Off-Lattice van der Waals Equations of State for Polymer Liquids

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Received November 23, 1992
Revised Manuscript Received May 1, 1993

Recently Rodgers[1] has correlated *PVT* data for 56 polymers with six equations of state and compared the accuracy of specific volume predictions. Reported absolute average deviations follow (10^{-4} cm^3/g): 6, Dee and Walsh modified cell model (MCM);[2] 7, Simha–Somcynsky hole model (SS);[3] 8, Prigogine cell model (CM);[4] 9, Hartmann and Haque model (HH);[5] 22, Flory, Orwoll, Vrij model (FOV);[6] 33, Sanchez–Lacombe lattice fluid model (LF).[7] At melt densities packing primarily determines pressure so that a Born–Green–Yvon integral approach on a lattice[8] is an improvement over the LF model but is not as good as the semiempirical HH model. We take the opposite tack and treat the attractive forces as a uniform background[9] by adding a van der Waals (vdW) term to the athermal pressure contribution $(\tilde{P}/\tilde{T})_0$ for tangent hard sphere (THS) chains

$$\frac{\tilde{P}}{\tilde{T}} = \left(\frac{\tilde{P}}{\tilde{T}}\right)_0 - \frac{\eta^2}{\tilde{T}} \qquad (1)$$

where the reduced variables $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, and $\eta = V^*/V$ are based on characteristic values

$$P^* = \epsilon/v_0 \qquad T^* = \epsilon/R \qquad V^* = (r/M)v_0 \qquad (2)$$

with r tangent spheres of volume $v_0 = \pi d^3/6$ forming a chain of molecular weight M. In Table I the athermal terms for the generalized Flory (GF),[10] Flory–Huggins (GFH),[10] and Flory dimer (GFD)[11] (incorporating either the Tildesley–Street (TS)[12] or Boublik–Nezbeda (BN)[13] dimer equation of state) models, first-order thermodynamic perturbation theory (TPT1)[14] (using either Carnahan–Starling (CS) or Percus–Yevick (PY) hard-sphere equations of state and pair distribution contact values[15]) and the adhesive hard sphere (AHS)[16] model with PY closure are given for $M \to \infty$. For pressure ranging from atmospheric to 200 MPa all equations have absolute average specific volume deviations similar to the HH value; with V^* set equal to the van der Waals volume V_{vdW}[17] the deviations are near those for the FOV equation. Note that V_{vdW}/V^* is generally greater than 1 and its magnitude increases with $(\tilde{P}/\tilde{T})_0$ at constant η, i.e., the opposite of $\eta \sim V^*$ at constant $(\tilde{P}/\tilde{T})_0$ since $\partial(\tilde{P}/\tilde{T})_0/\partial\eta > 0$.

Consider briefly the effects of stiffness, branching, overlap of adjoining segment spheres, and association on V_{vdW}/V^*. The polymer reference interaction site model (PRISM)[18,19] predicts that isothermal compressibility decreases with stiffness[20] for THS chains. Therefore, pressure increases and so must η or V^* if a flexible chain is used as a model. On the other hand, the units of a stiff chain are exposed to more intermolecular interactions which should lower both P and the model V^* if the vdW term does not absorb this properly. It is hard to say which has the larger influence. For branching, the athermal part increases only a few percent but the loss of adhesion boosts P considerably.[21] Overlap of adjacent spheres increases the stiffness but also decreases the ratio of hard contact surface to hard volume; this surface can be modeled by a smaller tangent sphere V^*.[22] Association effectively increases molecular weight which leads to lower P[14,23,24] and model V^*, but as $M \to \infty$ cohesive effects dominate. Branching might best be described by higher order TPT[14,25] and chain stiffness by an anisotropic AHS model.[26] Stiffness and the interpenetration of adjoining segment spheres may be incorporated into either the GFD model[27] or Wertheim's association theory.[14,25] With tabulated bond lengths and angles and vdW radii such considerations might be used to eliminate the parameters v_0 and r/M.

