Molecular thermodynamics of primitive models of complex fluids

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Recibido el 25 de marzo de 2006; aceptado el 5 de junio de 2006

The phase behaviour and structural properties of complex fluids can be studied using primitive models (PM) of real molecules, that satisfy two requirements: (a) the molecular model has the basic elements that determine the most relevant features observed meso and macroscopically, and (b) a PM system can be systematically studied through computer simulation and perturbation theories. In this paper we review some advances in the molecular thermodynamic modeling of colloids and liquid crystals using primitive models.

Keywords: Ionic fluids; liquid crystals; computer simulation.

El comportamiento de las fases y las propiedades estructurales de fluidos complejos pueden estudiarse utilizando modelos primitivos (PM) de las moléculas reales que satisfagan dos condiciones: (a) el modelo molecular debe poseer los elementos básicos que determinen las características observadas más relevantes a nivel meso y macroscópico, y (b) un sistema PM puede ser estudiado sistemáticamente mediante simulaciones por computadora y teorías de perturbaciones. En éste artículo se revisan algunos de los avances en el modelaje molecular-termodinámico de coloides y cristales líquidos utilizando modelos primitivos.

Descripores: Fluidos iónicos; cristales líquidos; simulación computacional.

PACS: 64.70.Md; 64.10.+h

1. Introduction

Over the past two decades considerable advances in the field of equations of state for complex fluids have been made, motivated by the rapid development of molecular-based theories and computer simulation methods. Both approaches are based on a knowledge of the intermolecular interactions between the molecules. One of the molecular equations of state derived following this scheme is the Statistical Associating Fluid Theory (SAFT) [1,2], which is probing to be a very reliable and accurate approach to model complex fluids. This approach incorporates separate contributions that account for non-sphericity, directional attractive interactions, dispersion and electrostatic forces. The SAFT approach is based on the thermodynamic perturbation theory of Wertheim [3-6], and has been used to predict the phase behaviour of a wide variety of pure components and their mixtures of industrial interest, such as hydrogen-bonded fluids, electrolytes and polymers. See references [7-9] for reviews on the applications of SAFT, as well as references [10-12] where SAFT has been used to model asphaltene precipitation.

In the specific case of liquid-crystalline (LC) materials, we know that real mesogens present molecular features such as flexible tails and anisotropic forces (π−π interactions between phenyl cores, dipole-dipole and hydrogen bonding interactions, etc.), that are not essential for mesophase formation, but they are the fine details that determine their phase behaviour [13-22]. Among other things, we know that the spatial exclusion due to harsh repulsive forces is the dominant factor in determining the fluid structure, and that a variety of liquid-crystalline phases can be induced by steric forces [23-28].

In order to model LC substances, we require to determine which are the basic molecular features that we need to take into account for a proper modelling. Although the detailed atomistic description of LC molecules could be used for obtaining information about mesoscopic phases, this route is computationally very demanding. Over the years, the use of primitive molecular models has been very useful to obtain qualitative predictions. By primitive model (PM) we mean a crude representation of real molecules but containing the basic microscopic information, such as molecular shape and intermolecular forces. Computer simulations can then be used for these simplified models in order to understand the interplay of the different molecular parameters, and this information can be included in molecular theories, as for example SAFT, to predict the phase behaviour of real substances.

In this work we review recent advances in the development of molecular thermodynamic models for ionic fluids and liquid crystals, using a method to simulate charged systems proposed by Wolf and coworkers [29,30], that can be combined with a version of the SAFT approach for systems interacting with potentials of variable range [31], in order to predict structural and thermodynamic properties of complex fluids.

2. Computer simulation of charged systems

One of the technical problems that arises in the computer simulation of complex fluids is the correct modelling of the long-
range electrostatic interactions. Standard methods such as the Ewald sum (ES) and Onsager Reaction-Field (RF) methods [32,33] are the most common procedures to deal with these interactions. Whereas the ES method is exact, a well-known shortcoming of this method is that it is expensive in computing time. On the other hand, the RF method requires to know the dielectric constant of the surrounding media, an information that is not known a priori and that requires to be calculated in a self-consistent way [34,35]. The total energy $E^{\text{tot}}$ for a system of $M$ ions is given by

