An Equation of State for Polymer Molecules: From Flexible Chains to Rigid Rods

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ABSTRACT: The scaled particle theory of Sato and Teramoto (ST)[1−3] for rigid rods and semiflexible polymers is extended to polymers with a wide range of flexibility. To formulate the free energy of polymer interactions, the polymer molecule is considered to be a collection of freely jointed subchains, envisioned as a series of shorter rods (Kuhn segments). The connectivity between the Kuhn segments is accounted for by using first-order perturbation theory for associating fluids. For polymers with a Kuhn segment number (N) smaller than 1, the model reduces to the ST theory. For polymers with N larger than 1, the model is tested against experimental data for isotropic−nematic phase equilibria. The comparison between the calculated and experimental results is favorable when use is made of experimental persistence length q values and hard-core diameter d values fairly close to those obtained from independent measurements. For flexible chains, the model reduces to a hard-sphere-chain equation of state which has been tested using computer simulation data for compressibility.

Introduction

Mixtures comprised of both flexible chains and rigid rods, such as polymer dispersed liquid crystals[4] and polymer blends that contain a flexible polymer and a liquid crystalline polymer,[5] are of interest due to their potential for a variety of applications. The phase diagrams for such mixtures have been generally simulated based on a simple summation of the free energies for isotropic mixing and nematic ordering. The Flory−Huggins (FH) theory is commonly used for the isotropic mixing. For the nematic ordering, Ballauff[6] utilized the Flory−Ronca theory. Brochard[7] and Shen et al.[8] employed the Maier−Saupe theory for binary nematic mixtures. Although these theories may be reasonable for the nematic phase, for the isotropic phase they reduce to the FH theory, which is applicable to flexible chains but not to rigid rods. Therefore, to realistically describe these mixtures, we need a unified model that is applicable both to flexible chains and to rigid rods.

For flexible polymers, a large amount of work has been done during the last decades usually based on the FH formalism. Recently, hard-sphere-chain equations of state[9−14] based on statistical mechanics have been developed to describe the behavior of flexible chain molecules made of freely jointed hard spherical segments. Despite their simplicity, the properties of these hard-sphere-chain models take into account some significant features of real polymer molecules, including segment excluded-volume effects and segment connectivity. For example, in the approach of Chapman et al.,[10] the excluded-volume effect is taken into account by using the Carnahan−Starling equation of state and the connectivity is approximated by using Wertheim's first-order perturbation theory. These equations have been tested against molecular simulation results for flexible chains of hard-sphere segments and have been used to correlate the thermodynamic properties of a wide variety of normal fluids including polymers. The results are very promising.

On the other hand, rodlike polymers can be modeled as spherocylinders. Their behavior can be described by using the Onsager theory[15] or the scale particle theory[16] depending on the polymer concentration. To extend these hard-body theories to semiflexible polymers, several modifications have been proposed. Khokhlov and Semenov[17] (KS) applied Lifshitz theory[18] to formulate the orientational entropy loss of semiflexible polymers using the wormlike chain model. Because the KS theory uses the second virial approximation to formulate the free energy of steric interactions, it may not be accurate for high polymer concentration solutions. In fact, it was found experimentally that even at concentrations much lower than the phase boundary concentration, the third and higher virial terms in the osmotic pressure could not be neglected.[19] To correct the defect, Sato and Teramoto[1,2] extended the scaled particle theory of Cotter[16] for straight hard spherocylinders to wormlike spherocylinders. Although good agreement between experimental and theoretical phase diagrams for isotropic−nematic equilibria was obtained, the applicability of the ST theory is limited to semiflexible polymers with small flexibility.[2] The limitation is due to the fact that they equate the free energy of polymer interactions for semiflexible polymers to that for rigid rods, as KS[17] did.

It is the intention of this work to extend the ST theory[1−3] to polymers with a wide range of flexibility by combining it with the approach of Chapman et al.[10] This paper presents the basic equations of the new model and tests them using experimental and computer simulation data.