In Table II more information is given of the GF + vdW fit because it is generally best for two parameters (at low P the GFH + vdW model is better because V^* decreases a couple percent). The characteristic values for the 56 listed polymers are determined by a least-squares regression of pressure from volumetric data (generated by a Tait equation for the second group of polymers) with temperature and pressure range described by Rodgers.[1] Large $|V_{vdW}/V^*-1|$ values and the corresponding deterioration of the two-parameter fit suggest that the hard-core descrip-

Table I. Comparison of seven van der Waals (vdW) Equations of State

equation of state	$(\tilde{P}/\tilde{T})_0$	V_{vdW}/V^{*a}	$\lvert\Delta V\rvert_{avg}$ (10^{-4} cm^3/g) 3 param	$\lvert\Delta V\rvert_{avg}$ (10^{-4} cm^3/g) $V_{vdW}/V^* \equiv 1$	ref
GF	$1.31659\frac{\eta^2}{(1-\eta)^3}(2-\eta)$	1.0108[b]	10.4	17.9	10
GFH	$0.55166\left[\ln(1-\eta)+\frac{\eta}{(1-\eta)^3}(1+2.9\eta-2.26667\eta^2)\right]$	0.9845	10.0	20.8	10
GFD(TS)	$0.95752\frac{\eta^2}{(1-\eta)^3}(1.45696+3.10386\eta-2.75503\eta^2)$	1.0464	11.6	20.3	11
GFD(BN)	$0.95752\frac{\eta^2}{(1-\eta)^3}(1.5+2.25\eta-1.25\eta^2)$	1.0709	11.7	24.1	11
TPT1(CS)	$\frac{\eta^2}{(1-\eta)^3}\left[(2+\eta-\eta^2)-\frac{(1-\eta)^2}{(2-\eta)}\right]$	1.0540	11.6	21.3	14
TPT1(PY)	$3\frac{\eta^2}{(1-\eta)^3}\left[1-\frac{(1-\eta)^2}{(2+\eta)}\right]$	1.0729	11.8	24.5	14
AHS(PY)	$1.5\frac{\eta^2}{(1-\eta)^3}(1+\eta)$	1.0887	11.8	27.5	16

[a] van der Waals volume. Reference 17, p 816, Table IX. [b] Average of all polymers in Table II. Excludes poly(tetrafluoroethylene).

0024-9297/93/2226-4970$04.00/0

Table II. Characteristic Parameters for the Generalized Flory (GF) + van der Waals (vdW) Equation of State