$$E^{\text{tot}} = \frac{1}{2} \sum_{i=1}^{M} \sum_{j\neq i=1}^{M} q_i q_j \frac{1}{r_{ij}} \tag{1}$$

where $q_i$ is the charge of ion $i$ and $r_{ij}$ is the distance between ions $i$ and $j$. Equation (1) is a conditionally convergent sum when $M \rightarrow \infty$, i.e., the result of the sum depends on the order followed to add pair interactions. Ewald [32,33] solved this problem considering a system of $N$ ions located into a cell, which is replicated periodically in all directions. Then, in order to screen the coulombic long-range interactions, a continuous charge density distribution is added to the original system in such a way that the sign of the charge of this distribution is opposite to the sign of each one of the original charges. The corresponding energy of this new composite system is now a convergent sum of pair interactions that can be evaluated directly in real space. To recover the original system, the effect of the continuous charge distribution is canceled in the reciprocal space of the periodic arrangement of cells. The energy associated to this charge density in $k$-space is expressed as a Fourier sum, that is also absolutely convergent. By a proper selection of a screening parameter $\alpha$ related to the charge density distribution and the number of $k$ vectors required for the evaluation of the Fourier sum, a computational scheme can be implemented to simulate the properties of charged systems in an optimal time that, however, is considerably longer than the time required to perform a simulation for a system interacting with a short-ranged pair potential.

According to the Wolf method [29,30,36], the conditional convergence of the pairwise $r^{-1}$ summation can be understood in the following way. Considering the radial symmetry of the coulombic interaction, the sum of charge pair interactions can be done using spherical shells of radius $R_c$. The absence of electroneutrality in these shells contributes to the non convergence of the sum in Eq. (1). However, the evidence that the effective pair potential between ions is short-ranged when we consider an electrolyte composed of many ions, suggests to perform the calculation of the energy of the system using an effective pair potential under the restriction of the electroneutrality of the spherical shells. Based on these facts, the energy of the system is obtained using a spherically truncated sum, corrected by a charge-neutralizing potential, which is assumed to be localized exactly at the sphere surface. In this way, the net charge of the complete system (charges within $R_c$ plus charges over the spherical surface of radius $R_c$) is null. In other words, this method reduces the problem to the calculation of the energy of an electroneutral finite system. This method has the main advantage of requiring a simulation time of the same order of a standard periodic boundary conditions simulation for a short-ranged potential.

The effective screened potential proposed by Wolf is the same potential used in the Ewald method when the real sum is restricted to the first cell, corrected by the potential due to the neutralizing charge in the surface of a sphere of radius $R_c$:

$$V_W(r_{ij}) = \frac{q_i q_j \operatorname{erfc}(\alpha r_{ij})}{r_{ij}} - \frac{q_i q_j \operatorname{erfc}(\alpha R_c)}{R_c} \tag{2}$$

when $r_{ij} < R_c$, otherwise $V_W(r_{ij}) = 0$. The Wolf potential is then shifted to zero at $r_{ij} = R_c$. Using this potential, the energy of the system, $E(R_c)$, can be expressed as

$$E(R_c) \approx \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} q_i q_j \frac{1}{r_{ij}} \operatorname{erfc}(\alpha r_{ij}) - \frac{1}{2} \sum_{i=1}^{N} \frac{\Delta q_i(R_c) \operatorname{erfc}(\alpha R_c)}{R_c} - \frac{\alpha}{\pi^{1/2}} \sum_{i=1}^{N} q_i^2 \tag{3}$$

where $\Delta q_i(R_c)$ is the net charge enclosed in the spherical truncation shell, given by

$$\Delta q_i(R_c) = \sum_{j=1}^{N} q_j (r_{ij} < R_c) \tag{4}$$

The last term in Eq. (3) is a self-energy term that must be subtracted to obtain the proper energy of the system, as also happens in the Ewald method.

The main advantage of Eq. (3) in comparison with the Ewald sum method is that it is not necessary to evaluate a reciprocal space sum, the most time-consuming procedure in the Ewald method. The required simulation time for obtaining equilibrated states using the Wolf method is of the same order of a standard periodic boundary conditions simulation for a short-ranged potential.

