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Living polymers in a size-asymmetric electrolyte

Sorin Bastea*
Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550

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A living polymers transition is found in molecular dynamics simulations of a charge-symmetric size-asymmetric electrolyte with no anisotropic interactions. The fluid has strong polymeric character at low temperatures, where it consists of large, alternating-charge linear chains and rings in chemical equilibrium. A mean-field theory of chain association is consistent with the existence of such a transition. In the polymeric phase, the system is very weakly conducting or electrically insulating.

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Ionic systems are rather ubiquitous in nature, ranging from molten salts to the electrolyte solutions crucial for the functioning of living cells, to even pure water at very high densities [1]. A decisive step in understanding how the long-range character of the Coulomb potential determines the behavior of ionic systems has long proved to be the Debye-Hückel theory of screening by counterions [2]. The introduction of the physically appealing notion of ionic pairing led to an additional refinement of these ideas and has allowed the recent development of successful theories for criticality in simple electrolyte models [3]. The formation of ionic pairs and higher-order clusters was initially observed and characterized in symmetric electrolytes [4] and it is now understood to be an essential feature of ionic systems [5–9]. Recent work has revealed that ionic clustering is even more pronounced in size-asymmetric model electrolytes and it is associated with an unexpected behavior of their phase coexistence regions [6,7]. Size asymmetry is of course the norm in numerous circumstances, e.g., colloid science [10] or systems with significant ionic character such as LiCl, NaH, etc. We present molecular dynamics simulations of a size-asymmetric electrolyte with isotropic interactions, where strong ionic clustering produces a continuous polymerization transition to a phase with very weakly conducting or insulating character.

We study a system of $N/2$ positive charges $+q$ and $N/2$ negative charges $-q$ interacting through potentials

$$v_{ij}(r)=u_{ij}(r)+\frac{q_i q_j}{4\pi D_0 r} \tag{1}$$

$(i,j=+,-)$. D_0 is the vacuum dielectric permeability, and $u_{ij}(r)$ are exponential-6 potentials,

$$u_{ij}(r)=\epsilon\left[Ae^{-\alpha(r/r_{ij})}-B\left(\frac{r_{ij}}{r}\right)^6\right] \tag{2}$$

with well depth ϵ corresponding to distance r_{ij}; $A=6e^{\alpha}/(\alpha-6)$, $B=\alpha/(\alpha-6)$, and $\alpha=13$. The Born-Mayer exponential term provides a good description of the repulsive short-range interactions that occur between closed-shell atoms or ions, e.g., in molten salts [11]. When modified to include many-body effects, such simple ionic models appear to have a rather wide range of applicability [12]. We set $q=1$ in units of the electron charge e and impose an extreme size asymmetry by choosing $r_{++}=0$ and $r_{+-}=r_{--}/2$, i.e., the positive ions are point charges. We choose as a relevant length scale the position of the minimum of $v_{+-}(r)$, which we denote by d_{+-}, $d_{+-}\simeq 0.67 r_{+-}$. This is appropriate at low temperatures where it should allow a comparison with the charged hard-core models usually studied. The total reduced number density is $\rho^*=\rho d_{+-}^3$, $\rho=N/V$, and the reduced temperature $T^*=k_B T/E_0$, with $E_0=q^2/4\pi D_0 d_{+-}$. Most of the simulations were performed with $N=2048$ particles in the microcanonical (*NVE*) ensemble, in a box with periodic boundary conditions, at reduced density $\rho^*=0.12$ and reduced temperatures T^* in the range 0.0065 to 0.0365. The reduced simulation box length was $L^*=L/d_{+-}\simeq 26$; simulations with $L^*\simeq 35$ $(N=5324)$ were also performed to verify the influence of finite-size effects. The energy scale of the short-range potentials was set to $\epsilon/E_0\simeq 2.4\times 10^{-3}$. The Coulomb interactions were handled using the Ewald summation technique with conducting boundary conditions. The system was typically equilibrated for $5\times 10^4-10^5$ time steps, using successively velocity rescaling, Andersen thermostat, and normal (*NVE*) molecular dynamics. The accumulation runs consisted of at least 5×10^5 time steps.