polymer	ref	density range V_{vdW}/V[a]	V_{vdW}/V^*[a]	V^* (cm³/g)	P^* (bar)	T^* (K)	n/r[b]	d (Å)	$\lvert\Delta V\rvert_{avg}$ (10^{-4} cm³/g)
high-density polyethylene	28	0.5516–0.6295	0.9354	0.7795	5529	12755	8.77	6.83	20.0
low-density polyethylene	28	0.5605–0.6354	1.0354	0.7043	9886	8844	3.77	4.98	19.1
polystyrene	29	0.5877–0.6506	0.9451	0.6386	6856	15701	2.87	6.81	7.2
poly(*o*-methylstyrene)	29	0.6001–0.6535	0.9709	0.6450	7638	15433	2.21	6.53	4.3
poly(vinyl acetate)	30	0.6013–0.6446	1.0204	0.5223	11038	10018	1.68	5.00	1.4
poly(methyl methacrylate)	31	0.6295–0.6816	1.0307	0.5437	10058	13388	2.04	5.69	3.5
poly(cyclohexyl methacrylate)	31	0.5991–0.6713	0.9996	0.5901	7890	13635	1.45	6.20	10.1
poly(*n*-butyl methacrylate)	31	0.5697–0.6704	1.0037	0.6080	8829	11425	1.25	5.63	18.5
branched polyethylene	31	0.5495–0.6332	0.9996	0.7295	8258	9901	4.87	5.49	10.9
linear polyethylene	31	0.5495–0.6299	1.0548	0.6913	10584	8426	3.41	4.79	4.7
high MW linear polyethylene	31	0.5428–0.6201	1.0884	0.6700	13297	7456	2.48	4.26	7.2
polyisobutylene	32	0.6373–0.6880	0.9818	0.7426	6334	15824	4.99	7.01	4.1
poly(dimethylsiloxane)	32	0.5988–0.6740[c]	1.0519	0.6116	5646	8096	2.63	5.83	7.2
poly(4-methyl-1-pentene)	33	0.4947–0.6129	0.9812	0.7431	6278	9818	2.08	6.00	8.8
poly(tetrafluoroethylene)	34	0.4511–0.5185	1.4559	0.2098	17156	4396	1.02	3.28	14.0
cis-1,4-polybutadiene	35	0.5031–0.6764	0.9500	0.7277	6809	12303	3.82	6.30	12.5
poly(ethylene oxide)	36	0.5342–0.6082	1.0037	0.5466	12004	9446	2.72	4.77	7.9
poly(tetrahydrofuran)	36	0.5510–0.6163	0.9524	0.6498	8325	11091	2.36	5.69	7.4
poly(vinyl methyl ether)	37	0.5412–0.6471	0.9304	0.6364	8108	12344	3.43	5.95	11.8
poly(methyl acrylate)	38	0.5472–0.6533	0.9748	0.5467	10161	11497	2.00	5.39	13.4
poly(ethyl acrylate)	38	0.5457–0.6618	0.9918	0.5650	8787	10692	1.79	5.52	16.8
poly(ethyl methacrylate)	38	0.5976–0.6697	1.0429	0.5572	10954	10630	1.27	5.12	9.3
tetramethyl-Bisphenol A polycarbonate	39	0.5653–0.6361	1.0912	0.5339	11003	9982	0.46	5.00	8.3
hexafluoro-Bisphenol A polycarbonate	39	0.5490–0.6358	1.1098	0.3769	11913	8626	0.44	4.64	6.5
Bisphenol chloral polycarbonate	39	0.5724–0.6451	1.0473	0.4351	12071	11556	0.60	5.09	6.3
poly(epichlorohydrin)	40	0.5967–0.6661	0.9392	0.4973	8024	15485	3.49	6.43	4.2
poly(ϵ-caprolactone)	40	0.5897–0.6563	0.9623	0.6049	7488	12868	2.07	6.19	5.1