Recently, we have used the Wolf method to study a wide range of PM electrolytes systems, using Monte Carlo computer simulations in the NVT and NPT ensembles and predicting thermodynamic and structural properties with the same accuracy than the Ewald method but with a significant reduction in computing time [37]. We found that all the systems studied can be simulated accurately using the same set of values for the Wolf parameters $\alpha$ and $R_c$, independently of the size and charge ratios of the systems, i.e., $R_c = 0.5 L$ and $\alpha = 4/L$, where $L$ is the length of the cubic simulation cell.

In Figs. 1 and 2 we present equilibrium configurations of 2:12 and 1:20 electrolyte systems using the Wolf method in NVT Monte Carlo computer simulations. The first system is composed of 384 cations and 64 anions, whereas the second one has 1280 cations and 64 anions. The corresponding size ratios for these systems are 1:10 and 2:15, respectively, and...
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Figure 1. Equilibrium configurations for a +2:-12 electrolyte system with a size ratio 1:10. Snapshots are for a temperature $T^* = 0.0641$ and the following densities $\rho^*$: (a) 0.0112, (b) 0.0280, (c) 0.0561 and (d) 0.1122.

Figure 2. Equilibrium configurations for a +1:-20 electrolyte system with a size ratio 2:15. Snapshots are for a temperature $T^* = 0.1188$ and the following densities $\rho^*$: (a) 0.0621, (b) 0.3093, (c) 0.6211 and (d) 1.2402.

Figure 3. Isotropic phase for an electroneutral system formed by charged hard spherocylinders of aspect ratio $L/\sigma = 5$, for a thermodynamic state $\rho^* = 0.1061$ and temperature $T^* = 2$. Ions and cations are depicted with different colors.

Figure 4. Nematic phase for an electroneutral system formed by charged hard spherocylinders of aspect ratio $L/\sigma = 5$, for a thermodynamic state $\rho^* = 0.1329$ and temperature $T^* = 2$. Anions and cations are depicted with different colors.

The Bjerrum length value was taken as 0.715 nm, that mimics aqueous solutions at 298 K. Simulations were obtained using the potential proposed by Hribar et al. [38] to model highly asymmetrical electrolytes of diameters $\sigma_i$ and $\sigma_j$, whose centers of mass are separated by a distance $r_{ij}$.

\[
\beta u_{ij} = A_{ij} \left[ \frac{\sigma_i + \sigma_j}{r_{ij}} \right]^9 + \frac{z_i z_j L_B}{r_{ij}}
\]

where $\beta = 1/kT$, $k$ is the Boltzmann’s constant, $T$ is the absolute temperature, $z_i$ is the valence of species $i$, $L_B$ is the Bjerrum length,

\[
L_B = \beta \frac{e^2}{D}
\]

and

\[
A_{ij} = \frac{L_B |z_i z_j|}{9(\sigma_i + \sigma_j)}
\]

where $e$ is the electron charge and $D$ is the dielectric constant. The reduced temperature and density are given by

\[
T^* = \frac{kT D \sigma_+ \sigma_-}{e^2 z_+ z_-}
\]
and

\[ \rho^* = \frac{N \sigma^3_{++}}{V} \quad (9) \]

where \( \sigma_{+-} = (\sigma_{++} + \sigma_{--})/2 \) and \( V \) is the volume of the system. Simulated states were obtained using \( 3 \times 10^5 \) cycles for equilibration and another \( 9 \times 10^5 \) cycles for averaging, where a cycle is the average number of movements per particle. The predicted values for pressures, internal energies, heat capacities and radial distributions functions for these systems, and their comparison with the Ewald method and integral equation theories, are reported in Ref. 37.

Besides the sizes and charges of the particles in a charged fluid, another interesting effect to study is the shape of the particles. We are currently studying a prototype of a simple model of a cationic-anionic system formed by hard spherocylinders of diameter \( \sigma \) and length \( L \), with a point charge located at the center. As in the case of spherical particles, we have found agreement between the Ewald and Wolf predictions for this system. In Figs. 3 and 4 we present equilibrium configuration for an isotropic and nematic phase observed for \( T^* = kT\sigma/\varepsilon^2 = 2 \). Preliminary results obtained for the simulated phase diagram of this system indicates that isotropic-nematic transition is not very different from the hard-spherocylinders system [28]. However, the behaviour of the charged system at low temperatures would have an interesting behaviour due to the association of charges, particularly in the smectic phase, similarly to what has been observed with hard-spherocylinders with transverse point dipoles [39].

