

Effective magnetic Hamiltonian and Ginzburg criterion for fluids

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We develop further the approach of Hubbard and Schofield [Phys. Lett. **40A**, 245 (1972)], which maps the fluid Hamiltonian onto a magnetic one. We show that *all* coefficients of the resulting effective Landau-Ginzburg-Wilson (LGW) Hamiltonian may be expressed in terms of the compressibility of a reference fluid containing only repulsive interactions and its density derivatives; we calculate the first few coefficients in the case of the hard-core reference fluid. From this LGW Hamiltonian we deduce approximate mean-field relations between critical parameters and test them on data for Lennard-Jones, square-well, and hard-core Yukawa fluids. We estimate the Ginzburg criterion for these fluids. [S1063-651X(98)07806-4]

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The modern theory of critical phenomena based on the renormalization group (RG) technique has demonstrated an impressive success in a variety of fields [1]. However, most of the studies using the RG approach have addressed the criticality of the Ising-like systems. Some effective computational schemes based on the RG technique have been developed for fluids [2], but they are not as convenient for the general analysis of criticality as those based on the so-called Ginzburg-Landau-Wilson (LGW) Hamiltonian. Effective magnetic Hamiltonians for fluids have been derived in a variety of ways. In Ref. [3] the fluid Hamiltonian was reduced to the magnetic one by means of coarse graining. In [4] the coefficients in an effective LGW Hamiltonian were obtained by comparing the critical amplitudes for the order parameter, compressibility, correlation length, etc., calculated within generalized mean-spherical approximation, with those derived from the LGW Hamiltonian. In [5] the functional generalization of the Mayer expansion for the single-component fluid was used; the attractive interactions were treated on the second-virial level and a few different approximation were adopted for the repulsive (hard-core) contribution to the free energy. Within these approximations Fisher and Lee evaluated the coefficients for the effective LGW Hamiltonian for a single-component fluid [5]; somewhat different approximations were employed to derive the LGW coefficients for the restricted primitive model of electrolytes [5].

Hubbard and Schofield [6] derived the effective LGW Hamiltonians for fluids by an *exact* mapping, based on the transformation of variables. Although they did not compute the coefficients of the effective Hamiltonian, they argued that fluids belong to the Ising universality class. In the present study we develop this approach further, showing in particular that *all* the coefficients of the effective LGW Hamiltonian may be expressed in terms of the known properties of the reference (hard-core) system: the compressibility and its density derivatives. We find explicit expressions for the first few coefficients. Applying the mean-field conditions for the critical point of the effective magnetic Hamiltonian, we formulate simple relations between some critical parameters and check them for some fluids; for these fluids we also estimate the parameter τ_G of the Ginzburg criterion.

We start from the fluid Hamiltonian

$$H = \sum_{i < j} \phi(r_{ij}) - \sum_{i < j} v(r_{ij}) = H_R + H_A. \quad (1)$$

Here $\phi(r)$ denotes the repulsive part of the interparticle interaction potential, while $-v(r)$ denotes the attractive part; $\{\vec{r}_j\}$ are coordinates of the particles and $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. The attractive part of the Hamiltonian, H_A , may be written in terms of the Fourier components of the density fluctuations, $n_{\vec{k}} = (1/\sqrt{\Omega}) \sum_{j=1}^N e^{-i\vec{k} \cdot \vec{r}_j}$ and the Fourier transform of the attractive potential $v_k = \int v(r) e^{-i\vec{k} \cdot \vec{r}} d\vec{r}$ as [6,7]

$$H_A = -\frac{1}{2} \sum_{\vec{k}} v_k n_{\vec{k}} n_{-\vec{k}} + \frac{1}{2} v(0)N, \quad (2)$$

where N is the number of particles, Ω is the volume of the system, and summation over the following set of \vec{k} is implied: $k_l = (2\pi/L)n_l$ with $L = \Omega^{1/3}$, $l = x, y, z$, and $n_l = 0, \pm 1, \pm 2, \dots$; the thermodynamic limit $L \rightarrow \infty$ is assumed. Let μ be the chemical potential of the system with the total Hamiltonian (1) and μ_R the chemical potential in the reference system having the Hamiltonian H_R , which includes only repulsive interaction. Then the grand partition function Ξ , may be expressed in terms of that of the reference fluid Ξ_R , as [6]