At the lowest temperatures, the pair correlation functions signal a strongly structured fluid, Fig. 1. The opposite-charge pair correlation function $g_{+-}(r)$ exhibits a very sharp peak at small distances, one that might be expected, for example, if significant ionic pairing takes place. An analysis of the coordination number as a function of distance, $N_{+-}(r)=(\rho/2)\int_0^r g_{+-}(r')4\pi r'^2\,dr'$, Fig. 1 (inset), reveals, however, the presence of two opposite-charge nearest neighbors, an indication of alternating-charge chain association. The importance of such polymeric structures for the thermodynamics of electrolytes has been suggested before in the context of size-symmetric systems [5] and has been recently reinforced by Monte Carlo simulations of size-asymmetric hard-core electrolytes [6,7]. Due to the large size asymmetry, their contribution is dominant here, apparently leading—see Fig. 1—to a continuous transition between a nonstructured isotropic fluid at high temperatures to a structured isotropic fluid at low temperatures.

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*Electronic address: bastea2@llnl.gov

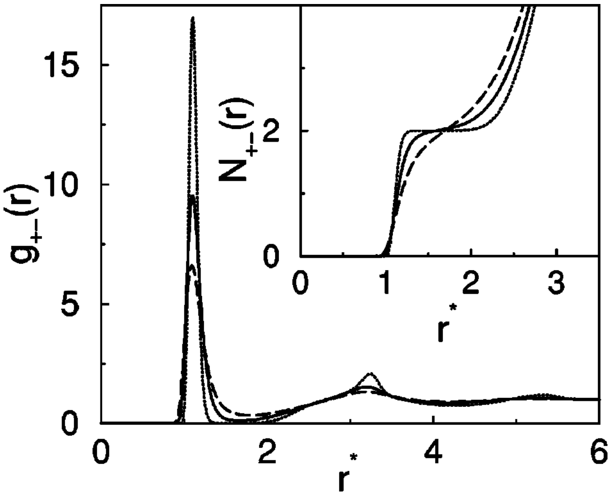

FIG. 1. Opposite-charge pair correlation functions $g_{+-}(r)$ at $T^*=0.0065$ (dotted line), $T^*=0.016$ (solid line), $T^*=0.024$ (dashed line), and corresponding coordination numbers $N_{+-}(r)$ (inset).

The formation of large structures in ionic systems can be understood using appropriate clustering definitions as first introduced for ionic systems by Gillan [4]. Gillan's original analysis of cluster populations labels an ion as belonging to a cluster if the smallest distance between the ion and other cluster ions is less than a certain distance R_C. We use $R_C=1.5d_{+-}$, which is a good approximation for the position of the first minimum of $g_{+-}(r)$. We note, however, that the low-temperature analysis is insensitive to the choice of R_C in a significant range. The same is true if we adopt a more restrictive definition of clustering, i.e., one that requires that an ion be "linked" to a cluster through an ion of opposite charge. We find that at low temperatures the system consists of large alternating-charge chains and rings that behave as living polymers, i.e., break and recombine continuously leading to a temperature-dependent equilibrium size distribution. The lifetime of these linear polymers, particularly the smaller ones, is rather long, which explains the extremely long times needed to equilibrate the system. Figure 2 shows snapshots of the motion of such a small ring at the lowest temperature simulated, which diffuses as a well-defined entity and exhibits the vibrational and rotational motions specific of a regular polymer.