poly(vinyl chloride)	40	0.6145–0.6690	0.9704	0.4819	8147	15560	5.27	6.41	4.7
a-polypropylene	40	0.5848–0.6445	1.0088	0.7227	7066	10022	3.88	5.81	6.8
ethylene/propylene 50 wt %	41	0.5336–0.5806	0.9344	0.7803	6551	12659	6.12	6.44	23.1
ethylene/vinyl acetate 18 wt %	42	0.5344–0.6278	0.9538	0.7274	7504	11131	5.31	5.89	11.7
ethylene/vinyl acetate 25 wt %	42	0.5286–0.6351	0.9616	0.7072	7410	10842	5.10	5.87	16.5
ethylene/vinyl acetate 28 wt %	42	0.5257–0.6313	0.9671	0.6972	8199	10471	4.41	5.61	15.4
ethylene/vinyl acetate 40 wt %	42	0.5322–0.6433	0.9702	0.6706	8007	10865	4.38	5.72	19.4
styrene/acrylonitrile 2.7 wt %	39	0.5630–0.6523	0.9984	0.6042	8146	12676	2.11	5.99	10.4
styrene/acrylonitrile 5.7 wt %	39	0.5580–0.6506	1.0235	0.5893	9460	11250	1.70	5.48	9.8
styrene/acrylonitrile 15.3 wt %	39	0.5779–0.6585	1.0091	0.5971	8431	13071	2.38	5.98	7.1
styrene/acrylonitrile 18.0 wt %	39	0.5839–0.6664	1.0059	0.5988	8185	13502	2.58	6.11	8.1
styrene/acrylonitrile 40 wt %	39	0.5911–0.6755	1.0137	0.5929	8304	14321	3.22	6.20	8.3
polysulfone	43	0.5623–0.6662	1.0627	0.4943	13457	12184	0.34	5.00	8.7
low-density polyethylene "A"	44	0.5431–0.6451	0.9734	0.7492	7474	11120	5.89	5.90	12.8
low-density polyethylene "B"	44	0.5443–0.6435	0.9596	0.7599	7137	11758	6.43	6.10	13.2
low-density polyethylene "C"	44	0.5443–0.6449	0.9709	0.7511	7484	11262	5.94	5.92	10.9
i-polypropylene	45	0.5150–0.6344	0.9713	0.7507	6122	10780	4.64	6.24	11.6
i-poly(1-butene)	45	0.5410–0.6502	0.9723	0.7499	6115	11451	3.70	6.37	13.8
poly(ethylene terephthalate)	46	0.5507–0.6317	1.0970	0.4468	16413	9904	0.59	4.37	4.6
poly(2,6-dimethylphenylene oxide)	47	0.5418–0.6522	1.1170	0.5167	12660	8802	0.93	4.58	8.4
Bisphenol A polycarbonate	48	0.5492–0.6616	1.0491	0.5106	12245	11312	0.59	5.03	12.7
polyarylate (Ardel)	48	0.5779–0.6655	1.0339	0.5156	11402	13040	0.52	5.40	5.7
phenoxy	48	0.5641–0.6814	1.0183	0.5526	12123	12822	0.56	5.27	19.8
poly(ethyl ether ketone)	49	0.5536–0.6386	1.1234	0.4603	15047	10305	0.43	4.56	6.0
polyamide 6	50	0.7157–0.8037	1.1259	0.5549	5052	21086	5.53	8.32	12.6
polyamide 6,6	50	0.6704–0.7728	1.2106	0.5161	8044	12353	1.09	5.96	6.3
styrene/acrylonitrile 70 wt %	51	0.6181–0.7118	0.9918	0.6042	7542	18885	5.54	7.02	12.3
styrene/methyl methacrylate 20 wt %	51	0.5664–0.6750	0.9926	0.5993	7568	13265	2.36	6.23	14.9
styrene/methyl methacrylate 60 wt %	51	0.5763–0.6878	1.0135	0.5699	7847	13205	2.42	6.15	16.9