$$\Xi = \Xi_R \left\langle \exp \left\{ \beta \mu' N + \frac{1}{2} \beta \sum_{\vec{k}} v_k n_{\vec{k}} n_{-\vec{k}} \right\} \right\rangle_R, \quad (3)$$

where $\mu' \equiv \mu - \mu_R + \frac{1}{2}v(0)$ and $\langle \rangle_R$ denotes an average over configurations of the reference system, at the temperature T with chemical potential μ_R . Note that the reference system (with only *repulsive* interactions) does not have a liquid-gas transition; i.e., its grand partition function Ξ_R is regular in the vicinity of the critical point of the fluid of interest. Following Hubbard and Schofield [6], we use the identity $\exp(\frac{1}{2}a^2x^2) = (2\pi a^2)^{-1/2} \int_{-\infty}^{+\infty} \exp(-\frac{1}{2}y^2/a^2 + xy) dy$ and after some algebra obtain the ratio $Q = \Xi/\Xi_R$ of the grand partition functions [6]

$$Q^\infty \int \prod_{\vec{k}} d\sigma_{\vec{k}} \exp \left\{ \frac{\mu'}{v_0} \Omega^{1/2} \sigma_0 - \frac{1}{2} \beta^{-1} \sum_{\vec{k}} v_{\vec{k}}^{-1} \sigma_{\vec{k}} \sigma_{-\vec{k}} \right\} \times \left\langle \exp \left\{ \sum_{\vec{k}} \sigma_{\vec{k}} n_{-\vec{k}} \right\} \right\rangle_R ; \quad (4)$$

here integration is to be performed under the restriction $\sigma_{-\vec{k}} = \sigma_{\vec{k}}^*$ (the complex conjugate of $\sigma_{\vec{k}}$); $\sigma_0 = \sigma_k$ for $k=0$ and we omit a factor regular at the critical point since it does not affect the subsequent analysis. Applying the cumulant theorem [8] to the factor $\langle \exp\{\sum_{\vec{k}} \sigma_{\vec{k}} n_{-\vec{k}}\} \rangle_R$ one obtains [6]

$$Q^\infty \int \prod_{\vec{k}} d\sigma_{\vec{k}} \exp\{-\mathcal{H}\}, \quad (5)$$

with

$$\mathcal{H} = -h' \sigma_0 \Omega^{1/2} + \sum_{n=2}^{\infty} \frac{1}{\Omega^{n/2-1}} \times \sum_{\vec{k}_1, \dots, \vec{k}_n} u'_n(\vec{k}_1, \dots, \vec{k}_n) \sigma_{\vec{k}_1} \cdots \sigma_{\vec{k}_n},$$

$$h' = [\mu - \mu_R + v(0)/2] v_0^{-1} + \rho,$$

$$u'_2(\vec{k}_1, \vec{k}_2) = \frac{1}{2!} \delta_{\vec{k}_1 + \vec{k}_2, 0} \{ \beta^{-1} v_{\vec{k}_1}^{-1} - \langle n_{\vec{k}_1} n_{-\vec{k}_1} \rangle_{cR} \},$$

$$u'_n(\vec{k}_1, \dots, \vec{k}_n) = -\frac{\Omega^{n/2-1}}{n!} \langle n_{\vec{k}_1} \cdots n_{\vec{k}_n} \rangle_{cR}, \quad n \geq 3.$$

Here $\rho = N/\Omega$ is the fluid density and $\langle \rangle_{cR}$ denotes the *cumulant* average calculated in the reference system. In Eq. (5) Q has been written in the same way as the partition function for a magnetic system having an Ising-like Hamiltonian: $\sigma_{\vec{k}}$ are the Fourier components of the ‘‘spin field’’ $\sigma(\vec{r})$ and h' is the ‘‘magnetic field.’’