Theory

We start with the case of semiflexible macromolecules which interact only by means of the forces of steric repulsion (athermal system). The asymmetric shape of the molecule can be approximated by a wormlike hard spherocylinder characterized by the persistence length q, the hard-core diameter d, and the cylinder length L_c; the total contour length L of the spherocylinder is equal to $L_c + d$ ($=M/M_L$), with M being polymer molecular weight and M_L being the molar mass per unit contour length. The wormlike spherocylinder model is a reasonable representation of the conformation of a linear

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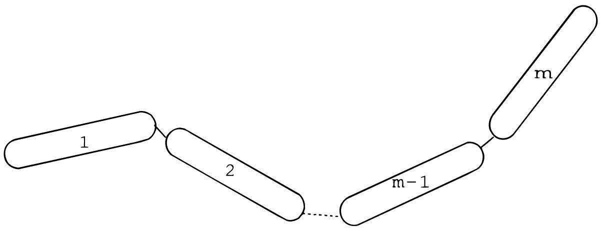

Figure 1. Schematic representation of a semiflexible polymer.

polymer chain in the unperturbed state, and the flexible chain and straight hard spherocylinder can be considered as its extremes. In the wormlike chain model, the stiffness is expressed in terms of q, which is a measure of the proximity of the conformation to that of rigid spherocylinders. Thus $q = \infty$ for a rigid cylinder and $q = d/2$ for flexible chains made of freely jointed hard spherical segments.

By analogy with the treatment of Onsager,[15] as ST[1,2] and KS[17] did, we write the Helmholtz free energy of the system as follows:

$$\frac{F}{nkT} = \ln(n/V) + \frac{F_{\mathrm{conf}}}{nkT} + \frac{F_{\mathrm{ster}}}{nkT} \qquad (1)$$

Here n is the total number of polymer molecules in the system, V is the volume, k is Boltzmann's constant, and T is the temperature. The first term on the right side corresponds to the translational entropy of the system, the term F_{conf} describes the entropy loss due to orientational ordering, and the last term F_{ster} describes the free energy of polymer interactions.

Orientation Entropy Contribution. Khokhlov and Semenov[17] were the first to calculate the entropy contribution F_{conf} for semiflexible polymers. Using the wormlike chain model and assuming the average orientational distribution function of the tangent vector along the chain contour to be described by the Onsager trial function,[15] they obtained explicit expressions of F_{conf} for the cases in which the Kuhn statistical segment number N $(=(L_c + d)/2q)$ is much larger than unity and much smaller than unity. To handle the situation where N is intermediate, several interpolation formulas have been proposed.[20,21] In this work, we use the empirical expression of Dupre and Yang.[20]

$$\frac{F_{\mathrm{conf}}}{nkT} = \ln(\alpha) - 1 + \pi\exp(-\alpha) + \frac{N}{3}(\alpha - 1) + \frac{5}{12}\ln\left\{\cosh\left[\frac{2N}{5}(\alpha - 1)\right]\right\} \qquad (2)$$

where α is the orientation parameter contained in the Onsager trial function. Equation 2 correctly approaches the Khokhlov and Semenov limits and is thought to be applicable to polymers with arbitrary flexibility.

Contribution Due to Polymer Interactions. Unlike the ST theory[1-3] and the KS[17] theory, where a semiflexible polymer is treated as a rigid cylinder with a fixed cylinder contour length in formulating F_{ster}, we have taken into account the polymer flexibility. Although F_{conf} may depend on the distribution of flexibility along the contour of the polymer chain,[17] we assume that, as far as F_{ster} is concerned, the wormlike polymer chain is equivalent to a chain formed by m freely jointed subchains, as shown in Figure 1. The subchain is modeled as a straight hard spherocylinder with the same hard-core diameter d, but with the cylinder length L_{sc}. If $L_c + d < 2q$, the polymer is treated as a rigid cylinder in the calculation of F_{ster}, and also $m = 1$ and $L_{\mathrm{sc}} = L_c$; If $L_c + d > 2q$, then polymer flexibility must be included in F_{ster}, and we have $m = (L_c + d)/2q$ and $L_{\mathrm{sc}} = (L_c - (2/3)(m - 1)d)/m$ to conserve polymer volume.

Using standard thermodynamics, we have

$$\frac{F_{\mathrm{ster}}}{nkT} = -\frac{1}{n}\int\left[\frac{n}{V}(Z_c - 1)\right]\mathrm{d}V \qquad (3)$$

where Z_c is the compressibility factor of the semiflexible polymer chain.