The association of neutral monomers in linear polymers under conditions of chemical equilibrium leads to a continuous polymerization transition accompanied by a maximum of the specific heat signaling the onset of chain formation [13]. The position of the maximum is a measure of the association, or "bond" energy within a chain. Such a transition is also apparently taking place in the ionic size-asymmetric system that we are simulating. We therefore calculate the constant volume specific heat, $c_V=(\partial E/\partial T)_V/N$, as a function of temperature in the microcanonical ensemble using the equilibrium kinetic energy fluctuations, $\langle \mathcal{K}^2\rangle-\langle \mathcal{K}\rangle^2=(3/2)Nk_B^2T^2(1-3k_B/2c_V)$ [14]. The maximum of c_V, Fig. 3, places the continuous polymerization transition at $T_p^*\simeq 0.016$, in agreement with the position of energy $E=E(T)$ and pressure $p=p(T)$ inflection points.

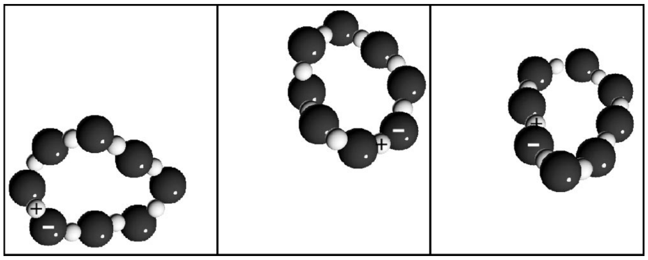

FIG. 2. Snapshots of the motion of a small alternating-charge ring at intervals of 150 000 time steps; $T^*=0.0065$.

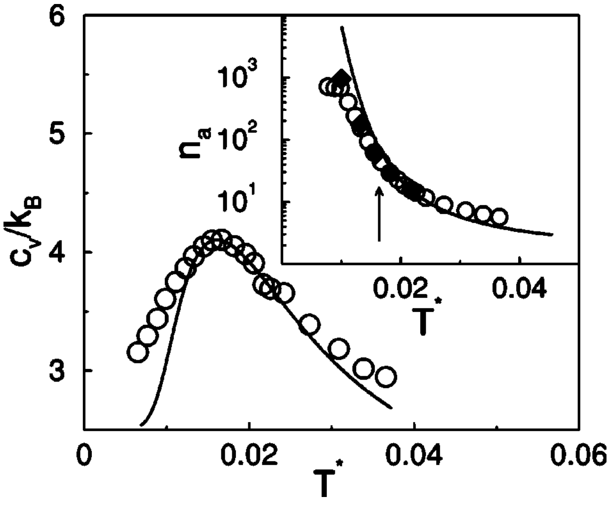

FIG. 3. Specific heat c_V from simulations (circles) and mean-field theory (solid line) after a temperature rescaling (see text). Inset: average chain size n_a from simulations with $N=2048$ particles (circles), $N=5324$ (filled diamonds), and mean-field theory (solid line); arrow indicates T_p^*.

It is remarkable that in the living polymers systems previously studied, the association of monomers into chains is driven by strong anisotropic interactions, which many times are of a dipolar nature [15]. While in the present case no such anisotropy is present, isotropic long-range (Coulomb) interactions mediated by extreme size asymmetry lead to similar characteristic behavior. This could perhaps be attributed to an enhanced tendency for dipolar pairing due to size asymmetry. However, although the chain size distribution above the polymerization temperature is peaked at $n=2$ (dipolar pairs), the distribution of ion fractions making up identical size chains is not, with the value for pairs remaining very small, of the order 10^{-2}. Nevertheless, energy considerations also suggest that the formation of chains is favored in systems with large size asymmetry [6,7]. If the propensity for chain formation is assumed to prevail for such electrolytes, a mean-field theory for charged associating chains can be formulated, as in the case of neutral living polymers [16]. At the simplest level such a theory (see below) does not include the size asymmetry *per se*, but only implicitly in the chain association assumption. The system is assumed to be a mixture of alternating-charge chains which are electrically neutral when containing equal numbers of positive and negative ions and with charge $\pm q$ otherwise. At low densities, the free energy of such a system can be written as