The coefficients of the effective Hamiltonian depend on the correlation functions of the reference fluid having only repulsive interactions. Using the definitions of the particle correlation functions of fluids [9] and definitions of the cumulant averages [8], one can *directly* evaluate $\langle n_{\vec{k}_1} \cdots n_{\vec{k}_n} \rangle_{cR}$ and thus the coefficients $u'_n(\vec{k}_1, \dots, \vec{k}_n)$. It is straightforward to show that u'_n may be expressed in terms of the Fourier transforms of the correlation functions h_1, h_2, \dots, h_n of the reference system, defined as $h_1(\vec{r}_1) \equiv \delta(\vec{r}_1)$, $h_2(\vec{r}_1, \vec{r}_2) \equiv g_2(\vec{r}_1, \vec{r}_2) - 1$, $h_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) \equiv g_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) - g_2(\vec{r}_1, \vec{r}_2) - g_2(\vec{r}_1, \vec{r}_3) - g_2(\vec{r}_2, \vec{r}_3) + 2$, etc., where $g_l(\vec{r}_1, \dots, \vec{r}_l)$ are l -particle correlation functions [9]. In particular, the first few coefficients read

$$u'_2 = \delta_{1,2} \rho \left[\frac{k_B T}{v_0 \rho} - (1 + \rho \tilde{h}_2(\vec{k}_1)) \right], \quad (6)$$

$$u'_3 = -\delta_{1,2,3} \rho \{ 1 + \rho [\tilde{h}_2(\vec{k}_1) + \tilde{h}_2(\vec{k}_2) + \tilde{h}_2(\vec{k}_3)] + \rho^2 \tilde{h}_3(\vec{k}_1; \vec{k}_2) \}, \quad (7)$$

where \tilde{h}_l are the Fourier transforms of h_l and we use the shorthand notation $\delta_{1,2,\dots,n} = \delta_{\vec{k}_1 + \vec{k}_2 + \dots + \vec{k}_n, 0} / n!$.

Now we consider the small- k expansion of the coefficients. First we note that the function $\tilde{h}_2(\vec{k})$ may be expressed in terms of the Fourier transform of the direct correlation function $\tilde{c}_2(\vec{k})$, as $\tilde{h}_2(\vec{k}) = \tilde{c}_2(\vec{k}) / [1 - \rho \tilde{c}_2(\vec{k})]$ and its zero k value in terms of the isothermal compressibility $\chi_R = \rho^{-1} (\partial \rho / \partial P_R)_\beta$ (where P_R is the pressure of the reference fluid) as $1 + \rho \tilde{h}_2(0) = \rho k_B T \chi_R \equiv z_0$. Using the expansions $v_{\vec{k}} = v_0 - v''_0 k^2 + \dots$ [10] and $\tilde{c}_2(k) = \tilde{c}_2(0) - \tilde{c}_2(0)'' k^2 + \dots$, one obtains for u'_2 , omitting terms of $\mathcal{O}(k^4)$,

$$u'_2 = \delta_{1,2} [a'_2 + b'_2 k^2 + \dots],$$

$$a'_2 = (\beta v_0)^{-1} - \rho z_0, \quad (8)$$

$$b'_2 = \rho^2 [z_0^2 \tilde{c}_2''(0) + \beta v_0'' (\rho \beta v_0)^{-2}]. \quad (9)$$

The LGW Hamiltonian does not have terms with powers of k higher than k^2 ; moreover, the only term of order k^2 is proportional to $\propto k^2 \sigma_{\vec{k}} \sigma_{-\vec{k}}$. Thus only zeroth order terms should be kept in the expansion of u'_n for $n > 2$. Hence we may write the contribution of such terms using this approximation:

$$u'_3 = -\delta_{1,2,3} \rho [1 + 3\rho \tilde{h}_2(\vec{0}) + \rho^2 \tilde{h}_3(\vec{0})], \quad (10)$$

$$u'_4 = -\delta_{1,2,3,4} \rho [1 + 7\rho \tilde{h}_2(\vec{0}) + 6\rho^2 \tilde{h}_3(\vec{0}) + \rho^3 \tilde{h}_4(\vec{0})],$$

etc., where $\tilde{h}_l(\vec{0}) \equiv \tilde{h}_l(0, \dots, 0)$. There exists a relation between successive correlation functions [9]

$$\chi \rho^2 \frac{\partial}{\partial \rho} \rho^l g_l = \beta \rho^l \left[l g_l + \rho \int d\vec{r}_{l+1} (g_{l+1} - g_l) \right], \quad (11)$$