Since the application of the Wolf method to study charged systems seems to be very promising, due to the significative reduction in computing time and by theoretical considerations that we will discuss in the next section, we have been looking at their application to model dipolar systems. The simple model that we have been studying is shown in Fig. 5, formed by a hard sphere particle with two opposite charges located along the particle axes \( e_i \). The dipolar moment, \( p \), is given by

\[ p = |z|e\mathbf{b} \quad (10) \]

where \( z \) is the valence, \( e \) is the electron charge, and \( \mathbf{b} \) is the relative position vector between charges. We have studied the low density/low temperature behaviour of this model, using the NVT ensemble for MC simulations of 256 particles, and with the same Wolf parameters used for electrolyte systems, \( R_c L = 0.5 \) and \( \alpha/L = 4.0 \). We have looked at the effect of varying the distance between charges and valence, \( |\mathbf{b}| \) and \( |z| \), respectively, keeping fixed the value of the dipolar moment. We select the thermodynamic state \( T^* = kT\sigma/\varepsilon^2 = 0.005352 \) and \( \rho^* = 0.049 \), that corresponds to the same state studied previously by Camp et al. [40] using dipolar hard spheres with point dipoles. In Fig. 6 four configurations for this model are presented, corresponding to different values of the parameters \( |\mathbf{b}| \) and \( |z| \). These configurations reproduce the same behaviour observed in Ref. 40, i.e., the associating dipolar interaction gives rise to chain and ring formation. However, notice that the associating mechanism depends on the values used for the relative distance \( |\mathbf{b}| \) and the valence \( |z| \), and, more interesting, they also have an important effect on the chain and loops lengths. Similar associating dipolar configurations have been reported previously for smectic phases of primitive models of liquid crystals, with molecules having a transverse dipole [39]. Since by increasing the temperature the chain and loop formation is lost, the associating behaviour observed in these type of models suggests an interesting transition between smectics: from a phase with dipolar chain and ring configurations to another phase with an isotropic distribution of dipoles.

3. Molecular Thermodynamics approach

The Wolf method also results an interesting approach due to its relevance in the framework of molecular-based theories for variable ranged systems of complex fluids based on the SAFT approach [7,12,41], as we explain now.

Under the approximation of primitive models for electrolytes, a useful theoretical approach consists in to represent the binary interaction \( u_{ij} \) between ions \( i \) and \( j \) a distance \( r \) apart as the sum of non-Coulombic and Coulombic interactions [41],

\[ u_{ij}(r) = u_{ij}^{HS}(r) + \psi_{ij}(r) \quad (11) \]

where \( \psi_{ij} \) is a binary interaction given by two contributions,

\[ \psi_{ij}(r) = u_{ij}^C + u_{ij}^{CS} \quad (12) \]

where \( u_{ij}^C \) is the bare Coulomb potential between two ions and \( u_{ij}^{CS} \) is a "co-sphere" potential, which takes into account the oppositely charged co-ions surrounding each one of the interacting ions \( i \) and \( j \), as well as the polarization effects of the solvent due to all the ions present. As it is well known, the effective potential \( \psi_{ij} \) derived in the Debye-Hückel theory [42] is given by a Yukawa potential

\[ \psi_{ij} = \frac{e^2 z_iz_j}{Dr_{ij}} \exp\left[-\kappa(r - \sigma)\right] \quad \frac{1 + \kappa \sigma}{1 + \kappa \sigma} \quad (13) \]

where \( \kappa^{-1} \) is the Debye length. Although this result is strictly valid only at low densities, the Wolf method follows a similar approach, where not only a screened interaction is taken into account, but also the electroneutrality of a subsystem contained within a radius \( R_c \) is considered. The resulting effective potential \( \psi_{ij} \) is given by Eq. (2). However, Heyes [43] has shown that the Ewald effective potential is not unique and that it is possible to use other representations. Basically, the shape of the charge density used to screen the electrostatic interactions in the Ewald method is arbitrary, and the effective potential to be used depends on the mathematical form of the density distribution that is being considered. The standard effective Ewald potential corresponds to a gaussian density.
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F I G U R E 5. Dipolar hard sphere model. The dipolar moment of the particle is obtained by an array of two charges of opposite sign \( q_i \), located along the particle main axis, whose orientation is given by the unit vector \( e_i \). The relative position between charges is described by \( b \).

