

A GE study of square-well vapor–liquid equilibrium was conducted by Vega et al. [78]. It includes the coexistence lines for $\lambda = 2.0$ and 1.75, which together present a good estimate of the critical point for the $\lambda = 1.95$ system. We perform the GE calculation at $\beta = 0.425$, between this estimate of the critical temperature ($\beta = 0.40$) and the cell-model estimate of the triple point ($\beta = 0.50$). The simulation yields a saturation pressure of $\beta P = 0.0575$. We initiate the GDI series from this point and integrate ($\beta$ vs. $\ln(\beta P)$, although Eq. (3.15) would work just as well) toward lower temperatures, going just beyond the expected triple point. The resulting coexistence line is included in Figure 4.

The solid–liquid and liquid–vapor coexistence lines intersect at $\beta = 0.491, \beta P = 0.028$. Further verification is obtained by examining the chemical potential $\beta \mu$, which is computed along the integration path as described in Section III.B.3. Free-energy values for the initial points are available; for the solid–liquid line the hard-sphere value is known [76,77] ($\mu = 16.898$), and for the liquid–vapor, it was measured during the GE simulations ($\mu = -3.191$). Curves for both integrations are included in Figure 4, and at $\beta = 0.488$ they indeed intersect very close to the triple-point temperature just established.

The triple point is a key “landmark” on the phase diagram, and with the point just established, we can begin to trace out a whole line of three-phase coexistence as a function of the well extent $\lambda$. We cannot proceed very far if considering only the fcc phase, for as $\lambda$ increases, the hcp and bcc phases gain in stability. The cell model calculations alerted us to the possibility of this outcome, so we performed “shadow” free-energy calculations of the hcp and bcc phases as they follow the coexistence path just established in the pressure-temperature plane. The bcc phase is so unstable at the outset of the series (hard spheres) that its structure cannot be maintained, and a single-occupancy constraint was applied [76]. The initial hcp free energy is indistinguishable from the fcc value [77], but as the solid–liquid coexistence series proceeds, it clearly rises above the free energies of the coexisting phases (Fig. 4); this behavior proves that hcp is not the stable solid at freezing. The single-occupancy bcc free energy for the hard-sphere initial condition has been established [43] ($\mu = 16.32$). The bcc phase gains relative stability as it follows the fluid–fcc coexistence path, but not enough to unseat fcc as the stable solid at freezing. The shadowing process can continue as the triple-point integration proceeds in the direction of increasing
Figure 5. Chemical potential of the fcc, hcp, and bcc phases along a path of increasing square-well extent \( \lambda \), with pressure and temperature set to ensure coexistence between the vapor, liquid, and fcc phases.

\( \lambda \). The density conjugate to the "field" \( \lambda \) is measured for each phase (liquid, vapor, fcc, hcp, and bcc) in the simulation according to Eqs. (3.10), (3.11), and (3.13). Results are described in Figure 5. The figure indicates that bcc becomes increasingly unstable, but the hcp phase achieves stability at freezing for \( \lambda \) greater than about 2.05. The integration could continue from this point by following the liquid–vapor–hcp coexistence (or other combinations of two or three phases, if interested) as \( \lambda \) increases further, with the fcc and bcc phases shadowing to continue to gauge their stability with respect to hcp.

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