from which follows a relation between the functions $\tilde{h}_l(\vec{0})$:

$$\chi \rho^2 \frac{\partial}{\partial \rho} \rho^l \tilde{h}_l(\vec{0}) = \beta \rho^l [l \tilde{h}_l(\vec{0}) + \rho \tilde{h}_{l+1}(\vec{0})], \quad (12)$$

expressing each $\tilde{h}_{l+1}(\vec{0})$ in terms of $\tilde{h}_l(\vec{0})$ and its density derivative. Using Eq. (12) iteratively one finally finds each $\tilde{h}_l(\vec{0})$ expressed in terms of the reference system compressibility χ_R and its density derivatives. Explicitly, we obtain

$$u'_3 \equiv \delta_{1,2,3} \rho_c u_3 = -\delta_{1,2,3} \rho z_0 (z_0 + z_1), \quad (13)$$

$$u'_4 \equiv \delta_{1,2,3,4} \rho_c u_4 = -\delta_{1,2,3,4} \rho z_0 [z_1^2 + z_0 (z_0 + 4z_1 + z_2)], \quad (14)$$

defining u_n , where ρ_c is the critical density, $z_0 \equiv \rho \chi_R / \beta$ as before, $z_1 = \rho \partial z_0 / \partial \rho$, and $z_2 = \rho^2 \partial^2 z_0 / \partial \rho^2$. In this way one can evaluate *all* the coefficients of the effective LGW Hamiltonian of the fluid and express them in terms of the compressibility of the reference system and its density derivatives. This solves the problem of finding the effective LGW Hamiltonian provided the compressibility of the reference system is sufficiently well known.

For the reference system with only repulsive interactions one can often usefully adopt the hard-sphere system with an

appropriately chosen hard-core diameter [11,12]. For soft (not impulsive) repulsive forces a simple relation [12] $d = d_{BH} = \int_0^\sigma \{1 - \exp[-\phi(r)/kT]\}$ gives the effective diameter d of the hard-sphere system corresponding to a repulsive potential $\phi(r)$ that vanishes at $r \geq \sigma$. For the hard-sphere system one has the fairly accurate Carnahan-Starling equation of state [12], for which

$$z_0 = (1 - \eta)^4 (1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4)^{-1}, \quad (15)$$

where $\eta = (\pi/6) d^3 \rho$. The value of $\tilde{c}_2(0)''$ may be found from the Wertheim-Thiele solution [13] for the direct correlation function, which gives

$$\tilde{c}_2(0)'' = -(\pi d^5/120) (16 - 11\eta + 4\eta^2)(1 - \eta)^{-4}. \quad (16)$$

To recast the effective Hamiltonian in the conventional form, we perform a transformation from the variables $\sigma_{\vec{k}}$ to ‘‘field’’ variable $\sigma(\vec{r})$. Under this transformation integration over the set $\{\sigma_{\vec{k}}\}$ becomes field integration over $\sigma(\vec{r})$ and the term $\sim k^2 \sigma_{\vec{k}} \sigma_{-\vec{k}}$ transforms into $\sim [\nabla \sigma(\vec{r})]^2$. Using $\rho_c^{-1/3}$ as a scaling factor for the length we finally arrive at the effective LGW Hamiltonian

$$\mathcal{H} = \int d\vec{r} \left[-h\sigma + \frac{a_2}{2} \sigma^2 + \frac{u_3}{3!} \sigma^3 + \frac{u_4}{4!} \sigma^4 + \dots + \frac{b_2}{2} (\nabla \sigma)^2 \right], \quad (17)$$

where $h = [\mu - \mu_R + v(0)/2](v_0 \rho_c)^{-1} + \rho/\rho_c$, $a_2 = k_B T / \rho_c v_0 - z_0(\rho/\rho_c)$, and u_3, u_4 are given by Eqs. (13) and (14). The coefficient b_2 reads

$$b_2 = \frac{1}{80} \left(\frac{36}{\pi^2 \eta_c} \right)^{1/3} \left[\frac{\lambda_{\text{eff}}^2}{\beta \epsilon_{\text{eff}}} - B \right], \quad (18)$$

where $B = 4\eta^2(1 - \eta)^4(16 - 11\eta + 4\eta^2)/(1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4)^2$ and constants ϵ_{eff} and λ_{eff} characterize zeroth order v_0 and second-order $v_0'' = \frac{1}{6} \int r^2 v(r) d\vec{r}$ moments of the attractive potential:

$$\frac{4\pi d^3}{3} \epsilon_{\text{eff}} = \int v(r) d\vec{r} = v_0, \quad (19)$$

$$\lambda_{\text{eff}}^2 d^2 = \frac{5}{3} v_0^{-1} \int v(r) r^2 d\vec{r}. \quad (20)$$