F I G U R E 6. Equilibrium configurations for dipolar spheres with the same dipolar moment. In order to maintain the dipolar moment fixed, the relative distance between charges and the valence, \( |b|/\sigma \) and \( |z| \), respectively, were changed simultaneously: a) \( |b|/\sigma = 0.8049 \) and \( z = 0.25 \), b) \( |b|/\sigma = 0.4024 \) and \( z = 0.50 \), c) \( |b|/\sigma = 0.2012 \) and \( z = 1.00 \) and d) \( |b|/\sigma = 0.1341 \) and \( z = 1.50 \). Simulations were obtained for the same temperature, \( T^* = 0.005352 \).

distribution. The same result applies to the Wolf method, and we can represent \( \psi_{ij} \) in terms of a generic screened potential \( V(r_{ij}) \). We then can write the more general effective potential to be used in the Wolf method as

\[
\psi_{ij} = V(r_{ij}; \alpha) - V(R_c; \alpha)
\] (14)

This potential is a variable-ranged interaction, that can be used within the SAFT-VR approach [31] to obtain an equation of state for charged systems. This theory provides a unified method for describing the properties of systems with different monomer-monomer potentials such as the square-well potential. In the SAFT-VR approach the individual contributions to the free energy of associating chain molecules are given as explicit functions of the range of the attractive potential; the non-conformal properties of these systems can thus be studied in the context of the phase equilibria of a wide range of real substances. Molecules are modeled as chains of \( m \) hard-core segments of equal diameter \( \sigma \). The monomer-monomer interactions are described by a specific interaction, and additional bonding sites are included to deal with molecular association. The Helmholtz free energy \( A \) can be written in terms of separate contributions as

\[
\frac{A}{NkT} = \frac{A_{\text{ideal}}}{NkT} + \frac{A_{\text{MONO}}}{NkT} + \frac{A_{\text{CHAIN}}}{NkT} + \frac{A_{\text{ASSOC}}}{NkT},
\] (15)

where \( N \) is the total number of molecules, \( A_{\text{ideal}} \) is the ideal free energy, \( A_{\text{MONO}} \) is the excess free energy due to the monomer segments, \( A_{\text{CHAIN}} \) is the contribution due to chain formation, and \( A_{\text{ASSOC}} \) is the term that describes inter-molecular association. Each of these contributions are given in full detail in Ref. 31, and the reader also can find in Refs. 44 and 45 the corresponding SAFT-VR expressions for the Yukawa and soft repulsive potentials, respectively. Recently, it has been shown that the SAFT-VR version presented in Ref. 44 can describe in a very accurate way the heat capacities of different real substances, in comparison with other SAFT versions [46]. The SAFT-VR approach has been also extended to electrolyte solutions [7,41], by considering an explicit energy contribution for ions. Since the Yukawa potential is a natural screened interaction arising in electroneutral charged systems, the effective Wolf potential in Eq. (14) can be written in terms of the Yukawa pair interaction and used in the SAFT-VR formalism, following the results derived in Refs. 41 and 45, to obtain an equation of state for charged systems.

In the case of liquid crystals, the theoretical prediction of phase diagrams using PM models can be achieved also through a molecular-based theory following the pioneering work of Gelbart & Gelbart [47], and Parsons [48]. In order to have a proper description of the thermodynamic effects arising from the different molecular elements that characterise a LC system, the Helmholtz free energy for a substance comprised of \( N \) molecules can be expressed in similar way as in the SAFT approach, as the sum of contributions to the free energy due to different molecular mechanisms. In the case of non-polar PM models, the free energy can be expressed as [49]

\[
\frac{A}{NkT} = \frac{A_{\text{ideal}}}{NkT} + \frac{A_{\Omega}}{NkT} + \frac{A_0}{NkT} + \frac{A_{vdW}}{NkT}
\] (16)
where $A_{\text{ideal}}$ is the ideal contribution to the free energy, $A_{1\Omega}$ is the orientational free energy, according to the Onsager expression [23],

$$\frac{A_{1\Omega}}{NkT} = \int f(\Omega) \ln[4\pi f(\Omega)]d\Omega$$

(17)

where $f(\Omega)$ is the single particle orientational distribution function for a solid angle $\Omega$; $A_{1\Omega}$ is the Helmholtz free energy of the hard-core body, and $A_{vdW}$ is the contribution to the free energy from the van der Waals forces.