Similar to the treatment of Chapman et al.[10] for a flexible polymer chain, we write Z_c as

$$Z_c = mZ_{\mathrm{sc}} + Z_{\mathrm{fb}} \qquad (4)$$

Here Z_{sc} is the compressibility factor of the nonbonded subchains, and Z_{fb} is the contribution of the $m - 1$ flexible bonds between the subchains.

The subchain compressibility factor can be calculated using the equation of state for straight hard spherocylinders.[1-3] As a function of the subchain number density ρ $(=m(n/V))$, Z_{sc} is written as

$$Z_{\mathrm{sc}} = \left\{1 + V_0\rho + b\rho\delta\left[1 + \frac{1}{3}V_0\rho(1 + 2g)\right] + \left(\frac{2}{3}\right)(V_0\rho)^2\left(1 + g - \frac{g^2}{2}\right)\right\}/(1 - V_0\rho)^3 \qquad (5)$$

Here the parameter δ is determined by the orientation of the test rod with respect to the local director and can be written as[1,2]

$$\delta = \frac{4}{(\pi\alpha)^{1/2}}\left[1 - \frac{15}{16\alpha} + \frac{105}{512\alpha^2} + \frac{315}{8192\alpha^3} + O(\alpha^{-4})\right] \qquad (6)$$

and the parameters b and g are related to the subchain volume V_0 $(=\pi(d/2)^2L_{\mathrm{sc}} + \pi d^3/6)$ as

$$b = \frac{V_0}{\dfrac{d}{L_{\mathrm{sc}}} + \dfrac{2}{3}\left(\dfrac{d}{L_{\mathrm{sc}}}\right)^2} \qquad (7)$$

$$g = 1 - \frac{d}{L_{\mathrm{sc}}}\frac{b}{V_0} \qquad (8)$$

To write the expression for Z_{fb}, we use the result derived by Chapman et al.,[10]

$$Z_{\mathrm{fb}} = -(m - 1)\left[1 + \rho\left(\frac{\partial \ln \Delta}{\partial \rho}\right)\right] \qquad (9)$$

Here Δ is defined by

$$\Delta = \int g_{\mathrm{R}}(12)\, f(12)\, \mathrm{d}(12) \qquad (10)$$

$f(12) = \exp(-E(12)/kT) - 1$ is the Mayer f-function, $g_{\mathrm{R}}(12)$ is the reference fluid (straight hard spherocylinder fluid) pair correlation function, and $\int\mathrm{d}(12)$ denotes an unweighted average over all orientations of molecules 1 and 2 and integration over all separations of molecules 1 and 2. The only density dependence in Δ is given by the reference fluid pair correlation function.

To obtain an explicit expression for Z_{fb}, we assume that the rigid subchains can be regarded as chains composed of j tangent spheres in a linear rigid configuration. If the $j - 1$ bonds in the subchains become fully flexible, our reference fluid would become identical to that of Ghonasgi et al.[22] It is shown in the work of Ghonasgi et al.[22] and Chang et al.[23] that the site−site correlation function of a hard-sphere fluid is different from that of a disphere fluid due to the "correlation hole" effect.[24] In the work of Ghonasgi et al.,[22] it is also assumed that all chains longer than dispheres have the same density dependence of the site−site correlation function for the terminal segments at contact as dispheres do. Their work implies that the bonding contribution to the compressibility depends on the properties of the terminal spheres and their closest neighboring spheres, but not on the properties of the other internal spheres. Unlike the bonds in the work of Ghonasgi et al.[22] and Chang et al.,[23] the $j - 1$ bonds in the subchains in our case are completely rigid. As a first-order approximation, we assume that the $g_R(12)$ can be approximated by the pair correlation function of hard spheres. This approximation implies that the bonding contribution to the compressibility depends only on the properties of the terminal spheres of the subchains. Clearly, this approximation awaits a molecular theoretical justification.