$$
\begin{aligned}
f=\frac{F}{Vk_BT}=&-\frac{3}{2}\rho\ln T+\sum_{n=1}\rho^0_{2n}(\ln\rho^0_{2n}-1)\\
&+\sum_{n=0}[\rho^+_{2n+1}(\ln\rho^+_{2n+1}-1)\\
&+\rho^-_{2n+1}(\ln\rho^-_{2n+1}-1)]-\sum_{n=1}\rho_n\ln K_n+f_{\mathrm{DH}}(\rho_c),
\end{aligned}
\tag{3}
$$

where ρ^0_{2n} and $\rho^{\pm}_{2n}$ are densities of uncharged and charged chains, respectively. K_n is the partition function of an n chain and ρ_c is the total density of charged chains $\rho_c=\Sigma_{n=0}(\rho^+_{2n+1}+\rho^-_{2n+1})$. The Debye-Hückel term

$$
f_{\mathrm{DH}}(\rho_c)=-\frac{1}{4\pi d^3}\left[\ln(1+\kappa d)-\kappa d+\frac{(\kappa d)^2}{2}\right]
\tag{4}
$$

includes an effective hard core d, that we set to d_{+-} independent of polymerization effects; $\kappa^2=q^2\rho_c/D_0k_BT$. For the n-chain partition function we use $K_n=[K_2(T)]^{n-1}$, with $K_2(T)$ the dimer association constant in the low-temperature Bjerrum approximation, $K_2(T)=4\pi d^3_{+-}T^*\exp(1/T^*)$ [3], neglecting interactions beyond nearest neighbors along a chain. [Here we treat the short-range potential $u_{+-}(r)$ as effectively hard core, but this should introduce only small errors at low temperatures.] We note that if only $+-$ "dimerization" is allowed, the above theory reduces to the so-called Debye-Hückel-Bjerrum (DHBj) theory [3]. The energy of the system is the sum of kinetic, "bond," and ionic terms,

$$
e=\frac{E}{V}=\frac{3}{2}k_BT+(\rho-\rho_t)e_2+e_{\mathrm{DH}}(\rho_c)
\tag{5}
$$

with ρ_t the total chains density, $\rho_t=\Sigma_{n=1}\rho_n$, $e_2=-E_0+k_BT$ the average $+-$ "bond" energy, and e_{DH} the Debye-Hückel contribution,

$$
e_{\mathrm{DH}}(\rho_c)=-\frac{E_0T^*}{8\pi d^3_{+-}}\frac{(\kappa d_{+-})^3}{1+\kappa d_{+-}}.
\tag{6}
$$

The chain size distribution ρ_n is then obtained by minimizing f at fixed density ρ and temperature T, with the constraint of particle conservation, $\Sigma_{n=1}n\rho_n=\rho$, and charge neutrality, $\Sigma_{n=0}[\rho^+_{2n+1}-\rho^-_{2n+1}]=0$. We obtain

$$
\rho^0_{2n}=K_2^{-1}e^{2n\lambda},
\tag{7}
$$

$$
\rho^+_{2n+1}=\rho^-_{2n+1}=K_2^{-1}e^{(2n+1)\lambda}\exp\left(-\frac{\partial f_{\mathrm{DH}}}{\partial\rho_c}\right),
\tag{8}
$$

where $\rho^+_{2n+1}=\rho^-_{2n+1}$ is a consequence of charge neutrality and λ can be interpreted as the monomer chemical potential. The particle conservation condition can be recast as an equation for the charge density ρ_c, which after being solved numerically also allows the calculation of ρ_t. Substitution into the energy equation yields the specific heat through $\rho c_V=\partial e/\partial T|_\rho$.