This effective LGW Hamiltonian may be used for the analysis of the critical behavior, using, for example, the RG technique.

Now we perform a mean-field (MF) level analysis based on the effective Hamiltonian. To do so we first remove the cubic term by making the shift $\sigma \rightarrow \sigma + \bar{\sigma}$, with $\bar{\sigma}$ chosen to make the cubic term vanish; this leads to new coefficients $\bar{h} = h + a_2 u_3 / u_4 - u_3^3 / 3u_4^2$ and $\bar{a}_2 = a_2 - u_3^2 / 2u_4$ with $\bar{u}_3 = 0$, $\bar{u}_4 = u_4$, and $\bar{b}_2 = b_2$. Then the MF condition at the critical point (CP) $\bar{a}_2 = 0$ and $\bar{h} = 0$ gives the approximate relations

$$\frac{k_B T_c}{\rho_c v_0} = \left[z_0 + \frac{u_3^2}{2u_4} \right]_{CP}, \quad (21)$$

$$v_0 \rho_c \left[1 + \frac{u_3^3}{6u_4^2} \right]_{CP} = -[\mu - \mu_R + v(0)/2]_{CP}. \quad (22)$$

Equation (21) relates the critical density and the critical temperature of the system; Eq. (22) relates the difference of the chemical potentials $\mu - \mu_R$ at the critical point to the critical density. We have tested these relations using simulation data for Lennard-Jones (LJ) [14], hard-core Yukawa (HCY) [15], and square-well (SW) [16–18] fluids. The Weeks–Chandler–Andersen (WCA) partition [11] of the LJ potential $u_{LJ}(r) = 4\epsilon_{LJ}[(\sigma/r)^{12} - (\sigma/r)^6]$ gives, for the attractive part,

$$v(r) = \begin{cases} \epsilon_{LJ} & r \leq 2^{1/6} \sigma \\ -u_{LJ}(r), & r \geq 2^{1/6} \sigma, \end{cases} \quad (23)$$

which is perfectly smooth in the core region. This partition gives the best estimates for the thermodynamic functions in the WCA perturbation scheme [11]. The repulsive part $\phi(r) = u_{LJ}(r) + v(r)$ is then used to find the effective hard-core diameter using the expression quoted above. Similarly, we use the WCA partition for the SW and HCY fluids. The square-well fluid has the interaction potential $\phi(r) - v(r) = +\infty$ if $r < d$, $-\epsilon$ if $d \leq r < \lambda d$, and 0 if $r \geq \lambda d$; the reference system is the hard-sphere system with the diameter d . We take the attractive part of the potential as $v(r) = 0$ for $r \geq \lambda d$ and $v(r) = \epsilon$ for $0 < r < \lambda d$. For the HCY potential, $\phi(r) - v(r) = +\infty$ if $r < d$ and $-\epsilon_Y \exp[-\kappa(r-d)]/r$ for $r \geq d$; the WCA partition gives $v(r) = \epsilon_Y/d$ for $r < d$ and $v(r) = \epsilon_Y \exp[-\kappa(r-d)]/r$ for $r \geq d$.

Table I gives the ratio of the right- to the left-hand side of the MF Eq. (21) as W_c and that of Eq. (22) as Y_c . As one can see from the table, these MF relations hold rather satisfactorily except for HCY fluids with short-ranged attractive potentials, where the MF description and Monte Carlo (MC) results appear to differ. In Table I we also give some coefficients of the LGW Hamiltonian at the critical point.