Based on this approximation, eq 9 can be simplified to

$$Z_{\mathrm{fb}} = -(m-1)\left[1 + \rho\left(\frac{\partial \ln g_{\mathrm{HS}}(d)}{\partial \rho}\right)\right] \qquad (11)$$

The contact value of the pair correlation function of hard spheres, $g_{\mathrm{HS}}(d)$, can be derived from eqs 5−8 with $L_{\mathrm{sc}} = 0$.

$$g_{\mathrm{HS}}(d) = \frac{4 - 2\phi + \phi^2}{4(1-\phi)^3} \qquad (12)$$

where the $\phi(=\rho V_0)$ is the reduced density of the subchains. After some algebra, we obtain

$$Z_{\mathrm{fb}} = -\frac{(m-1)}{1-\phi}\,\frac{4 + 4\phi + \phi^2}{4 - 2\phi + \phi^2} \qquad (13)$$

By combining the above equations, we obtain an expression for the Helmholtz free energy of the system, that is,

$$\frac{F}{nkT} = \ln\left(\frac{n}{V}\right) + \frac{F_{\mathrm{conf}}}{nkT} + m\left[\ln\left(\frac{1}{1-V_0\rho}\right) + \frac{3V_0\rho}{1-V_0\rho} + b\rho\delta\frac{\left[1-(1-g)\frac{V_0\rho}{3}\right]}{(1-V_0\rho)^2} + \frac{(V_0\rho)^2}{3}\,\frac{\left(4+g-\frac{g^2}{2}\right)}{(1-V_0\rho)^2}\right] + (m-1)\ln\left(\frac{(1-\rho V_0)^3}{4-2\rho V_0+(\rho V_0)^2}\right) \qquad (14)$$

Although eq 14 is proposed for a one-component system of polymer molecules, it can be applied to an athermal polymer solution, as mentioned by Onsager.[15] Under this condition, F should be considered as the excess free energy over that of the pure solvent.

Test of the Model

For polymers whose Kuhn segment number N is smaller than 1, eq 14 is the same as the ST theory.[1−3] Extensive comparisons have been made by their group using the theory to interpret experimental data. The systems they treated range from rigid rodlike polymers to semiflexible polymers with N as high as 50, although they realized that their theory should not be applied to polymers with large flexibility.

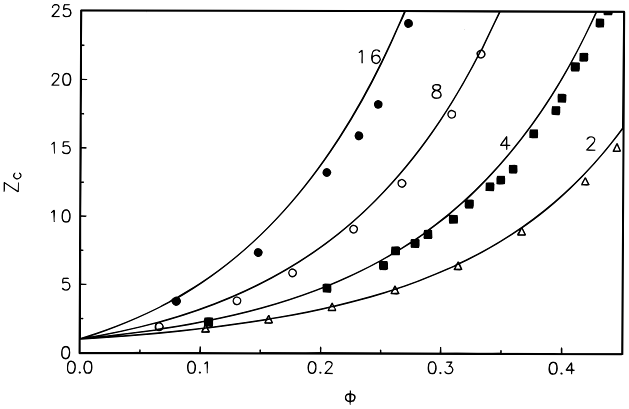

Figure 2. Compressibility factor for chains of $m = 2$, 4, 8, and 16 hard spheres as a function of the hard-sphere site volume fraction. The simulation results of Tildesley et al.[25] for $m = 2$ and of Dickman et al.[26] for $m = 4$, 8, and 16 are represented by the data points; the calculation results are represented by the solid curves.

In the following, eq 14 is tested for polymers with $N > 1$, that is, $q < (L_c + d)/2$. Our reasoning is that the influence of polymer flexibility on the excluded-volume effect may become significant for polymers with large N (small q). For polymers with $q = d/2$, eq 14 is tested against computer simulation data for the compressibility factor. For polymers with $d/2 < q < (L_c + d)/2$, the model predictions are compared with experimental data for isotropic−nematic phase boundary concentrations.

Testing for Polymers with $q = d/2$. The polymer with $q = d/2$ is made of freely jointed hard spheres. Because the connection between two closest neighboring spheres can be at any point on the spherical surface, the direction of the spheres cannot be specified. Therefore, the entropy loss due to the orientational ordering is zero and our model reduces to a hard-sphere-chain equation of state

$$Z_c = m\frac{1+\phi+\phi^2}{(1-\phi)^3} - \frac{(m-1)}{(1-\phi)}\,\frac{4+4\phi+\phi^2}{4-2\phi+\phi^2} \qquad (15)$$