We find that c_V displays the characteristic maximum [13] of a living polymers transition at $T^*_{p0}\simeq 0.11$. This is higher than the transition temperature obtained in the simulations, but it is not surprising given the many approximations involved. In particular, the K_n approximation used leads to a large overestimate even for the energy of long, straight alternating-charge chains, while size-asymmetry-dependent packing and solvation effects, neglected here, should decrease the polymerization temperature by weakening the $+-$ "bonds" [17]. After a suitable rescaling of the temperature, the calculated c_V is qualitatively compared with the simulation results in Fig. 3. We note that the height of the c_V maximum is very well reproduced, along with the higher-temperature behavior. The low-temperature deviations, however, are significant, probably due to the neglect of ring structures that appear to be very important below the transition temperature. In fact, the cluster analysis yields mostly neutral structures at low temperatures, which is not well reproduced by the above mean-field model.

Another signature of a continuous polymerization transition is the rapid chain growth below T^*_p [13]. We show in Fig. 3 (inset) the average chain size $n_a=\Sigma_{n=1}n\rho_n/\Sigma_{n=1}\rho_n$ found in the simulations and with the above mean-field treatment after the same rescaling of the temperature used for c_V. The chain size at T^*_p is in good agreement with the theory, as it is the overall behavior. The slower rise of n_a in the simulations than in the theory at low temperatures may be due to a depletion of linear chains due to rings formation, as noted before. It is worth pointing out that the finite-size effects that appear to affect n_a for the smaller system size occur only at the lowest temperatures, far away from T^*_p. We also estimate an effective lifetime τ of the polymeric chains by assuming an initial exponential decay $\exp(-t/\tau)$ of the time correlation function $C(\Delta t)=\langle\rho_t(t_0)\rho_t(t_0+\Delta t)\rangle-\langle\rho_t\rangle^2$ of the total number of chains ρ_t; τ is, for example, of the order of 20 MD time steps at $T^*=0.01$ (compared with $\simeq 5\times 10^5$ total simulation steps), although it may be significantly longer for the smaller chains and rings.

The formation of large chains and rings and the dominance of the neutral ones has important consequences for the conduction properties of the polymeric phase. We calculate the electrical conductivity σ using the Green-Kubo expression

$$
\sigma(t)=\frac{1}{3Vk_BT}\int_0^t\langle\mathbf{j}(t')\cdot\mathbf{j}(0)\rangle dt',
\tag{9}
$$

where $\mathbf{j}(t)=\Sigma_{k=1}^N q_k\mathbf{v}_k(t)$ is the charge current; σ is evaluated from the large times value of $\sigma(t)$, $\sigma=\lim_{t\to\infty}\sigma(t)$. Below the transition temperature, $\sigma(t)$ exhibits very strong oscillatory behavior and decays apparently to zero, i.e., the polymeric phase is very weakly conducting or insulating; the conductivities above T^*_p are shown in Fig. 4. As the temperature increases, the conductivity also increases exhibiting an

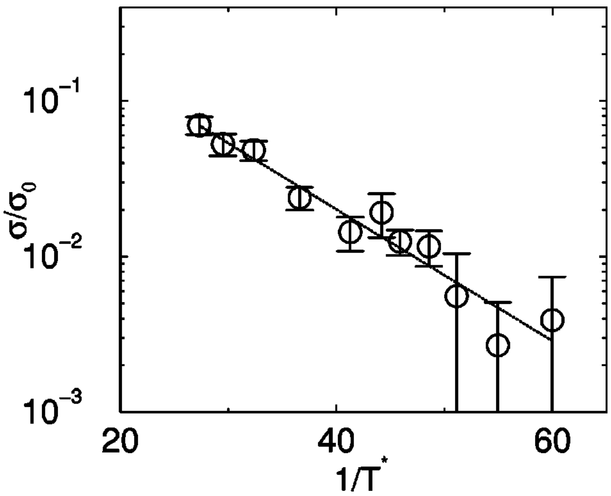

FIG. 4. Electrical conductivity for $T^* > T_p^*$ (circles) and fit with $\sigma = \sigma_0 \exp(-E_b^*/T^*)$ (dotted line).