[a] van der Waal volume. Reference 17, p 816, Table IX. [b] Number of mers per tangent hard sphere. [c] Reference 17, p 74, Table 4.2.

tion of some polymers could be improved. For others this is indicated by the monomer units per THS

$$\frac{n}{r} = \frac{RT^*}{M_{mer}P^*V^*} \tag{3}$$

where M_{mer} is the molecular weight of a repeat unit. Hydrocarbons and their copolymers, poly(tetrahydrofuran), poly(epichlorohydrin), poly(ϵ-caprolactone), poly(vinyl chloride), nylon, and styrene/acrylonitrile 70 wt % have unreasonably large n/r values, while the acrylates and methacrylates have ratios of THS diameter, d, to mer length that are far too big. Only poly(tetrafluoroethylene) has an excessively large V_{vdW}/V^* value and the PVT fit deteriorates badly when this is set to 1. The reduced density range V_{vdW}/V is greater than that for liquids but is bounded by the cylinder close-packing value $\eta = \pi/2\sqrt{3} \approx 0.91$. Remarkably V^*/V is also bounded by the sphere close-packing value $\eta = \pi/3\sqrt{2} \approx 0.74$. Presumably the reduced density of random close packing and the solid–liquid transition of athermal THS chains increase with chain length.

While mixture thermodynamic properties have to be symmetrized with respect to chain insertion order for the first four models[52] of Table I at lower molecular weights, the integral equations on which the last three are based naturally incorporate segment size difference effects like athermal phase separation at constant pressure (the thread

limit of PRISM[53] seems anomalous here). Only the vdW term requires a mixing rule. These simple models cannot describe the phase envelope for UCST (where nonrandom mixing is important[54]) but should improve upon the LCST correlation (where a good account of component cohesive energy density is necessary[55]) of other vdW models (LF, FOV). Of course, vdW theory is accurate for weak and long-range potentials[56] (e.g., a square-well (SW) with extent 2–3 times the hard core[57]), but realistic potentials are short ranged and the inclusion of several atoms into a THS should shorten this further ($d >$ atomic diameter). We expect that this makes $(P - P_0)/\eta$ ($=-\eta P^*$ for eq 1) convex with respect to η, which would explain the observed decrease of P^* with increasing pressure range (since the slope effectively increases). The opposite trend for LF and FOV models may result from a poor description of the hard core while the better PVT fits of CM, MCM, and the SS model benefit from the convexity of the potential employed at liquid and melt densities. The mean-spherical approximation (MSA), which is accurate for SW[58] and Yukawa[59] fluids in addition to SW chains,[60] can be extended to all models in Table I. A Yukawa + MSA theory is of special interest because (1) the algebraic results for spheres become coupled diffusion equations that incorporate branching (see ref 61 for a perturbative lattice description of this) along the THS chain (with $V_{vdW}/V^*=1$ or a fixed decay rate for the potential this would be a three-parameter theory), (2) a series of Yukawa terms can approximate any continuous potential,[62] including Lennard-Jones,[63] and (3) added terms could also improve the consistency of structural and thermodynamic predictions.[62,64,65]

Acknowledgment. We thank Dr. P. Rodgers for supplying us with PVT data files and a regression routine. This research was sponsored by AFOSR.