which is very similar to that of Chapman et al.[10] with only the minor difference that we use eqs 5−8 with $L_{\mathrm{sc}} = 0$ to describe the properties of a hard-sphere system while the Carnahan−Starling equation was used in their work. A comparison of eq 15 with computer simulation results for various chain lengths is shown in Figure 2. The curves are labeled with m, the number of spheres in the chain. It can be seen that good agreement is found between the results of theory and simulations for the hard-disphere fluid, $m = 2$. Similar results are also found for chains of four spheres, $m = 4$, and for chains of eight spheres, $m = 8$. The agreement is not as good for chains with $m = 16$, which indicates the inability of the theory to account for the steric self-hindrance of longer chains. It is concluded that for flexible chains up to a chain length of eight, the equation of state (15) is a good representation, although its adequacy decreases as the chains get longer.

Testing for Polymers with $d/2 < q < (L_c + d)/2$. For polymers with $d/2 < q < (L_c + d)/2$, we compare

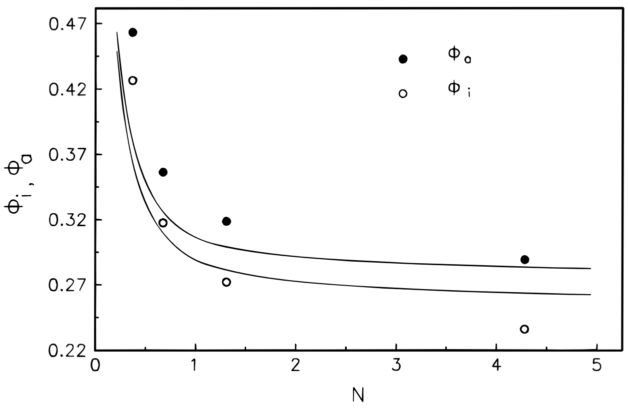

Figure 3. Isotropic–nematic phase boundary volume fractions as a function of Kuhn segment number for the system of PHIC in DCM at 20.0 °C. The data points are experimental results,[29] and the solid curves are calculated from the model.

experimental data for isotropic–nematic phase boundary concentrations with the theoretical values calculated using eq 14. The isotropic–nematic phase boundary concentrations can be calculated from the free energy minimization condition with respect to the degree of orientation in the nematic phases:

$$\frac{\partial F}{\partial \alpha} = 0 \tag{16}$$

and the phase coexistence equations

$$\Pi_i = \Pi_a \tag{17}$$

$$\mu_i = \mu_a \tag{18}$$

where the subscripts i and a represent the quantities associated with the isotropic and anisotropic phases, respectively. In the isotropic state, $F_{\text{conf}} = 0$ and $\delta = 1$. The osmotic pressure Π of the solution and the chemical potential μ of the solute are derived from eq 14, $\Pi = -\partial F/\partial V$ and $\mu = \partial F/\partial n$.

In the calculations, three molecular parameters are required: the contour length L, the number of Kuhn segments N, and the diameter d of each polymer. The values of L and N are calculated from the molecular weight M of each sample using the experimental molecular weight M_L per unit contour length and the persistence length q. The value of the remaining parameter d is chosen so that the calculated isotropic–nematic phase boundary concentrations give the best agreement with experiment. The same method was used by Kubo et al.,[27] Brian et al.,[28] and Sato et al.[1]

Figures 3 and 4 compare experimental data for phase boundary concentrations with theoretical values calculated from the model for dichloromethane (DCM) and toluene solutions of poly(hexyl isocyanate) (PHIC), respectively. Experimental data for the onset of the appearance of the anisotropic phase are compared with the model calculation in Figure 5 for (hydroxypropyl)cellulose (HPC) in dimethylacetamide (DMAc) and for (acetoxypropyl)cellulose (APC) in dibutyl phthalate (DBP). These figures show that reasonably good agreement between experiment and calculation is obtained when d is treated as an adjustable parameter. It can be seen from Table 1, in which the parameters used in the calculation are given, that for all four systems investigated, the values of d used in the calculation are fairly close to those estimated from independent measurements. Due to the great sensitivity of F_{conf} to the