activated behavior well described by $\sigma = \sigma_0 \exp(-E_b^*/T^*)$, with $E_b^* \simeq 0.1$. The conductivity increase is driven by an increasing charged clusters density, which occurs through the break-up of $+-$ "bonds." E_b can therefore be interpreted as an effective "bond" strength, yielding $T_p^*/E_b^* \simeq 0.16$, which is comparable with the value found in neutral living polymers of 0.25 [13]. The possibility of an electrolyte insulating phase has been discussed before in the light of strong ionic pairing at low densities, in the vapor region of symmetric ionic systems [11,18,19]. An insulating phase may arise here in connection with a living polymers transition in the liquid region of the phase diagram. It should be noted that the very slow dynamics of the system at low temperatures, leading to the observed Arrhenius temperature dependence of the conductivity, may render the question of the conducting or insulating character of the polymeric phase rather moot.

The chain associating tendency of size-asymmetric electrolytes, underscored by the continuous polymerization transition reported here, may interfere with the vapor-liquid coexistence and perhaps explain the observed reduction of the vapor-liquid phase separation region in electrolytes as the size asymmetry increases [6,7]. The competition between chain association and liquid condensation has been studied before for the case of neutral monomers, where it was found that vapor-liquid coexistence can become metastable under strong chain association conditions [20]. This is also worth exploring in the case of ionic systems, particularly because simulation results suggest that vapor-liquid coexistence may persist in charge-symmetric size-asymmetric electrolytes even for the extreme case of point cations [6], while theoretical calculations find no such coexistence [10]. Finally, we note that polymeric behavior has been observed in molten $BeCl_2$ [21], where it was found to be due to the strong polarizability of the anion, coupled with the size-asymmetry of the ions. We find here that size-asymmetry alone may lead to living polymers behavior.

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[1] C. Cavazzoni *et al.*, Science **283**, 44 (1999).
[2] P.W. Debye and E. Hückel, Phys. Z. **24**, 185 (1923).
[3] M.E. Fisher and Y. Levin, Phys. Rev. Lett. **71**, 3826 (1993).
[4] M.J. Gillan, Mol. Phys. **49**, 421 (1983).
[5] Y. Levin and M.E. Fisher, Physica A **225**, 164 (1996).
[6] J.M. Romero-Enrique, G. Orkoulas, A.Z. Panagiotopoulos, and M.E. Fisher, Phys. Rev. Lett. **85**, 4558 (2000).
[7] Q. Yan and J.J. de Pablo, Phys. Rev. Lett. **86**, 2054 (2001).
[8] Q. Yan and J.J. de Pablo, J. Chem. Phys. **114**, 1727 (2001).
[9] J.J. Weiss and D. Levesque, Chem. Phys. Lett. **336**, 523 (2001).
[10] R. van Roij and J.-P. Hansen, Phys. Rev. Lett. **79**, 3082 (1997).
[11] Y. Guissani and B. Guillot, J. Chem. Phys. **101**, 490 (1994).
[12] P.A. Madden and M. Wilson, J. Phys.: Condens. Matter **12**, A95 (2000).
[13] Y. Rouault and A. Milchev, Phys. Rev. E **51**, 5905 (1995).
[14] J.L. Lebowitz, J.K. Percus, and L. Verlet, Phys. Rev. **153**, 250 (1967).
[15] M.A. Osipov, P.I.C. Teixeira, and M.M. Telo da Gama, Phys. Rev. E **54**, 2597 (1996).
[16] M.E. Cates and S.J. Candau, J. Phys.: Condens. Matter **2**, 6869 (1990).
[17] Preliminary simulations with $\rho^* = 0.3$ yield $T_p^* \simeq 0.02$.
[18] H. Weingärtner, V.C. Weiss, and W. Schröer, J. Chem. Phys. **113**, 762 (2000).
[19] J.M. Callilol, J. Chem. Phys. **102**, 5471 (1995).
[20] R. van Roij, Phys. Rev. Lett. **76**, 3348 (1996).
[21] M. Wilson and P.A. Madden, Mol. Phys. **92**, 197 (1997).