References and Notes

(1) Rodgers, P. A. *J. Appl. Polym. Sci.* **1993**, *48*, 1061.
(2) Dee, G. T.; Walsh, D. J. *Macromolecules* **1988**, *21*, 811, 815.
(3) Simha, R.; Somcynsky, T. *Macromolecules* **1969**, *2*, 342. Simha, R. *Macromolecules* **1977**, *10*, 1025.
(4) Prigogine, I.; Trappeniers, N.; Mathot, V. *Discuss. Faraday Soc.* **1953**, *15*, 93. Prigogine, I.; Bellemans, A.; Mathot, V. *The Molecular Theory of Solutions*; North-Holland Publishing Co.: Amsterdam, The Netherlands, 1957.
(5) Hartmann, B.; Haque, M. A. *J. Appl. Polym. Sci.* **1985**, *30*, 1553.
(6) Flory, P. J.; Orwoll, R. A.; Vrij, A. *J. Am. Chem. Soc.* **1964**, *86*, 3507.
(7) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352; *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 71.
(8) Lipson, J. E. G.; Andrews, S. S. *J. Chem. Phys.* **1992**, *96*, 1426.
(9) Longuet-Higgins, H. C.; Widom, B. *Mol. Phys.* **1964**, *8*, 549.
(10) Dickman, R.; Hall, C. K. *J. Chem. Phys.* **1986**, *85*, 4108.
(11) Honnell, K. G.; Hall, C. K. *J. Chem. Phys.* **1989**, *90*, 1841.
(12) Tildesley, D. J.; Streett, W. B. *Mol. Phys.* **1980**, *41*, 85.
(13) Boublik, T.; Nezbeda, I. *Chem. Phys. Lett.* **1977**, *46*, 315. Boublik, T. *Mol. Phys.* **1981**, *44*, 1369.
(14) Wertheim, M. S. *J. Chem. Phys.* **1987**, *87*, 7323; *J. Stat. Phys.* **1984**, *35*, 19, 35; **1986**, *42*, 459, 477.
(15) Reed, T. M.; Gubbins, K. E. *Applied Statistical Mechanics*; McGraw-Hill: New York, 1973; pp 254–7.
(16) Chiew, Y. C. *Mol. Phys.* **1990**, *70*, 129.
(17) Van Krevelen, D. W. *Properties of Polymers*; Elsevier: New York, 1990.
(18) Schweizer, K. S.; Curro, J. G. *Phys. Rev. Lett.* **1987**, *58*, 246. Curro, J. G.; Schweizer, K. S. *J. Chem. Phys.* **1987**, *87*, 1843.
(19) Schweizer, K. S.; Curro, J. G. *J. Chem. Phys.* **1988**, *89*, 3342, 3350.
(20) Honnell, K. G.; Curro, J. G.; Schweizer, K. S. *Macromolecules* **1990**, *23*, 3496.
(21) Yethiraj, A.; Hall, C. K. *J. Chem. Phys.* **1991**, *94*, 3943.
(22) Amos, M. D.; Jackson, G. *J. Chem. Phys.* **1992**, *96*, 4604.
(23) Chapman, W. G.; Jackson, G.; Gubbins, K. E. *Mol. Phys.* **1988**, *65*, 1057.
(24) Panayiotou, C.; Sanchez, I. C. *J. Phys. Chem.* **1991**, *95*, 10090.
(25) Phan, S.; Kierlik, E.; Rosinberg, M. L.; Yu, H.; Stell, G., submitted to *J. Chem. Phys.*
(26) Cummings, P. T.; Blum, L. *J. Chem. Phys.* **1986**, *84*, 1833. Blum, L.; Cummings, P. T.; Bratko, D. *J. Chem. Phys.* **1990**, *92*, 3741.
(27) Yethiraj, A.; Curro, J. G.; Schweizer, K. S.; McCoy, J. D. *J. Chem. Phys.* **1993**, *98*, 1635. Boublik, T.; Vega, C.; Diaz-Pena, M. *J. Chem. Phys.* **1990**, *93*, 730.
(28) Hellwege, K.-H.; Knappe, W.; Lehmann, P. *Kolloid Z. Z. Polym.* **1962**, *183*, 110.
(29) Quach, A.; Simha, R. *J. Appl. Phys.* **1971**, *42*, 4592.
(30) McKinney, J. E.; Goldstein, M. *J. Res. Natl. Bur. Stand.* **1974**, *78A*, 331.
(31) Olabisi, O.; Simha, R. *Macromolecules* **1975**, *8*, 206.
(32) Beret, S.; Prausnitz, J. M. *Macromolecules* **1975**, *8*, 536.
(33) Zoller, P. *J. Appl. Polym. Sci.* **1977**, *21*, 3129.
(34) Zoller, P. *J. Appl. Polym. Sci.* **1978**, *22*, 633.
(35) Barlow, J. W. *Polym. Eng. Sci.* **1978**, *18*, 238.
(36) Jain, R. K.; Simha, R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1929.
(37) Ougizawa, T.; Dee, G. T.; Walsh, D. J. *Macromolecules* **1991**, *24*, 3834.
(38) Data for poly(methyl acrylate), poly(ethyl acrylate), and poly(ethyl methacrylate) were provided by D. J. Walsh of Central Research and Development, Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, DE 19880.