The calculation of $A_0$ can be done using a scaling procedure proposed by Parsons [48], that consists in giving the non-spherical hard body properties in terms of the hard-spheres fluid properties,

$$A_0 = \frac{V_{exc}}{8V_m} A_{HS}$$

(18)

where $V_{exc}$ is the volume excluded by two non-spherical particles, $V_m$ is the molecular volume per particle and $A_{HS}$ is the Helmholtz free energy of a hard-spheres fluid at the same packing fraction value than the non-spherical system. The brackets denote an angular average over all the orientational configurations between a pair of particles. The same approach can be used to evaluate $A_{cdW}$ in a high-temperature perturbation expansion.

This approach has been used for the description of the phase diagram of a typical LC substance, such as p-azoxyanisole [50], using a mean-field approach for LC [47] together with results for a a first-order perturbation theory for a square-well isotropic fluid [51-54]. The molecular parameters of the molecule were obtained by a standard fitting method to thermodynamic properties. The accuracy of this approach can be substantially improved if a more realistic estimation of the hard-body geometric parameters is taken. This can be accomplished by quantum mechanical calculations, minimizing the total energy of the real molecule with respect to all or some structural parameters. For example, the PM3 [55] semiempirical method uses experimental values of the angles and distances between atoms in order to get the molecular structure, This optimization procedure leads to the most stable structure observed in ideal conditions. In Ref. 56 we have shown that the combined use of a second-order perturbation theory and PM3 calculations, obtaining the molecular volume of p-azoxyanisole by PM3 instead of the value obtained by fitting to thermodynamic properties, improves substantially the accuracy of the theoretical prediction of the phase diagram for this substance.

The thermodynamic modeling of polar LC substances is more challenging, since polar interactions give rise to a complexity in the stability of LC phases, as has been already established in a series of Monte Carlo studies for dipolar PM models, such as hard spherocylinders with point dipoles [21,22,39].

Different theories for polar PMs have predicted opposite effects. For example, Vega and Lago [14], and Vanakaras and Photinos [15] predicted that elongated hard-core molecules with longitudinal central dipoles should stabilize the nematic phase with respect to the isotropic phase, in contradiction with computer simulation results by McGrother et al. [21]. The explanation for this discrepancy has been given by Emelyanenko and Osipov [57] in terms of the associating behaviour observed for polar fluids at low temperatures. These authors included an associating contribution to the free energy in order to take into account the pairing observed in the simulated systems. For small values of the dipolar moment the nematic phase is stabilized but there is a critical value where the effect is reversed and for dipolar moments above this value the nematic phase is destabilized. This theory is based on the same scheme of the SAFT approach, where the Helmholtz free energy has five different contributions: the usual ideal and dipole-dipole contributions, plus the contributions of the dimers formed by the pairing of dipoles, and the monomer-dimer and dimer-dimer interactions. Notice that by neglecting the associating free energy arising from the dimer formation, the inversion mechanism for the isotropic-nematic range of stability can not be obtained, a clear indication that a proper thermodynamic modeling of polar substances is incomplete if the associating mechanism is not included.

4. Conclusions

In this paper we have summarized recent work in the application of molecular based theories and computer simulation methods to predict properties of primitive models of ionic and polar systems. We have discussed how the Wolf procedure to simulate charged systems has the advantage of offering a unified method to deal theoretically and by computer simulations with systems of particles interacting via potentials like Eq. (14). The combined use of the Wolf method, associating fluid theories and quantum mechanical calculations for the characterization of molecules seems to be a promising scheme for the development of realistic molecular thermodynamic theories for complex fluids in the near future.

Acknowledgements

This work was supported under CONACYT grants 2002-C01-41678 and 2003-C03- 42439/A-1, and CONCYTEG grant 04-16-K119-092. C. Avendaño, Niza Ibarra-Avalos, and Jorge Medina thank Ph.D. scholarships from CONACYT. Carla M. Quezada thanks a Bachelor scholarship from CONCYTEG.