Using coefficients of the effective LGW Hamiltonian obtained, one can also estimate the Ginzburg parameter τ_G [1]. This defines the domain of validity of the classical critical behavior: The classical description fails for $|\tau| \equiv |T/T_c - 1| \ll \tau_G$. Following [5], we write for this parameter

$$\tau_G = \frac{1}{32 \pi^2} \frac{u_4^2}{\alpha_2 b_2^3}, \quad (24)$$

where $\bar{a}_2 = \alpha_2 \tau$. From Eqs. (18) and (24) it follows that for the infinite-range Kac-Baker potential $\lambda_{\text{eff}} \rightarrow \infty$ [with $\epsilon_{\text{eff}} \propto v_0$ finite; see Eqs. (19) and (20)], $b_2 \rightarrow \infty$ and thus $\tau_G \rightarrow 0$ as expected (cf. [5]).

To estimate α_2 we use the MF condition (21) and approximate $z_0(\rho/\rho_c) + u_3^2/2u_4$ by its value at the critical point $k_B T_c / \rho_c v_0$. This yields:

$$\bar{a}_2 \approx \frac{k_B T}{\rho_c v_0} - \frac{k_B T_c}{\rho_c v_0} = \alpha_2 \tau. \quad (25)$$

TABLE I. The Ginzburg criterion τ_G , the ratio of the right- to the left-hand side of Eq. (21) as W_c and that of Eq. (22) as Y_c , and coefficients of the effective LGW Hamiltonian $b_{2,c}, u_{4,c}, \alpha_2$. Here λ_{eff} is the effective range of the attractive potential ($\lambda_{\text{eff}}=\lambda$ for the SW fluid). $T^*=k_B T/\epsilon_{\text{eff}}$ and $\rho_c^*=\rho_c d^3$ are, respectively, the reduced critical temperature and density. The critical data for the SW fluid are from [17], [16] (for $\lambda_{\text{eff}}=1.5$), and [18] (for $\lambda_{\text{eff}}=3.0$); for the HCY fluid from [15]; and for the LJ fluid from [14].

λ_{eff}	T_c^*	ρ_c^*	τ_G	W_c	Y_c	$b_{2,c}$ (units of 10^{-2})	$u_{4,c}$ (units of 10^{-2})	α_2 (units of 10^{-2})
SW								
1.25	0.391	0.370	0.272	1.07		1.21	0.62	25.2
1.375	0.375	0.355	0.259	1.06		1.55	0.88	25.2
1.500	0.370	0.329	0.301	1.06	1.01	2.00	1.46	26.9
1.75	0.338	0.284	0.407	1.12		2.89	2.96	28.4
2.00	0.346	0.225	0.334	1.09		4.58	6.10	36.7
3.00	0.433	0.181	0.012	0.87		15.7	9.02	57.0
HCY								
1.396	0.298	0.377	0.336	1.45	0.56	1.91	0.52	18.8
1.579	0.307	0.375	0.096	1.39	0.62	1.70	0.55	19.5
2.137	0.328	0.313	0.054	1.16	0.95	4.40	1.91	25.0
LJ								
2.215	0.347	0.320	0.027	1.06	0.94	5.09	1.70	25.9

Thus $\alpha_2=k_B T_c/\rho_c v_0=k_B T_c/8\eta_c \epsilon_{\text{eff}}$. Using this value of α_2 and u_4, b_2 given by Eqs. (14), and (18) (the coefficients in this relation computed at the critical point), we calculate an approximate Ginzburg parameter τ_G for some of the SW, HCY, and LJ fluids. The results are given in Table I [19].

As we see in Table I, the derived value of τ_G is of the order of 10^{-1} for most of the fluids studied in computer simulations and lies within the range of τ_G values predicted in Ref. [5]. On the other hand, for the SW fluid with the most long-ranged attraction ($\lambda_{\text{eff}}=3$), $\tau_G \approx 10^{-2}$ is much smaller and may explain the MF-like behavior observed [18]. For the

LJ fluid, with an attractive potential proportional to r^{-6} , similar to that of real fluids, τ_G is of the order of 10^{-2} ; real simple fluids are supposed to have similar values of τ_G [20]. However, it may be noted that in MC simulations of the LJ fluid [14] (where a cutoff of the LJ potential and tail corrections were used) Ising-like behavior was observed to values of $|\tau|$, at least a few times larger than the τ_G given in Table I.

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