(39) Kim, C. K. Ph.D. Thesis, The University of Texas at Austin, Austin, TX, 1992.
(40) Data for poly(epichlorohydrin), poly(ε-caprolactone), poly(vinyl chloride), and atactic polypropylene were determined by P. A. Rodgers and I. C. Sanchez at the Center for Polymer Research, The University of Texas at Austin, Austin, TX 78712.
(41) Griskey, R. G.; Waldman, N. *Mod. Plast.* **1966**, *43*, 245.
(42) Zoller, P.; Jain, R. K.; Simha, R. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 687.
(43) Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1261.
(44) Zoller, P. *J. Appl. Polym. Sci.* **1979**, *23*, 1051.
(45) Zoller, P. *J. Appl. Polym. Sci.* **1979**, *23*, 1057.
(46) Zoller, P.; Bolli, P. *J. Macromol. Sci., Phys.* **1980**, *B18*, 555.
(47) Zoller, P.; Hoehn, H. H. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1385.
(48) Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1453.
(49) Zoller, P.; Kehl, T. A.; Starkweather, H. W., Jr.; Jones, G. A. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 993.
(50) Wang, Y. Z.; Chia, W. J.; Hsieh, K. H.; Tseng, H. C. *J. Appl. Polym. Sci.* **1992**, *44*, 1731.
(51) Kim, C. K.; Paul, D. R. *Polymer* **1992**, *33*, 2089.
(52) Honnell, K. G.; Hall, C. K. *J. Chem. Phys.* **1991**, *95*, 4481.
(53) Curro, J. G.; Schweizer, K. S. *Macromolecules* **1990**, *23*, 1402. Schweizer, K. S.; Curro, J. G. *Chem. Phys.* **1990**, *149*, 105.
(54) Sariban, A.; Binder, K. *Macromolecules* **1988**, *21*, 711. Deutsch, H. P.; Binder, K. *Europhys. Lett.* **1992**, *17*, 697. Schweizer, K. S.; Curro, J. G. *J. Chem. Phys.* **1989**, *91*, 5059. Yethiraj, A.; Schweizer, K. S. *J. Chem. Phys.* **1992**, *97*, 5927.
(55) Sanchez, I. C. *Macromolecules* **1991**, *24*, 908.
(56) Lebowitz, J. L.; Penrose, O. *J. Math. Phys.* **1966**, *7*, 98. Lebowitz, J. L.; Stell, G.; Baer, S. *J. Math. Phys.* **1965**, *6*, 1282.
(57) Vega, L.; de Miguel, E.; Rull, L. F.; Jackson, G.; McLure, I. A. *J. Chem. Phys.* **1992**, *96*, 2296. Benavides, A. L.; Alejandre, J.; del Rio, F. *Mol. Phys.* **1991**, *74*, 321. Henderson, D.; Scalise, O. H.; Smith, O. R. *J. Chem. Phys.* **1980**, *72*, 2431.
(58) Smith, W. R.; Henderson, D.; Tago, Y. *J. Chem. Phys.* **1977**, *67*, 5308.
(59) Arrieta, E.; Jedrzejek, C.; Marsh, K. N. *J. Chem. Phys.* **1991**, *95*, 6838. Hoheisel, C.; Zhang, R. *Phys. Rev. A* **1991**, *43*, 5332. Rey, C.; Gallego, L. J.; Gonzalez, L. E. *J. Chem. Phys.* **1992**, *96*, 6984. Konior, J.; Jedrzejek, C. *Mol. Phys.* **1985**, *55*, 187. Henderson, D.; Waisman, E.; Lebowitz, J. L.; Blum, L. *Mol. Phys.* **1978**, *35*, 241.
(60) Yethiraj, A.; Hall, C. K. *J. Chem. Phys.* **1991**, *95*, 8494; *Mol. Phys.* **1991**, *72*, 619.
(61) Dudowicz, J.; Freed, K. F. *Macromolecules* **1991**, *24*, 5076. Dudowicz, J.; Freed, K. F.; Madden, W. G. *Macromolecules* **1990**, *23*, 4803.
(62) Carraro, C.; Cicceriello, S. *Phys. Rev. A.* **1987**, *35*, 3472.
(63) Arrieta, E.; Jedrzejek, C.; Marsh, K. N. *J. Chem. Phys.* **1991**, *95*, 6806. Cummings, P. T.; Rudisill, E. N. *Mol. Phys.* **1989**, *68*, 629. Konior, J.; Jedrzejek, C. *Mol. Phys.* **1988**, *63*, 655.
(64) Waisman, E. *Mol. Phys.* **1973**, *25*, 45. Henderson, D.; Blum, L. *Mol. Phys.* **1976**, *32*, 1627. Giunta, G.; Abramo, M. C.; Caccamo, C. *Mol. Phys.* **1985**, *56*, 319. Hoye, J. S.; Stell, G. *Mol. Phys.* **1984**, *52*, 1071.
(65) Yethiraj, A.; Hall, C. K. *J. Chem. Phys.* **1990**, *93*, 5315.