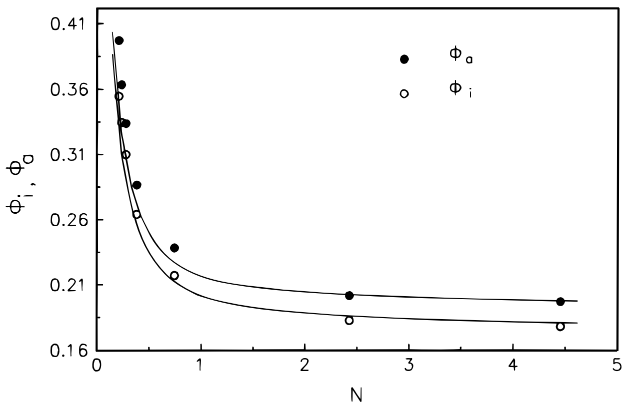

Figure 4. Isotropic–nematic phase boundary volume fractions as a function of Kuhn segment number for the system of PHIC in toluene at 25.0 °C. The data points are experimental results,[29] and the solid curves are calculated from the model.

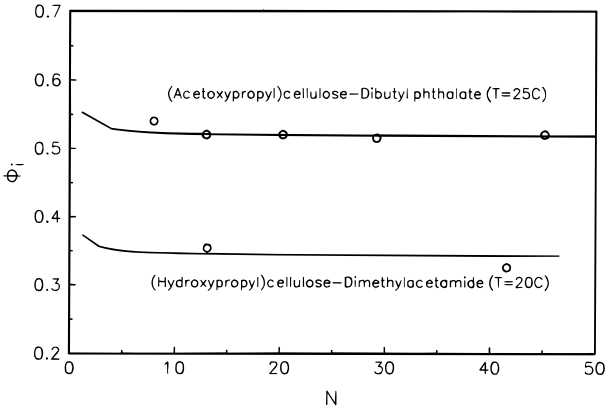

Figure 5. Phase boundary volume fraction ϕ_i as a function of Kuhn segment number for cellulose derivatives. The data points are experimental results,[30,31] and the solid curves are calculated from the model.

Table 1. Parameters Used in the Calculations

system	estimated			fitted
	M_L(nm^{-1})	q (nm)	d (nm)	d (nm)
PHIC in DCM	740.0[a]	21.0[a]	1.25[a]	1.55
PHIC in toluene	740.0[a]	37.0[a]	1.25[a]	1.60
APC in DBP	812.0[b]	5.9[b]	1.15–1.22[b]	1.65
HPC in DMAc	720.0[c]	8.0[d]	1.28[c]	0.95

[a] Itou et al.[29] [b] Laivins et al.[30] [c] Conio et al.[31] [d] Upper value, Conio et al.[31]

flexibility mechanism,[17] the model should be most accurate for wormlike chains, although the calculation has been done for both wormlike chains, such as PHIC, and polymers conforming to the Kuhn chain model, such as HPC.

Finally, a few words have to be said about the limitation of the equation of state. The new equation, like other hard-sphere-chain equations of state, fails to predict the correct scaling behavior in the semidilute region ($\Pi \sim (n/V)^{2.25}$). Therefore, the new equation is not applicable to random coils which correspond to $q = 0$.

Conclusions

As with other hard-sphere-chain models, the equation of state proposed in this work emphasizes two significant features of real polymer molecules: the excluded-volume effect and segment connectivity. Going beyond the hard-sphere-chain models, the new equation takes into account the stiffness of the bonds between polymer segments. The entropy loss due to the stiffness of the bonds is estimated using the interpolation formula proposed by DuPre and Yang for persistent chains. To account for the excluded-volume effect, we have assumed that the effect is independent of polymer flexibility and that the polymer is equivalent to a chain formed by several freely jointed rigid subchains. The contribution to thermodynamic properties due to the flexible bonds between the subchains is taken into account using first-order perturbation theory. The contribution from the excluded volume of the rigid subchains is modeled using hard-body scaled particle theory.

The new equation of state reduces to the ST theory for rigid rods and polymers with small flexibility. For flexible chains, the equation reduces to a hard-sphere-chain equation of state, which is similar to that of Chapman et al. In this sense, the new equation can be regarded as an interpolation equation between the ST theory and the hard-sphere-chain equation of state. For these two limiting situations, extensive work has been done and the results to date are very promising.[1−3,9−13,22] For polymers with intermediate flexibility, the model has been tested against experimental data for isotropic–nematic phase equilibria. Favorable results are obtained with only one fitted parameter *d* whose values are fairly close to those from independent measurements.

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